THIRD ANNUAL MEETING
UNIVERSITY OF STUTTGART, WEST GERMANY
April 7–10, 1987

PROGRAM AND ABSTRACTS

POLYMER PROCESSING SOCIETY

INTERNATIONAL

Organized by

INSTITUT FÜR KUNSTSTOFFTECHNOLOGIE
STUTTGART, WEST GERMANY

In association with

HANSER PUBLISHERS
MUNICH, NEW YORK

Plenary Speakers

Opening:
M. Herzog, Minister for Economics and Technology, State of Baden-Württemberg

Technical Lecture:
G. Wegner, Max-Planck-Institut für Polymerforschung, Mainz, West Germany

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Co-Organizers at Large

P. J. Carreau, Ec. Polytechnique, Montreal (Canada)
F. N. Cogswell, ICI Wilton, Middlesbrough (UK)
M. Crochet, U Catholique, Louvain (Belgium)
M. M. Denn, U of California, Berkeley (USA)
G. W. Ehrenstein, U Kassel (FRG)
M. Fleissner, Hoechst AG, Frankfurt/Main (FRG)
K. Fujiwara, Idemitsu Petrochem., Kimitsu (Japan)
M. Horio, Kyoto U (Japan)
R. Keunings, U of California, Berkeley (USA)
J. Meissner, ETH Zürich (Switzerland)
G. Menges, IKV Aachen (FRG)
A. Michel, CNRS, Vernaison (France)
K. Oberbach, Bayer AG, Leverkusen (FRG)
R. S. Porter, U of Massachusetts, Amherst (USA)
C. Rauwendaal, Raychem, Menlo Park (USA)
E. O. Reher, TH Leuna-Merseburg (GDR)
L. R. Schmidt, GE, Schenectady (USA)
J. E. Spruiell, U of Tennessee, Knoxville (USA)
T. Sun, Textile U, Shanghai (China)
J. Vlachopoulos, McMaster U, Hamilton (Canada)

Symposia Co-Organizers

1. Polymerization Processes
   E. D. Gilles, C. W. Macosko, S. Omi
2. Compounding, Mixing and Devolatilization
   Z. Tadmor, J. A. Biesenberger, M. Dienst
3. Rheology and Rheometry
   H. M. Laun, A. C. Papanastasiou, D. Boger
4. Continuous Shaping Processes
   E. Uhland, J. F. Stevenson, T. Kanai
5. Discontinuous Shaping Processes
   J. F. Agassant, M. R. Kamal, Y. Oyanagi
6. Reactive Processing
   M. Lambla, J. T. Lindt
7. Rubber Processing
   G. Pampus, L. F. Ramos de Valle
8. Fibers and Films (Drawing Operations)
   P. J. Lemstra, M.H.G. Deeg, S. Kase
9. Structure Development in Processing
   J. L. White, B. Qian, G. Perez
10. New Technologies (Processing of High Performance Materials
   H. Münstedt, A. E. Zachariades, T. Masuda
11. Composites
   G. Grüninger, L. A. Goettler, H. Hojo
12. Polyblends
   J. Lyngaae-Jorgensen, L. A. Utracki, S. Li

Conference Committee

General Chairman: *H.-G. Fritz,* IKT, U Stuttgart
Program Chairman: *H. Kühnle,* IKT, U Stuttgart
Treasurer: *E. Grünschloß,* IKT, U Stuttgart
Publicity Chairman: *W. Glenz,* Hanser Publishers, Munich

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President Elect.: *L. A. Utracki*
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Treasurer: *J. F. Stevenson*
Member at Large: *J. T. Lindt*

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Europe, Middle East and Africa: *H.-G. Fritz, Z. Tadmor*
East Asia and Australia: *B. Qian, J. Shimizu*
North and South America: *M. R. Kamal, L. F. Ramos de Valle*

Catering

During the breaks; coffee will be offered free of cost. Lunches are available at a preferential rate in the university canteen adjacent to the lecture rooms.

The City

Stuttgart (560,000 inhabitants) is the Capital of Baden-Württemberg, the state covering the South-West of the FRG. Lying in a spacious valley between wooded hills and vineyards, the city is a traditional center of culture, science and education.
Stuttgart is housing several theaters and the State Opera with its world-famed ballet (John Cranko's school).

Various museums are covering a wide range of cultural subjects:
The State Gallery of Fine Arts has, among other things, the most complete Picasso collection worldwide. The Linden Museum of Ethnology, featuring exotic cultures, and the Rosenstein Museum of Natural History are plainly unique.

There are numerous sites of historical and modern architecture:
The Old Castle and several palaces of the Counts (1135–1495), Dukes (1495–1806) and Kings (1806–1918) of Württemberg, the Weissenhof Colony (1927) with contributions of all the leading European architects of the first third of this century (e.g. le Corbusier, Mies van der Rohe, Gropius), the Television Tower (Leonhardt and Gutbrod, 1956) which is the ancestor of numberless pre-stressed concrete towers all over the world, and the New State Gallery building (J. Stirling, 1984).

A zoological-botanical garden, Wilhelma, accommodates fauna and flora from all the five continents (6000 animals of 1000 kinds).

There are two universities, two Max Planck Institutes and two technical colleges. Research fields in which the Stuttgart schools are worldwide leading include the Finite Elements (J. H. Argyris) and Solid State Physics (K. v. Klitzing, Nobel Prize 1985). An Art College and a Music Academy complete the educational facilities.

The region has brought forth many fundamental thinkers, e.g. J. Kepler (1571–1630), J. R. Mayer (Conservation of Energy, 1842) and even more inventors: W. Schickardt (First mechanical calculator, 1633), G. Daimler (Automobile, 1886), R. Bosch (Magneto ignition etc.) and Count Zeppelin (Rigid airship, 1900).

No wonder therefore that Stuttgart has also grown a metropolis of industry in which numerous companies with global activities, e.g. in automobiles, chemistry, machinery and electronics are established. Within the frame program, the conference participants will be given the opportunity to have a look at some of the most prominent firms.

Stuttgart's restaurants, snug or elegant ones, are offering regional (Swabian) and international cuisine and wine as well as the tasty beer from three large local breweries.

City Traffic

To travel about inside the City, we recommend to use the very fast city railway which, too, provides for the connection between the downtown Hotel locations and the University campus. The organizers will supply each participant free of extra cost, with an area ticket which is valid through four days (not on the Airport - Downtown route, however).

General Information

Introduction

The program of the Third Annual PPS Meeting again shows the Society's wide thematic scope as well as its international character.

The present state of research and technical innovation in Polymer Processing is comprehensively documented.

The schedule shows 217 technical contributions from 26 countries of four continents (Europe and Middle East: 45%, East Asia and Australia: 20%, Americas: 35%). It is also worth noting that 33 percent of the presentations come from the industry and 67 percent from the institutes (Universities and similar organizations).

The conference committee members wish to express their gratitude to the numerous co-organizers all over the world who enabled such an impressive collection of highly valuable papers and posters.

The Polymer Processing Society (PPS)

The PPS was founded on March 28–29, 1985 at Akron, Ohio (USA). The audience of the Founding Meeting, more than 200 experts from all over the world, of both industrial companies and universities, enthusiastically approved the objectives of the new society. On April 1–4, 1986 the Second Annual Meeting was held at Montreal, Canada. Attracting over 450 participants, the PPS continued its advancement.

The goal of the PPS as embodied in its constitution is to foster scientific understanding and technical innovation in polymer processing by providing a discussion forum for the worldwide community of engineers and scientists in this field. The thematic range of the PPS encompasses all formulation, conversion and shaping operations applied to polymeric systems in the transformation from their monomeric forms to commercial products.

Besides the international annual conferences, the PPS activities include the arrangement of regional and local meetings, publication of a journal, and sponsorship of educational seminars.

Membership in the PPS is open to all research workers in the field, and to all individuals who feel the activities of the society advance their professional development.

Technical Program

Running in four parallel streams, the program includes twelve thematic symposia and an extensive poster session.

The detailed schedule can be found on pages 6 to 23.

Working Parties

Reverting to a plan which was already conceived in the founding session, the Society at this meeting will start to form working parties on special topics of current interest.

A provisional outline is given on page 24.

Frame Program

Five prominent companies whose activities are related to the major conference topics (Bosch, Daimler, IBM, Porsche and Werner & Pfleiderer) are inviting the participants to have a look at their manufacturing plants.

On Saturday, April 11 there will be an excursion to the organizing Institut für Kunststofftechnologie.

A festive banquet with musical entertainment can be attended at extra cost.

Spouses' Program

Spouses' program registration covers the attendance of the banquet and sightseeing tours in the surroundings of Stuttgart. Fares and entrance fees are included.

Conference Fees

Registration is covering the reception on the evening of April 7, one or three days attendance of the sessions and one copy of the abstracts book.

The fees are quoted for early/late registration (before/after Februar 28, 1987)

Three days attendance:	
PPS members	420/500 DM
Non-members	550/660 DM
Students	120 DM
One day attendance:	200/240 DM
Banquet ticket:	120 DM
Spouses' Program:	150 DM
1 Abstracts book extra:	50 DM

PROGRAM AT A GLANCE

April 7	18h00 – 22h00	Reception Registration				Hotel Graf Zeppelin
April 8	8h00 – 9h00	Registration				University 47 Pfaffenwaldring Foyer
	9h00 – 10h15	Plenary Session				Room 47.1
	10h45 – 18h00	(Symposium 5) Discontinuous Shaping Processes – Injection Molding – Special Technologies	(Symposium 11) Composites – Composites Processing – Composites Rheology	(Symposium 2) Compounding, Devolatilization, Mixing	(Symposium 1) Polymerization	Rooms 47.2–47.5
	20h00 – 23h00	Banquet				Hotel Graf Zeppelin
April 9	8h15 – 16h30	(Symposium 10) New Technologies – High Performance Materials – Liquid Crystals	(Symposium 3) Rheology and Rheometry	(Symposium 9) Structure Development in Processing	(Symposium 6) Reactive Processing	University 47 Pfaffenwaldring Rooms 47.2–47.5
	17h00 – 18h00	Introduction to Posters				Rooms 47.2–47.5
		Rheology and Chemistry	Shaping Processes I	Shaping Processes II	Morphology and Properties	
(*)	18h00 – 22h00	Presentation and Discussion of Posters				Foyer
April 10	8h15 – 18h00	(Symposium 4) Continuous Shaping Processes – Die Flow – Dynamic Modeling and Control – Single Screws – Twin Screws	(Symposium 12) Polyblends	(Symposium 8) Fibers and Films (Drawing Operations)	(Symposium 7) Rubber Processing – Rubber – Rubber/Thermoplastics Blends	University 47 Pfaffenwaldring Rooms 47.2–47.5

(*) For the WORKING PARTIES' Program, see page 24

April 8, Morning Sessions

8h00 Registration

9h00 Plenary Session

Opening:
M. Herzog, Minister for Economics and Technology, State of Baden-Württemberg
Technical Lecture:
"Properties by Molecular Design of Materials"
G. Wegner, Max Planck Institute, Mainz (FRG)

10h15 Break

	Room 47.2	Room 47.3
	Symposium 5: **Discontinuous Shaping Processes** **Chairman** *J. F. Agassant,* Ecole Nat. Superieure des Mines de Paris (France)	Symposium 11: **Composites** **Co-chairmen** *G. Grüninger,* DFVLR, Stuttgart (FRG) *L. A. Goettler,* Monsanto, Akron (USA) *H. Hojo,* Tohoku U, Sendai (Japan)
10h45	*Injection Molding* 5/1 ***"Numerical Simulation of Transient Mold Filling"*** J. Vlachopoulos, H. Mavridis and A. N. Hrymak, Mc Master U, Hamilton (Canada)	*Composites Processing* 11/1 ***"Fibre Management in Composite Materials by Multi Live-feed Injection Moulding"*** P. S. Allan and M. J. Bevis, Brunel U, Uxbridge (UK)
11h30	5/2 ***"Numerical Simulation of Mold Filling with Polymers"*** A. Latrobe, H. Bung and M. E. Delalande, Informatique Intl., Grenoble (France).	11/2 ***"Manufacturing Processes of Continuous Fiber-reinforced Polyetheretherketone"*** G. Kempe, H. Krauss and G. Grüninger, DFVLR Stuttgart (FRG)
12h00	5/3 ***"Injection Molding of Reinforced Thermosets: Fiber Orientation Observations and Flow Calculation"*** R. Blanc, S. Philipon, M. Vincent, J. F. Agassant, Ecole des Mines de Paris, Valbonne, and H. Alglave, Inst. Charles Sadron, Strasbourg (France)	11/3 ***"Simulation of Compression Molding with Matrix-Fibre Separation and Fibre Orientation for Long Fibre-reinforced Thermoplastics"*** H. Hojo, E. G. Kim, H. Yaguchi and T. Onodera, Tohoku U, Sendai (Japan)
12h30	5/4 ***"Manifestation of the Effects of Fountain Flow and Packing in Real Injection Molding Systems"*** M. R. Kamal, E. Chu and S. Goyal, McGill U, Montreal (Canada)	11/4 ***"A Study of Fibre Attrition in the Processing of Long Fibre Reinforced Thermoplastics"*** H.-G. Kraft, ICI, Frankfurt (FRG) and R. S. Bailey, ICI, Middlesbrough (UK)

13h00 Lunch

University, 47 Pfaffenwaldring

Foyer

Room 47.1

10h15	Break	
	Room 47.4	Room 47.5
	Symposium 2: **Compounding, Mixing and Devolatilization** **Co-chairmen** *J. A. Biesenberger*, Stevens Inst., Hoboken (USA) *M. Dienst*, Berstorff GmbH, Hannover (FRG)	Symposium 1: **Polymerization Processes** **Co-chairmen** *E. D. Gilles*, U Stuttgart (FRG) *C. W. Macosko*, U of Minnesota, Minneapolis (USA) *S. Omi*, Tokyo U of Agriculture and Technology (Japan)
10h45	2/1 ***"Compounding, Mixing and Devolatilization"*** E. O. Reher, B. Poltersdorf and H. J. Radusch, TU Leuna-Merseburg (GDR)	1/1 ***"Features of Polymer Reaction Engineering"*** K. H. Reichert, TU Berlin (FRG)
11h30	***Compounding*** 2/2 ***"New Methods of Quality Assurance in Plastics Compounding"*** H. Herrmann, H. J. Nettelnbreker and K. Kapfer, Werner & Pfleiderer GmbH, Stuttgart (FRG)	1/2 ***"Modeling and Operation of a Continuous Polymerization Process to Obtain Extra-pure Polymers with Desired Molecular Weight and Molecular Weight Distribution"*** S. Omi, I. Iwata, K. Inubuse and M. Iso, U of Agriculture and Technology, and M. Suka, Nippon Plant Technology, Tokyo (Japan)
12h00	2/3 ***"Modelling of Flow in Modular Intermeshing Corotating Twin Screw Extruders and Preliminary Experimental Studies"*** W. Szydlowski and J. L. White, U of Akron (USA)	1/3 ***"Gel-Permeation Chromatography as a Tool for the Real-Time Estimation of the Chain Length Distribution in a Polymerization Reactor"*** S. A. Papadopoulou and E. D. Gilles, U of Stuttgart (FRG)
12h30	2/4 ***"The Open Shear Rolling Extruder for Processing of High Viscous Materials"*** A. Albers and E. Lotz, Color Metal GmbH, Heitersheim (FRG)	1/4 ***"Dynamic Scheme of the Polymerization of Caprolactam"*** C. L. Tang, N. S. Huang, M. H. Chow and Q. H. Zhang, Textile U, Shanghai (China)
13h00	Lunch	Canteen

April 8, Afternoon Sessions

	Room 47.2	Room 47.3
14h00	Injection Molding (continued) 5/5 *"A Visual Investigation on Flow Behaviour Around Inserts in Cavity of Injection Filling Process"* Y. Oyanagi and A. Tanaka, Kogakuin U, Tokyo (Japan)	Composites (continued) 11/5 *"Studies of Microstructure Development in Processing of Short-fiber Reinforced Thermoplastics"* M. R. Kamal, A. T. Mutel and P. Singh, McGill U, Montreal (Canada)
14h30	5/6 *"Analysis of Birefringence in the Injection Molded Disks"* A. Izuka, T. Katuki and S. Soejima, Daicel Chemical Ind., Aboshi-ku (Japan)	11/6 *"Continuous Processing of Composites"* A. N. Alexandrou and T. C. Papanastasiou, U of Michigan, Ann Arbor (USA)
15h00	5/7 *"Prediction of Viscosity and Molecular Orientation in Injection Moulding"* S. F. Bush, U of Manchester (UK)	*Composites Rheology* 11/7 *"Study on the Measurement of Fiber Orientation Distribution in the Fiber Reinforced Composites"* Z. Maekawa, H. Hamada and T. Horino, Kyoto Inst. of Tech., and S. Maeda, Nippon Glass Sheet Co., Osaka (Japan)
15h30	Break	
16h00	5/8 *"Optimizing the Application of Melting Cores in Injection Molding"* A. Schneiders and C. Hauck, BASF AG, Ludwigshafen (FRG)	11/8 *"Investigation of the Flow Behaviour of a Glass-fibre filled, Uncrosslinked Polyester Compound"* K. Geiger, IKT, Stuttgart, and A. Mandel, Bosch GmbH, Waiblingen (FRG)
16h30	*Special Technologies* 5/9 *"PVC Powder Slush"* R.Saffert,Deutsche Solvay-Werke, Rheinberg(FRG)	11/9 *"Measurement of the Damping of Flexural Properties of Short Fibre Reinforced Injection Mouldings"* H.El-Sobky,J.N.Ashton and S.Wray, UMIST, Manchester(UK)
17h00	*Special Technologies* 5/10 *"Finite Element Control Volume Simulation of Non-planar Compression Mold"* T. Osswald and C. L. Tucker III, U of Illinois, Urbana (USA)	11/10 *"Shear Flow of Carbon-fiber Filled Polyethylene Melts"* T. Kitano, M. Funabashi and H. Kanetsuna, Research Inst. for Polymers and Textiles, Ibaraki (Japan)
17h30 – 18h00	5/11 *"Injection Welding of Polyamides"* P. Maskus, Ems-Chemie AG, Domat (Switzerland)	11/11 *"The Surface Polymerization-modified $CaCO_3$ and Composites"* K. C. Gong and O. Meng, Inst. of Technology, Guangzhou (China)
20h00 – 23h00	Banquet	

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	Room 47.4	Room 47.5
14h00	Compounding etc. (continued) ***Devolatilization*** 2/5 ***"Foam-enhanced Devolatilization of Polymer Melts in Rolling Pools: Further Contributions Toward Understanding the Process"*** J. A. Biesenberger, Stevens Inst., Hoboken (USA)	Polymerization (continued) 1/5 ***"Micromixing and Macromixing in Polymerization Reactors"*** R. Thiele and J. Breme, Engineering College, Köthen (GDR)
14h30	2/6 ***"Design Aids for Vented Single Screws"*** H. Kühnle, U of Stuttgart (FRG)	1/6 ***"Continuous Melt Polymerization of Polyetherimide"*** L. R. Schmidt and E. M. Lovgren, General Electric Company, Schenectady (USA)
15h00	2/7 ***"Analysis of the High-mass Transfer Rate Regime of Extrusion Devolatilization"*** R. Chella, Florida State U, Tallahassee, R. W. Foster and J. T. Lindt, U of Pittsburgh (USA)	1/7 ***"Gas Phase Polymerization Process of Propylene"*** M. Ichimura, Mitsui Petrochemical Ind., Tokyo (Japan)
15h30	Break	
16h00	***Mixing*** 2/8 ***"Dynamics of Agglomerate Size Distribution in Linear Shear Flow Fields"*** D. L. Feke and I. Manas-Zloczower, Case Western Reserve U, Cleveland (USA)	1/8 ***"Continuous Reactive Extrusion of Crosslinkable Monomers"*** T. G. Charbonneaux, K. J. Mikkelsen and C. W. Macosko, U of Minnesota (USA)
16h30	2/9 ***"Laminar Shear Mixing in Plasticating Extruders"*** H. Potente and M. Koch, U of Paderborn (FRG)	1/9 ***"Polymer Crosslinking in Processing Operations Through Controlled Chemical Reactions: Polyvinylchloride and Polyethylene"*** A. Michel, M. Gonnu and E. Koerper, C.N.R.S., Vernaison (France)
17h00	2/10 ***"Static Mixers for the Processing of Thermoplastics"*** G. Schneider, Sulzer AG, Winterthur (Switzerland)	1/10 ***"Development of the Spherical Ultrafine Polymethyl Methacrylate Powder and Its Applications for Surface Modification"*** S. Kawase, F. Takeuchi, T. Takeuchi and Y. Takizawa, Soken Co., Tokyo (Japan)
17h30 – 18h00	2/11 ***"Novel Melt Mixing Device and Process"*** B. Alzner, Abbott Labs., Abbott Park (USA)	1/11 ***"The Flow of a Growing Viscosity Liquid in a Tube Under the Frontal Polymerization"*** P. V. Zhirkov, Inst. of Chemical Physics, Moscow (USSR)
20h00 – 23h00	Banquet	Hotel Graf Zeppelin

April 9, Morning Sessions

	Room 47.2	Room 47.3
	Symposium 10: **New Technologies** **Co-chairmen** *H. Münstedt,* BASF AG, Ludwigshafen (FRG) *A. E. Zachariades,* IBM, San Jose (USA)	Symposium 3: **Rheology and Rheometry** **Co-chairmen** *H. M. Laun, BASF,* Ludwigshafen (FRG) *A. C. Papanastasiou,* U Michigan, Ann Arbor (USA)
8h15	10/1 ***"New Technologies for Thermoplastic Morphology Development"*** R. S. Porter, U of Massachusetts, Amherst (USA)	3/1 ***"Conventional and New Modes of Deformation in Polymer Melt Rheometry"*** J. Meissner, ETH Zürich (Switzerland)
9h00	***High Performance Materials*** 10/2 ***Self-reinforcement of Thermoplastics in Injection Moulding"*** C. Maertin, G. W. Ehrenstein, L. Chwalisz and L. Macskasi, U of Kassel (FRG)	3/2 ***"The Relation Between the Stress-Tensor, the Deformation Tensor and the Orientation of Chain-Like Molecules"*** G. Nijman and R. J. J. Jongschaap, U Twente, Enschede (The Netherlands)
9h30	10/3 ***"High Modulus/High Strength Polyethylene Fiber Prepared by the Melt-drawn Orientation Method"*** K. Yagi, Mitsui Industries, Kuga-gun (Japan)	3/3 ***"Viscosity of entangled Polymer Melts"*** E. E. Schäfer, Bayer AG, Leverkusen (FRG)
10h00	10/4 ***"Ultra-High Molecular Weight Polyethylene Products from Pseudo-Gel Precursors"*** A. E. Zachariades, IBM, San Jose (USA)	3/4 ***"Melt Flow Index - Rheometry and Quality Control"*** W. Gleissle, U of Karlsruhe (FRG)
10h30	Break	
11h00	10/5 ***"Pultruded Thermoplastics - Manufacture and Product Properties"*** K. T. O'Brien, Celanese, Chatham (USA)	3/5 ***"Melt Fracture and Sharkskin Instabilities in Orifice Dies"*** J. M. Piau, B. Tremblay and N. El Kissi, Inst. de Mecanique de Grenoble (France)
11h30	10/6 ***"Injection Moulding of Hostalen GUR 812, a Special UHMW PE Grade"*** W. Payer, R. Kellersohn and M. Gusik, Ruhrchemie AG, Oberhausen (FRG)	3/6 ***"The Behaviour of Rigid Versus Flexible Molecule Solutions in Die Entry Flows"*** D. V. Boger, U of Melbourne, Parkville (Australia)
12h00	10/7 ***"Radio-frequency Assisted Processing of UHMW PE"*** R. Gauvin, Q. X. Nguyen and B. Fisa, Ecole Polytechnique, Montreal (Canada)	3/7 ***"A Study of Viscoelastic Fluid Flowing Through a Conical Die"*** X. L. Sun, Desige Inst., and G. J. Tang, Inst. of Technology, Guangzhou (China)
12h30	10/8 ***"Polymer Extrusion Through Oscillatory Dies"*** J. Casulli, J. R. Clermont, Inst. de Mecanique de Grenoble (France) and A. v. Ziegler, B. Mena, Nat. U of Mexico (Mexico)	3/8 ***"Effect of Contraction Ratio on the Viscoelastic Flow Transitions in an Axisymmetric Sudden Contraction"*** W. P. Raiford, L. M. Quinzani, R. C. Armstrong and R. A. Brown, M. I. T., Cambridge (USA)
13h00	Lunch	

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	Room 47.4	Room 47.5
	Symposium 9: **Structure Development in Processing** **Chairman** *J. L. White,* U of Akron (USA)	Symposium 6: **Reactive Processing** **Co-chairmen** *M. Lambla,* Ecole d'Application des Hauts Polymeres, Strasbourg (France) *J. T. Lindt,* U of Pittsburgh (USA)
8h15	9/1 ***"Concepts of Polymer Crystallization Under Varying Processing Conditions"*** H. Janeschitz-Kriegl and G. Krobath, Linz U (Austria)	6/1 ***"Evolution of Rheology During Chemical Gelation"*** H. H. Winter, U of Massachusetts, Amherst (USA)
9h00	9/2 ***"Development of Crystallization in Polymer Processing"*** N. Billon and J. Haudin, Ecole des Mines de Paris, Valbonne (France)	6/2 ***"Dynamics of Mixing-Initiated Foam Growth"*** J. T. Lindt and R. Chella, U of Pittsburgh (USA)
9h30	9/3 ***"Rate Controlled Non-Isothermal Crystallization of Polymers"*** J. Berger, W. Schneider and A. Köppl, TU Vienna (Austria)	6/3 ***"Computer Monitored Injection Moulding of Urea Formaldehyde: On-line Shear and Elastic Flow Characterisation"*** P. D. Coates and D. A. Sharp, U of Bradford (UK)
10h00	9/4 ***"Orientation and Crystallization During the Stretching of Polyester Films"*** G. le Bourvellec, L. Monnerie and J. P. Jarry, Rhone Poulenc Research, Saint Fons (France)	6/4 ***"A Contribution to the Silane Grafting and Crosslinking Process of Polyethylene"*** H. G. Fritz and H. Yu, IKT, Stuttgart (FRG)
10h30	Break	
11h00	9/5 ***"Structure Formation in Crystallizable Blend Flows"*** A. J. McHugh, S. J. Sakellarides and D. A. Tree, U of Illinois, Urbana (USA)	6/5 ***"Imidification Reaction by Reactive Extrusion"*** M. Lambla and J. Druz, Ecole d'Applic. des Hautes Polym., Strasbourg, T. Valla, Centre de Mise en Forme, Valbonne, and A. Nicco, CdF Chimie, Bully-les-Mines (France)
11h30	9/6 ***"Influence of Flow History on Polymer Blend Morphology"*** R. Ramanathan and D. G. Baird, Virginia State U, Blacksburg (USA)	6/6 ***"Coupling of Reactive Polystyrene and Polyethylene in Melts"*** W. E. Baker and M. Saleem, Queen's U, Kingston (Canada)
12h00	9/7 ***"Orientation Development in Plane Welding Flows-Modelling and Flow Birefringence Experiments"*** K.-H. Wei, M. Nordberg III and H. H. Winter, U of Massachusetts, Amherst (USA)	6/7 ***"Reactive Polymer Compounding"*** M. Rätzsch, Institut für Technologie der Polymere, Dresden (GDR)
12h30	9/8 ***"Entanglements as an Element of Polymer Texture"*** B. Qian, J. Qin, Z. Wu and P. Hu, Textile U, Shanghai (China)	6/8 ***"Ternary System of PVC, Unsaturated Polyester and Styrene Monomer for Reactive Polymer Processing"*** S. N. Abrahami, D. M. Vofsi and A. E. Bershadsky, Institute of Plastics, Haifa (Israel)
13h00	Lunch	Canteen

April 9, Afternoon Sessions

	Room 47.2	Room 47.3
14h00	New Technologies (continued) 10/9 ***"Solid-Phase Forming and Coforming of High-Performance Thermoplastics"*** O.C.Raspor,Dow Chemical Co.,Midland(USA) and H.Bongarts,Dow Chemical Europe, Horgen(Switzerland)	Rheology (continued) 3/9 ***"Flow Induced Crystallization of HDPE Observed by Capillary Rheometry"*** G. Titomanlio, Ist. Ing. Chimica, Palermo, and G. Marrucci, U of Naples (Italy)
14h30	10/10 ***"Multilayer Ceramics"*** H. J. Birkenbeil, IBM Deutschland, Sindelfingen (FRG)	3/10 ***"Dynamic Measurements on Liquid-Crystalline Solutions of Poly(p-Phenylene-2,6-Benzobisthiazole)"*** M. Horio, U of Kyoto, and E. Kamei, K. Matsunobu, Ube Industries, Osaka (Japan)
15h00	***Liquid Crystals*** 10/11 ***"Processing Influence on Properties of Liquid Crystal Polymers"*** A. Knutsson, J. Martinsson and M. Robertsson, Ericsson Telecom, Kristianstad (Sweden)	3/11 ***"Non-linear Viscoelasticity of ABS Polymers in the Molten State"*** T. Masuda, M. Takahashi and L. Li, Kyoto U (Japan)
15h30	10/12 ***"Properties of Liquid Crystal Injection Mouldings"*** G. Menges, T. Schacht and S. Ott, IKV Aachen (FRG)	3/12 ***"Rheological and Dielectric Properties of Short Fiber-Polymer Suspensions"*** D. R. Boyington and D. S. Soong, U of California, Berkeley (USA)
16h00	10/13 ***"Effects of Molecular Weight on Rheology and Molecular Orientation of Thermotropic Liquid Crystalline Copolyesters"*** K. Fujiwara, Idemitsu Petrochemical Co., Kimitsu, and M. Takahashi and T. Masuda, Kyoto U (Japan)	3/13 ***"Application of a Blending Rule for the Dynamic Viscosity of Polymer Melts"*** H. Schuch, BASF, Ludwigshafen (FRG)
16h30	Break	
17h00 - 22h00	***Poster Sessions*** Introduction, Presentation and Discussion	

	Room 47.4	Room 47.5
14h00	Structure Development (continued) 9/9 ***"Structure Development During Molding of the Thermotropic Copolyester XYDAR"*** J. Blackwell, H.-M. Cheng and A. Biswas, Case Western Reserve U, Cleveland, and N. D. Field, P. D. Frayer and R. Layton, Dartco Manufacturing, Augusta (USA)	Reactive Processing (continued) 6/9 ***"Interactions of Processing, Morphology and Mechanical Properties of Polyurethane-Polyester IPN"*** T. J. Hsu, K. J. Wang and L. J. Lee, Ohio State U, Columbus (USA)
14h30	9/10 ***"Microprocessing - Preparation of Langmuir Blodgett Monolayer and Multilayer Films"*** J. B. Lando, S. E. Rickert, G. Dipoto, L. Uitenham and M. Biddle, Case Western Reserve U, Cleveland (USA)	6/10 ***"Kinetics of the Reaction of Water and Tolulene Diisocyanate"*** B. Sethuram and G. A. Campbell, Clarkson U, Potsdam (USA)
15h00	9/11 ***"Lattice Deformation and Meso-phase Structure in PET Drawn by Solid State Coextrusion"*** T. Sun, A. Zhang, F. Li and H. Zhou, Textile U, Shanghai (China), and R. S. Porter, U of Massachusetts, Amherst (USA)	6/11 ***"Phase Localised Catalysis in Reaction Processing"*** B. G. Willoughby, Rapra Technology Ltd., Shrewsbury (UK)
15h30	9/12 ***"Production of Highly Oriented Polymers by Die-Drawing"*** G. Craggs and I. M. Ward, U of Leeds (UK)	6/12 ***"Ion Aggregation in Thickened Polyester Resins - S.A.X.S. Study on Models"*** C. Habassi, M. Brigodiot, A. Fradet and E. Marechal, U P. et M. Curie, Paris (France)
16h00	9/13 ***"Processing Characteristics and Structure Development in Cold Rolling Poly Ether Ether Ketone"*** M. Niemeyer and M. Cakmak, U of Akron (USA)	6/13 ***"A New Microwave Applicator for the Continuous Vulcanisation of Rubber"*** P. J. Luypaert, Katholieke U Leuven (Belgium)
16h30	Break	

See pages 14 to 17

April 9, Poster Sessions

17h00	Introduction to Posters	
18h00 - 22h00	Presentation and Discussion	
	Room 47.2	Room 47.3
	Rheology and Polymer Chemistry P/1 *"Relationship Between Steady-state and Dynamic Rheometry for Polymer Melts"* S. Venkatraman, Raychem, Menlo Park (USA)	**Shaping Processes I** P/16 *"Complete Viscoelastic Model for Non-isothermal Extrusion in a Channel"* N. Famili and A. I. Isayev, U of Akron (USA)
	P/2 *"Complex Melt Fluidity Concept as a New Viscoelastic Parameter"* V. Verney and A. Michel, CNRS, Vernaison (France)	P/17 *"A 3-D Finite Element Model for Non-Newtonian Fluid Flow"* M. Robichaud and P. A. Tanguy, U Laval, Quebec (Canada)
	P/3 *"A Predictive Model for the Effect of Molecular Properties on the Steady Shear Viscosity of Polystyrene"* M. Adams and G. A. Campbell, Clarkson U. Potsdam (USA)	P/18 *"Numerical Determination of the Swelling Ratio for Viscoelastic Incompressible Liquids in an Axisymmetric Geometry by Using the Concept of Stream Tubes"* P. Andre and J. R. Clermont, Inst. de Mecanique de Grenoble (France)
	P/4 *"Studies of the Deformation Behaviour of Thick Section Polypropylene at High Strain Rates in the Production of Oriented Geogrids"* P. D. Coates, D. I. Ellis and S. M. Pourmahnaei, U of Bradford (UK)	P/19 *"Calculating the Melting and Pressure Performance of Single Screw Extruders by Approximation Equations"* H. Potente and M. Koch, U. of Paderborn (FRG)
	P/5 *"A Modified Cone and Plate Rheometer for the Measurement of Material Functions"* L. M. Quinzani and E. M. Valles, UNS-Conicet, Bahia Blanca (Argentina)	P/20 *"Optimisation of Devolatilizing Single Screw Plasticating Machines"* H. Potente and A. Fornefeld, U of Paderborn (FRG)
	P/6 *"A New Shear Rheometer for Molten Polymers"* J.M.Dealy and A.J.Giacomin, McGill U, Montreal (USA)	P/21 *"A new Method of Profile Die Calculation"* Y. C. Peng and D. W. Sun, Inst. of Technology, Guangzhou (China)
	P/7 *"Rheological Properties of Filled and Blended Polymers"* D. Gu, D. Pu and D. Wu, U of Science and Technology, Chengdu (China), and W. Wen, Beijing Plastics Co. (China)	P/22 *"Molten Polymer Flow in a Spiral Mandrel Die"* J. Vlcek, J. Perdikoulias and J. Vlachopoulos, McMaster, U Hamilton (Canada)

University, 47 Pfaffenwaldring

Rooms 47.2–47.5

Foyer

Room 47.4	Room 47.5
Shaping Processes II P/31 ***"Static Mixing Technology in the Production of Polymers"*** A. Heierle, Sulzer Bros., Winterthur (Switzerland)	**Morphology and Properties** P/46 ***"Influence of the Processing Variables on the Electrical Conductivity of Poly(p-Phenylene Sulfide)"*** R. E. S. Bretas and G. Lunardi, U. Federale, Sao Carlos (Brazil)
P/32 ***"Blown Film Bubble Shape – the Influence of the Air Ring"*** B. Cao and G. A. Campbell, Clarkson U, Potsdam (USA)	P/47 ***"The Determination of Polymer-Polymer Compatibility in Polymer Blends by Ultrasonics"*** R. P. Singh, Indian Inst. of Technology, Kharagpur (India)
P/33 *"The Effects of Processing Variables on Carbon Fibres Properties in a Continuous Process "* Li Rengyuan, Z. Jun and L. Jie Anhui University, Hefei (China)	P/48 ***"A Theoretical Approach to Mechanical Model of Polyblends in Phase Inversion and Its Application"*** T. Sun, D. Chen and H. Zhou, Textile U, Shanghai (China)
P/34 ***"Calender Lines for the Manufacture of Plastic Films"*** K. Marquardt, Berstorff GmbH, Hannover (FRG)	P/49 ***"Studies on Polyblends of Polycarbonate with ABS"*** X. Xu, X. Zhu and L. Li, Shanghai Jiao Tong U (China)
P/35 ***"Experimental Research of Controll-Thickness Precision of Calendered Film"*** W. K. Sun, Second Light Industrial Bureau, Harbin (China)	P/50 ***"Thermal and Crystallization Behaviour of Blends of Polyphenylene Sulphide and High Density Polyethylene"*** V. M. Nadkarni, National Chemical Laboratory, Pune (India)
P/36 ***"Expanding Matrix Systems for New Laminating Processes"*** E. Kamps and U. Massen, Ciba-Geigy GmbH, Wehr (FRG)	P/51 ***"Study of Morphology and Structure in Polycarbonate Polyethylene Blends"*** Z. Zhang, S. Li and X. Tong, Tsinghua U, Beijing (China)
P/37 ***"A Laboratory Unit for Obtaining Realistic Processing Data for Elastomer Injection Moulding Processes"*** H.-J. Graf and W. P. Lauhus, Klöckner Ferromatik Desma, Achim (FRG)	P/52 ***"Morphological Characteristics of Thermotropic Liquid Crystalline Cellulose Derivatives During Processing"*** B. Liang, Textile U, Shanghai (China)

April 9, Poster Sessions (continued)

	Room 47.2	Room 47.3
–	Rheology and Polymer Chemistry (continued) P/8 ***"Rheology of Concentrated Fiber Suspensions"*** M. A. Bibbo and R. C. Armstrong, Massachussetts Inst. of Technology Cambridge (USA)	Shaping Processes I (continued) P/23 ***"Recent Advances in Wire-coating Simulation"*** E. Mitsoulis, U of Ottawa (Canada)
	P/9 ***"Testing the Die-swell Behaviour of Polymers During Extrusion"*** L. Schöne, Brabender OHG, Duisburg (FRG)	P/24 ***"System Analysis and Morphological Classification of Moulds for Injection Moulding of Polymers"*** I. Catic and P. Raos, U of Zagreb, and N. Razi, R. Koncar Oour Engnrg., Zagreb (Yugoslavia)
	P/10 ***"Predicting Spiral Flow of Thermoplastic Melts Using Similarity Criteria"*** N. S. Rao, Consultant, Lienen (FRG)	P/25 ***"Pressure and Temperature Distribution in Cavity During Injection Mould Filling (Part II)"*** Y. Oyanagi and K. Kubota, Kogakuin U, Tokyo (Japan)
	P/11 ***"The Speckle Photography in the Rheological Measurement of Polymer Systems*** Y. Ivanov, V. Kavardzikov and L. Hadzikov, Academy of Sciences, Sofia (Bulgaria)	P/26 ***"Flow Visualization of the Motions of Elastomers and Molten Plastics in Batch and Continuous Twin Screw Mixers"*** K. Min, M. Kim and J. L. White, U of Akron (USA)
	P/12 ***"Influence of Titanate Coupling on Rheological Properties of $CaCO_3$ Filler PVC System"*** Q. Cai and R. Jin, Polytechnical U, Hefei (China)	P/27 ***"Orientation Studies During Flow By Light Scattering Measurements"*** K. Sondergaard and J. Lyngaae-Jorgensen, Inst. for Kemiindustri, Lyngby (Denmark)
	P/13 ***"A Study on the Chemical Kinetics of Polyester Alkaline Hydrolysis"*** W. Qian, Inst. of Silk Textile Technology, Suzhou (China)	P/28 ***"Measurement of Three-dimensional Fiber Orientation in Fiber Reinforced Thermoplastics"*** T. Konicek and C. L. Tucker III, U of Illinois, Urbana (USA)
	P/14 ***"Halogenfree, Flame Retardant Compounds for Safety Cables"*** H. Widler, Standard Electric Lorenz AG, Stuttgart (FRG)	P/29 ***"Mathematical Modelling of Fibre Orientation in Polymer Processing"*** H. El-Sobky, UMIST, Manchester (UK)
	P/15 ***"Anionic Polymerization of Linear Ultra-high Molecular Weight Polyamide 6"*** J. L. Markhorst and J. A. Juijn, Enka Research Institute, Arnhem (The Netherlands)	P/30 *"On-line Particulate Analysis of Polymer Melts and Compounds"* D.Mettlen,Schwing Verfahrenstechnik GmbH,Neukirchen-Vluyn(FRG)

	Room 47.4	Room 47.5
	Shaping Processes II (continued) P/38 ***"Structure/Toughness Variations in Polypropylene Injection Mouldings"*** M.W. Murphy and M.J. Bevis, Brunel U, Uxbridge, and K. Thomas, NPL, Teddington (UK)	Morphology and Properties (continued) P/53 ***"Influence of Molecular Structure and Processing on the Thermal-Mechanical Performance of Thermotropic Copolyesters"*** H. N. Yoon and M. Jaffe, Celanese Res. Co., Summit (USA)
	P/39 ***"Packing-Cooling Stage in Injection Molding of Thermoplastics"*** D. Huilier, C. Lenfant, J. Terrisse and R. Deterre, Ecole d'Application des Hauts Polymeres, Strasbourg (France)	P/54 ***"Physical Properties of Films from LDPE/LLDPE and HDPE/LLDPE Blends"*** V. Musil, B. Pregrad and B. Zerjal, U of Maribor (Yugoslavia)
	P/40 ***"Injection Molding with Reduced Packing"*** W. Friesenbichler and W. Knappe, Montanuniversität Leoben (Austria)	P/55 ***"Boundary Layers of Injection Molded Polypropylene Pieces"*** J. Koppelmann and E. Fleischmann, Montan-U Leoben (Austria)
	P/41 ***"Experimental Study of the Filling Stage of Two Industrial Molds: A Skiing Shoe and a Car Bumper, Comparison With a Calculation Program"*** B. Alles, G. Dehay, P. Lerebours and G. Grosdidier, Atochem, Serquigny, B. Ginglinger, Billion, Oyonnax, and J. F. Agassant and M. Vincent, Ecole des Mines de Paris, Valbonne (France)	P/56 ***"Influence of Injection Moulding Variables on Knit Lines Structure of Nylon 6"*** S. Piccarolo, A. Rallis and G. Titomanlio, Ist. Ing. Chimica, Palermo (Italy)
	P/42 ***"Effects of Processing Parameters on the Strength of Weld Line in Injection Molded FRTP"*** H. Hamada, Z. Maekawa and T. Horino, Kyoto Inst. of Tech., and K. Tomari, Osaka Municipal Tech. Res. Inst. (Japan)	P/57 ***"The Deformation of PEEK-Carbon Fibre Laminates Under Strain Recoverable Conditions"*** D. J. Groves, ICI Petrochemicals & Plastics, Middlesbrough (UK)
	P/43 ***"Experimental Study and Mathematical Simulation of the Processing of Unsaturated Polyester by Pultrusion"*** D. Lalart, CdF Chimie, Mazingarbe, and G. Behar, CdF Chimie, Rouvroy (France)	P/58 ***"Creep Induced Buckling of Plastic Materials"*** A. Cohen and C. B. Arends, Dow Chemical Co., Midland (USA)
	P/44 ***"Rolling-Drawing: A Processing Technique to Produce High Performance Sheet Materials"*** K. R. Tate, A. R. Perrin and R. T. Woodhams, U of Toronto (Canada)	P/59 ***"Properties of Wolastonite/Mica Filled Polyamide 6"*** P. A. Järvelä, P. K. Järvelä and P. Törmälä, Tampere U of Technology, and J. C. Le Bell, Oy Partek Ab, Parainen (Finland)
	P/45 ***"Quality Improvement by Progress in Pneumatic Conveying and Small Chemicals Weighing"*** H. Hoppe, Waeschle GmbH, Ravensburg (FRG)	P/60 ***"A Mineral Wool Based Composite"*** P. K. Järvelä, P. A. Järvelä and P. Törmälä, Tampere U of Technology, and J. C. Le Bell, Oy Partek Ab, Parainen (Finland)

April 10, Morning Sessions

	Room 47.2	Room 47.3
	Symposium 4: **Continuous Shaping Processes** **Co-chairmen** *E. Uhland,* Werner & Pfleiderer, Stuttgart (FRG) *J. F. Stevenson,* GenCorp, Akron (USA) *T. Kanai,* Idemitsu Chemical Co., Ichihara (Japan)	Symposium 12: **Polyblends** **Co-chairmen** *J. Lyngaae-Jorgensen,* Inst. for Kemiindustri, Lyngby (Denmark) *L. A. Utracki,* IMRI, Boucherville (Canada) *S. Li,* East China Inst. of Chemical Technology, Shanghai (China)
8h15	4/1 ***"Structure Development During Processing"*** M. M. Denn, U of California, Berkeley (USA)	12/1 ***"The Processing Window for Block, Graft and Star Copolymers"*** I. C. Sanchez, Alcoa Labs., Alcoa Center, M. O. de la Cruz, Northwestern U, Evanston (USA)
9h00	***Die Flow*** 4/2 ***"Use of the Finite Element Method to Interpret Viscous and Viscoelastic Effects in Blade Coating"*** T. Sullivan, AT & T Bell Labs., Murray Hill, S. Middleman, U of California, La Jolla, and R. Keunings, U of California, Berkeley (USA)	12/2 ***"Entanglement and Friction Between Dissimilar Chains in Compatible Polymer Blends"*** S. Wu, Du Pont, Wilmington (USA)
9h30	4/3 ***"Interface Shape in Coextrusion"*** A. N. Hrymak, A. Karagiannis, H. Mavridis and J. Vlachopoulos, McMaster U, Hamilton (Canada)	12/3 ***"On the Influence of Interfacial Slip on Melt Flow Porperties of Polymer Blends"*** J. Lyngaee-Jorgensen, Inst. for Kemiindustri, Lyngby (Denmark)
10h00	4/4 ***"Recent Advances in the Finite Element Modelling of Viscoelastic Fluid Flow"*** A. Fortin, Ecole Polytechnique, Montreal, and M. Fortin, M. Gadbois and P. A. Tanguy, U Laval, Quebec (Canada)	12/4 ***"Modification and its Mechanism of PVC/CPE Blends with Coupling Agent"*** C. Song, K. Li and S. Li, East China Inst. of Chemical Technology, Shanghai (China)
10h30	Break	
11h00 – 13h00	Morning Sessions (Continued)	

	Room 47.4	Room 47.5
	Symposium 8: **Fibers and Films (Drawing Operations)** **Co-chairmen** *P. J. Lemstra,* TH Eindhoven (The Netherlands) *S. Kase,* Kyoto Inst. of Technology (Japan)	Symposium 7: **Rubber Processing** **Co-chairmen** *G. Pampus,* Deutsches Institut für Kautschuktechnologie, Hannover (FRG) *L. F. Ramos de Valle,* Centro de Investigacion en Quimica Aplicada, Saltillo (Mexico)
8h15	8/1 ***"A Comparison of Mathematical Modeling with On-line Experimental Measurements of Dynamics and Structure Development During High Speed Melt Spinning of Synthetic Filaments"*** J. E. Spruiell, J. Bheda, K. F. Zieminski, F. Lu and C. C. Bai, U of Tennessee, Knoxville (USA)	7/1 ***"Example of a Flexible Manufacturing Station for Thermoplast-Rubber Articles"*** G. Menges, IKV Aachen (FRG)
9h00	***Fibers*** 8/2 ***"Maxwell Viscoelasticity in Dynamic Melt Spinning Model"*** S. Kase, Kyoto Inst. of Technology (Japan)	7/2 ***"A New Concept for Processability Characterization of Raw Rubbers"*** J. Markert, Hüls AG, Marl (FRG)
9h30	8/3 ***"Influence of the Molecular Weight in the Polypropylene Spinning"*** C. Prost and A. Michel, CNRS, Vernaison, and R. Hagege and G. Nemoz, Inst. Textile, Lyon (France)	7/3 ***"Influence of the Macrostructure on Rheology and Processibility of Polybutadienes"*** R. Koopman, G. Marwede and B. Stollfuss, Bayer AG, Leverkusen (FRG)
10h00	8/4 ***"Studies on High Speed Spinning of PET – the Dynamic Analysis of Spinning Line at the Speed of 3600 m/min"*** J. Cheng, Inst. of Silk Textile Technology, Suzhou (China)	7/4 ***"Rheovulkameter – for Fast and Easy Testing Processability of Rubber Compounds"*** K.-H. Moos, Göttfert GmbH, Buchen (FRG)
10h30	Break	
11h00 – 13h00	See pages 20/21	

April 10, Morning Sessions (Continued)

	Room 47.2	Room 47.3
11h00	Continuous Shaping Processes (Continued) 4/5 ***"A Survey of Recent Developments in the Numerical Simulation of Viscoelastic Flows"*** R. Keunings, U of California, Berkeley (USA)	Polyblends (Continued) 12/5 ***"Rheology and Phase Separation in PS/PVME Blends"*** L. Choplin, R. E. Prud'homme and W. Zaldivar, U Laval, Quebec (Canada)
11h30	***Dynamic Modelling and Control*** 4/6 ***"Dynamic Modelling of a Single Screw Extruder"*** C. Guerrero, P. J. Carreau and I. Patterson, Ecole Polytechnique, Montreal (Canada)	12/6 ***"Linear Low Density Polyethylenes and Their Blends: Part 4, Shear Flow of LLDPE Blends with LLDPE and LDPE"*** L. A. Utracki and B. Schlund, IMRI, Boucherville (Canada)
12h00	4/7 ***"An Accumulator Device to Compensate for Short-term Cyclic Output Variation in a Continuous Process"*** T. E. Codispoti and J. F. Stevenson, GenCorp, Akron (USA)	12/7 ***"Flow-induced Textures in Multiphase Polymers and Their Effect on Physical Properties"*** M. J. Folkes, F. Ehtaiatkar and H. Nazockdast, Brunel U, Uxbridge (UK)
12h30	4/8 ***"State-Variable Temperature Controller for Extruders"*** S. Dormeier and G. Brüntrup, U Paderborn (FRG)	12/8 ***"A Study on Polymer Blending Microrheology: The Prediction of Domain Sizes"*** J. J. Elmendorp, Koninklijke Shell, Amsterdam, and A. K. van der Vegt, U of Technology, Delft (The Netherlands)
13h00	Lunch	

	Room 47.4	Room 47.5
11h00	Fibers and Films (Continued) 8/5 ***"Physical Structure in Relation to Process Conditions and Properties of Poly(Ethylene Terephthalate) Yarns"*** R. Huisman and H. M. Heuvel, Enka Res. Inst. Arnhem (The Netherlands)	Rubber Processing (Continued) 7/5 ***"Control of Plastication During Mixing Process"*** K. Miyasaka, Yokohama Rubber Co., Kanagawa (Japan)
11h30	8/6 ***"Gel Spinning of Flexible Macromolecules"*** P. Lemstra, TU of Eindhoven (The Netherlands)	7/6 ***"A Dispersive Mixing Testing Apparatus"*** R. K. Chohan, A. Nir and Z. Tadmor, Technion Haifa (Israel)
12h00	8/7 ***"Drawing and Heating Effects on the Morphology of Gel Spinning PE Filament"*** Z. Wu, P. Lu and A. Zhang, Textile U, Shanghai (China)	7/7 ***"Process Analysis of a Laboratory Internal Mixer"*** F. Grajewski and G. Menges, IKV Aachen (FRG)
12h30	8/8 ***"Coagulation Studies for Cellulose in the Ammonia/Ammonium Thiocyanate (NH_3/NH_4SCN) Direct Solvent System"*** C.-K. Liu and J. A. Cuculo, North Carolina State U, Raleigh (USA)	7/8 ***"Milling Behavior of Compounded and Fiber Reinforced Elastomers"*** L. A. Goettler, Monsanto, Akron (USA)
13h00	Lunch	Canteen

April 10, Afternoon Sessions

	Room 47.2	Room 47.3
14h00	Continuous Shaping Processes (continued) 4/9 *"A Criterion for Estimation of Polymer Temperature Fluctuation in a Single Screw Extrusion Process"* K. Wilczynski, Politechnika Warszawska (Poland)	Polyblends (continued) 12/9 *"Analysis of the Efficiency of a Mixing Device Through the Determination of Residence Time Distribution"* A. Poitou and J. F. Agassant, Ecole des Mines de Paris, and M. Dolidier, C. Herviou and G. Riglet, Rhône-Poulenc Rech., Aubervilliers (France)
14h30	***Single Screws*** 4/10 *"Flow Patterns in the Melting Zone of a Single-screw Extruder"* I. Bruker and G. S. Balch, General Electric, Schenectady (USA)	12/10 *"Phase Morphology of a Model Polyblend/Alloy Concomitant to the Melt Flow in a Twin-Screw Industrial Mixer"* A. P. Plochocki, S. S. Dagli and M. Mack, Stevens Institute, Hoboken (USA)
15h00	4/11 *"Extrusion Characteristics of Power Law Fluids in Screw Pumps"* C. J. Rauwendaal, Raychem, Menlo Park (USA) and J. F. Ingen Housz, TH Twente, Enschede (The Netherlands)	12/11 *"A Basic Study on Polymer Blends Containing a Thermotropic Liquid Crystalline Copolyester and Polyamides"* B. Liang, C. Dai, Q. Yu, Textile U, and Y. Shi, Inst. of Synthetic Resins, Shanghai (China)
15h30	4/12 *"Flow-Induced Torque in a Barrel Screw System"* G. Mennig, Deutsches Kunststoff-Institut, Darmstadt (FRG)	12/12 *"Polyethylene Terephtalate Blends – Effect of Selective Crosslinking on Permeability and Morphology"* P. M. Subramanian, Du Pont, Wilmington (USA)
16h00	Break	
16h30	***Twin Screws*** 4/13 *"Statistical Evaluation of Process Parameters in a Counter Rotating Twin Screw Extruder: Effects on Mixing"* S. F. Quigley and S. P. Petrie, U of Lowell (USA)	12/13 *"Bulk Versus Surface Compatibility of Polycarbonate/Poly(Hexamethylene Sebacate) Blends as a Function of Molecular Weight"* K. S. Shih and C. L. Beatty, U of Florida, Gainesville (USA)
17h00	4/14 *"On the Modelling of Corotating Twin Screw Extruders"* H. E. H. Meijer, DSM Research, Geleen, and P. H. M. Elemans, TU Eindhoven (The Netherlands)	12/14 *"Structure-Property Relationships in Polyamide-ABS Blends"* D. V. Howel and M. D. Wolkowicz, Borg Warner Chemicals, Washington (USA)
17h30 – 18h00	4/15 *"Model Formulation for Material Feeding in Twin Screw Extruders"* B. Poltersdorf and L. Fiedler, TU Leuna-Merseburg (GDR)	12/15 *"Studies on the Simultaneous Interpenetrating Networks of Polybutadiene-based Polyurethane/Poly(methyl methacrylate-co-Glycol Dimethacrylate)"* D. M. Jia, M. Z. Wang, C. J. You and B. Wu, South China Inst. of Technology, Guangzhou (China)

	Room 47.4	Room 47.5
14h00	Fibers and Films (continued) 8/9 ***"Two-stage Drawing of Ultra-high Molecular Weight Polyethylene Reactor Powders"*** T. Kanamoto, T. Ohama, K. Tanaka and M. Takeda, Science U Tokyo (Japan), and R. S. Porter, U of Massachusetts (USA)	Rubber Processing (continued) 7/9 ***"Basic Studies of Extrusion of Rubber Compounds"*** R. Brzoskowski, J. L. White, K. Kubota, N. Nakajima, F. C. Weissert and K. Min, U of Akron (USA)
14h30	8/10 ***"Transient Elongational Viscosities and Drawability of Polymer Melts"*** H. M. Laun and H. Schuch, BASF, Ludwigshafen (FRG)	7/10 ***"Temperature Development in a Rubber Processing Pin Barrel Extruder"*** H.-J. Laake and N. Räbiger, Deutsches Institut für Kautschuktechnologie, Hannover (FRG)
15h00	***Films*** 8/11 ***"Elongational Flow of High Density Polyethylene Samples and Bubble Instability in Film Blowing"*** M. Fleissner, Hoechst AG, Frankfurt (FRG)	7/11 ***"The Extrusion of Tire Profiles – Free of Tension and without Air Bubbles"*** W. Schiesser, Interplastica, Zürich (Switzerland)
15h30	8/12 ***"TEM, WAXS and Laser Doppler Anemometry Studies of Highly Oriented LDPE Film"*** A. J. M. S. Robeerst, DSM Research, Geleen (The Netherlands)	7/12 ***"Mill Processability, Rheology and Structure Differences of Polyacrylate Elastomers"*** N. Nakajima, R. A. Miller, U of Akron and E. R. Harrell, BF Goodrich Comp., Avon Lake (USA)
16h00	Break	
16h30	8/13 ***"Isothermal and Non-isothermal Models for Film Extrusion"*** P. Barq, J. F. Agassant, and J. M. Haudin, Ecole des Mines de Paris, Valbonne (France)	***Rubber/Thermoplastics Blends*** 7/13 ***"Rubber/Thermoplastic Blends: Viscoelastic and Thermal Properties"*** L. F. Ramos de Valle, CIQA, Saltillo (Mexico)
17h00	8/14 ***"Processability of T-Die Film Extrusion"*** T. Kanai and A. Funaki, Idemitsu Petrochemical Co., Ichihara (Japan)	7/14 ***"Polyblend of Polystyrene and Polyacrylate Rubber Modified by Polystyrene Macromer and Butyl Acrylate Graft Copolymer"*** S. Ying, C. Hu and K. Ma, Inst. of Chemical Technology, Shanghai (China)
17h30 – 18h00	8/15 ***"Mechanical Properties of Uniaxially and Biaxially Rolled Polymer Sheets"*** T. Kikuma, Y. Higashida, I. Tanaka and T. Kawanami, Nippon Steel Corp., Kitakyushu City (Japan)	7/15 ***"Morphology and Properties of HDPE/Butyl Rubber Blends*** G. Liu, X. Dong, L. Cai and X. Xu, U of Science and Technology, Chengdu (China)

Working Parties

The PPS offers an environment conducive to solving a wide range of polymer processing related problems through a network of its ad-hoc Working Parties.

Membership in a Working Party is open to industrial, academic and governmental organizations from all parts of the world. In a given area of interest, the Working Party will bring together the enrolled persons and, if necessary, outside specialists, in order to help establish working relationships among the participating organizations and disseminate information produced by the Working Party.

Each Working Party will choose its own mode of operation, including sharing of information, depending on the nature of its interest. It is expected, however, that the activities of the Working Parties will culminate in their open sessions at the Annual PPS Meetings to ensure continuous contact to the PPS membership at large.

The purpose of the below scheduled first meetings is to initially form the Parties and to precisely state their thematic ranges.

THURSDAY, April 9, 1987

18h30–19h00	General discussion	Room 47.2
19h00–20h00	Special discussions of the proposed topics	
	– Simulation of injection molding and extrusion	Room 47.2
	– Structure development in polymer processing	Room 47.3
	– Compounding: Technology and characterization for polymer blends and composites	Room 47.4
	– Reactive polymer processing	Room 47.5

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- Annual meetings of international membership focused on processing of plastics and rubber.
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  April 1988; New Jersey Meadowlands (USA)
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  Next regional meeting:
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THE POLYMER PROCESSING SOCIETY

THIRD ANNUAL MEETING

Stuttgart, West Germany: April 7-10, 1987

ABSTRACTS

Plenary Lecture

PROPERTIES BY MOLECULAR DESIGN OF MATERIALS

G. Wegner, Max-Planck-Institut für Polymerforschung
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The molecular origin of the macroscopic behaviour and performance of polymer materials is reasonably well understood. The design of new materials is based on these insights and takes advantage of newly developed or considerably improved methods to achieve and handle supramolecular architectures.

The fine tuning of attractive and dispersive forces between different molecules or segments of the same molecule allows for the defined production of self-reinforcing systems, high-impact resistent materials and colloidal systems of unsurpassed stability. Understanding of the electronic interaction between molecules leads to the design of so-called organic metals, i.e. polymer materials of adjustable electric conductivity. The fact that a small number of individual molecules can be handled by the Langmuir-Blodgett-technique leads to unconventional polymer structures with promissing optical and non-linear optical properties. Thus, polymer science has entered another age of innovation with a large number of new challenges ahead.

Use polymer layers (like a soap film - by dipping) and run a laser through layers to make a "chip".

1/1 FEATURES OF POLYMER REACTION ENGINEERING

K.H. Reichert, Institut fuer Technische Chemie
der Technischen Universitaet Berlin, 1 Berlin 12,
Strasse des 17. Juni 135

After a short introduction concerning the classification of polymerization reactions, polymerization techniques and polymerization reactors the first part of the talk will be devoted to reactor design. Emphasis will be put on the performance of different polymerization reactors their selectivity with respect to polymer properties especially on molecular weight distribution. Another point of interest will be the stability and safety of polymerization reactors. In the second part of presentation, characteristic features of polymerization reactions will be presented from the point of view of polymer reaction engineering. Attention will be paid to the increase of viscosity of the reactor contents during the course of polymerization and its influence on kinetics, mass and heat transfer as well as on mixing and residence time distribution in the case of continuous reactors.
A further characteristic chemical engineering aspect of polymerization reactions is the removal of heat and its dependency on conversion. Some remarks will be made on this topic as well as on the sensitivity of polymerization reactions towards impurities.

1/2 MODELING AND OPERATION OF A CONTINUOUS POLYMERIZATION PROCESS TO OBTAIN EXTRA-PURE POLYMERS WITH DESIRED MOL. WT. AND DISTRIBUTION

SHINZO OMI, INEO IWATA, KIYOSHI INUBUSE, MAMORU ISO AND MOTOSHI SUKA*, DEPT OF CHEMICAL ENGINEERING, TOKYO UNIVERSITY OF AGRICULTURE & TECHNOLOGY, KOGANEI, TOKYO 184, JAPAN

A particular continuous polymerization process was designed and operated in order to produce contamination-free polymers in a small scale. The system is operated with a conventional stirred tank reactor (STR) or with a loop reactor (LR), either one designed to carry out bulk polymerizations without causing troubles which may arise from treating fairly viscous fluid. Both reactors have 1 litre capacity, and the agitation is driven by a magnetic device to prevent possible contaminations through the agitation seal if one employs an ordinary device. Monomer feed pump is also selected so that direct contact of monomer with driving shaft of the pump can be prevented. Polymer-monomer mixture leaving the reactor is introduced to a small-scale extruder, where monomer is separated, and pure polymer is extruded through the die.

Thermally initiated bulk polymerization of styrene was carried out at 403 K to investigate the feasibility of this particular system. Performance of the system was quite satisfactory, so far 40 % conversion was achieved with the mean residence time of 2.4 hr employing a single STR.

An all-purpose computerized reaction model, which is capable to simulate behaviours of monomer conversion, average molecular weight and molecular weight distribution, was developed. The performance of the system was monitored from the theoretical point of view using this model. Observed data agreed quite well with the calculated values. This particular model can predict the performance of any commercial reactor system (CSTR, tubular, tower or combination of these) regardless isothermal or nonisothermal operation. We believe this reactor system is quite feasible for the productions of polymers which are required extra-pure qualities such as optical fibers. Bulk polymerization of methyl methacrylate will be investigated soon after the capacity of a loop reactor was established.

*) Motoshi Suka is with Nippon Plant Technology Co. LTD.

1/3 GEL-PERMEATION CHROMATOGRAPHY AS A TOOL FOR THE REAL-TIME ESTIMATION OF THE CHAIN LENGTH DISTRIBUTION IN A POLYMERIZATION REACTOR

S. Ar. Papadopoulou and E.D. Gilles
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Universitaet Stuttgart,
Pfaffenwaldring 9, D-7000 Stuttgart 80

The distribution of the polymer molecules over their chain length determines many important technological properties of the polymeric product. If this fact is to be taken into account when controlling the quality of the produced polymer, especially under non-stationary conditions, sufficient information about the chain length distribution (CLD) should be continually available during the polymerization process.

Model-aided measurement methods (Kalman filter) provide the possibility of reconstructing on-line not directly accessible process states from the available measurements. These methods have found a wide area of application in order to estimate conversions of the reactants as well as characteristics of the CLD in polymerization reactors.

In the case of free radical polymerization in solution model-aided measurement methods have been developed and implemented considering easily available measurements such as the measurements of temperature, refractive index (R.I.), density etc. Nevertheless the CLD and its characteristics are not observable if only such measurements are used for filtering. The presence of disturbances influencing primarily the CLD, as well as the high parametric sensitivity of the filter algorithm for estimation under extreme but industrially important reaction conditions demand additional experimental information about CLD.

Gel-Permeation Chromatography (GPC) is a measuring procedure, which allows only time-discrete CLD measurements and introduces significant time delays in the system.

In order to overcome the deficiencies of both GPC (time delay of the measurement system) and estimation algorithms (non-observability of the states characterizing the CLD if only easily available measurements are used for filtering) a Kalman filter can be used considering on the one hand continuous measurements of temperature and R.I. and on the other hand sporadic time lagged GPC measurements.

The results obtained from the real-time implementation of this filter have proved its efficiency and practical importance.

1/4

DYNAMIC SCHEME OF THE POLYMERIZATION OF CAPROLACTAM

C.L.Tang, N.S.Huang, M.H.Chow and Q.H.Zhang
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The foundation of polymerization engineering in PRC is comparatively recent. During the first stage of the past 20 years, production of Nylon-6 was exclusively carried out in a large number of small sized VK tubes. This kind of operation can hardly fulfill the market demand both in quality and quantity. Critical situation requires a theoretical insight into the reacting system in the equipment.

(1)Taking into account the ring-opening,condensation and chain growth as the basic reactions, a system of chemical kinetic equations is developed, of which the general form is

$$\frac{du_n}{dt} = -2k_2\left[u_n C - \frac{W(C-\sum_{i=1}^{n} u_i)}{K_2}\right] - k_3\left[x(u_n - u_{n-1}) - \frac{u_{n+1}-u_n}{K_3}\right] + \begin{cases} 2k_2 \sum_{i=1}^{\frac{n+1}{2}} \left[u_{n-i}u_i - \frac{u_n W}{K_2}\right] & (\text{for odd } n) \\ 2k_2 \sum_{i=1}^{\frac{n}{2}-1} \left[u_{n-i}u_i - \frac{u_n W}{K_2}\right] + k_2\left[u_{\frac{n}{2}}^2 - \frac{u_n W}{K_2}\right] & (\text{for even } n) \end{cases}$$

(2)The heat generation is mainly charaterized by the formation of amide linkage in the polymers.

(3)A practical objective function $J=-Q_x\frac{dx}{dt}+Q_p\frac{dp}{dt}$ is set up,aiming at the optimization of operation conditions,where Q_x and Q_p are weights intentionally selected at any stage to intensify the monomer consumption or reinforce the degree of polymerization. Combination of (1)(2)(3) gives a host of rational operation conditions,i.e.,the distribution of temperature and water along the tube, at distinctive values of Q_x and Q_p.

(4)The temperature distribution is also critically observed in the radial direction. Therefore, heat conduction is considered to investigate this problem.

(5)A flow patten in stead of plug flow should be incorporated with (1)(2)(3)(4) to elaborate the original mathematical model.

1/5 MICROMIXING AND MACROMIXING IN POLYMERIZATION REACTORS

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Engineering College, 4370 Koethen, GDR

Experimental investigations of the styrene-acrylonitrile copolymerization have been carried out in a specially constructed reactor /1/ using different stirrer speeds.The residence time distribution of the reactor is that an ideally mixed countinuously operating tank reactor in the whole range of the investigated stirrer revolutions. There are steady state operating points for witch both the polymer mass fraction and the molecular nonuniformity may be increasing or decreasing as functions of stirrer speed. For model calculations of the reactor behaviour the idealized mixing limit cases-the micromixing model and the segregation model-were used. The kinetic model considers 2 thermic start reactions, 4 propagation reactions, 3 termination reactions by combination, 4 monomer transfer reaction, 4 solvent transfer reactions, and the gel effect. High stirrer speed approximates micromixing while for small stirrer revolutions the segregation degree increases. The influence of the stirrer speed on the polymer mass fraction can be explained by the autocatalytic reaction behaviour, while the dependence of the molecular nonuniformity on the stirrer revolution is a result of varying parts of transfer and termination reactions with increasing conversion. The Experiments and model calculations show that the results of Gerrens /2/and Biesenberger /3/ can not be generalised and that segregated flow for the considered reaction is not dangerous with respect to the product properties in a wide region of operating parameters unless temperature gradients are present in the reactor.

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Institution of Chemical Engineers,Symp.Ser. 87,1984, 125
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Chemie-Ing.-Techn.,Weinheim 52, 1980, 477
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1/6 CONTINUOUS MELT POLYMERIZATION OF POLYETHERIMIDE

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A new process for continuous melt polymerization of aromatic dianhydrides and diamines has been developed. The process consists of several integrated stages: feeding, melting, devolatilization, mixing, and advanced polymerization. The transport phenomena and coupled reaction rates have been studied in a corotating, intermeshing twin-screw reactor/extruder. Each stage in this process has been analyzed. The results show the importance of viscous heat for melting monomers, free surface generation in mass transfer, total shear strain in distributive mixing, and back mixing for extended residence time and advanced polymerization. High molecular weight polyetherimide ($\overline{M}_w = 50x10^{-3}$) was obtained with this process for a variety of conditions. The reactions were run with 3 mole % of monofunctional anhydride to cap the polymer ends at a specific molecular weight for the most desirable balance of mechanical and physical properties.

1/7

Gas Phase Polymerization Process of Propylene

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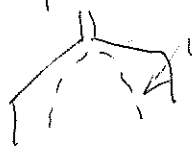
Through joint research with Montedison (now with Himont Inc., U.S.A.), Mitsui Petrochemical Industries, Ltd. (MPC) developed an ULTRA-HIGH PERFORMANCE CATALYST for polypropylene. MPC started the development of a gas phase process in 1974 and constructed in 1984 a commercial plant which has been operating smoothly to date.

The performance of the CATALYST is as follows: (1) It has extremely high activity, reaching more than, 1,000,000 g-PP/g-Ti (100 times higher than any conventional catalyst) and has long-sustained activity. Thus, the CATALYST eliminates deashing section in the process. (2) It simultaneously realizes sufficently high stereospecificity of the product (98% isotactivity index) without the need for atactic polymer removal. (3) The polymer particles obtained with the CATALYST are of good rigidity, spherical in shape and uniform in size, with excellent flowability (with no stickiness and formation of lumpy polymer), and does not necessarily call for pelletization. This superb morphology serves to ensure trouble-free operation of the said gas phase process, particularly in the case of high-ethylene-content impact copolymer production.

The characteristics of MPC's gas phase process technology with the use of such excellent CATALYST are as follows: (1) Low operation cost (consumptions of monomer and energy are 1,010 kg and 1.3 MM Kcal respectively, per ton of polypropylene), (2) Low investment cost (60 to 80% of that of conventional process), (3) Wide product coverage all with excellent quality ((a) homopolymers with good optical properties, high rigidity, good stretchability and good spinnability, (b) random copolymers with good optical properties and easy heat sealability, (c) directly polymerized impact copolymers with best balance of impact strength/rigidity, having a very wide MFR range (0.5 - 60) without using peroxide, (4) Stable operation (continuous yearlong operation without any formation of polymer build-up on the internal surface of reactors and their associated equipment); (5) Clean and safe process (these comes out no waste water and minimal off-gas with the latter being recoverable. Far less hydrocarbon inventory than conventional processes greatly contributes to operational safety.)

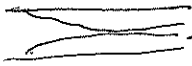
The said process and catalyst technologies have been highly evaluated throughout the world. Hence, they have been licensed to two U.S. and one Chiness companies, as well as the catalyst technology which has been licensed to over ten companies in the world.

thermosetting



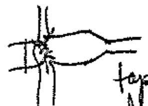
← plugging.
get narrower product.

Strasbourg 01.
Published Polymer Process Engineering Journal
went to prevent plugging
is there a critical wall shear stress? – e.g. continuous crosslinking polyethylene.
use a tube first,


← critical radius. –

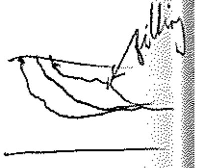
2nd order kinetics
Bosch pumps
~200 bar
critical nozzle
Re > 300
for good mixing

1/8 CONTINUOUS REACTIVE EXTRUSION OF CROSSLINKABLE MONOMERS


tapered channel.

T.G. Charbonneaux , K.J. Mikkelsen and C.W. Macosko
Department of Chemical Engineering and Materials Science
University of Minnesota, Minneapolis, MN 55455


polyol.


filling

at end of ~~pt~~ shot shoot polyol to kill rxn. & flush
get constant pressure at critical radius

To eliminate drying costs and solvent pollution problems there is a trend today in the coating industry toward coating a mixture of monomer and polymer, the monomer being polymerized either by heat or radiation. However, these thermal or radiation steps are still expensive, and add considerably to the size of a continuous coating operation. An alternative to initiating the polymerization of monomers by heat or radiation is to use mixing activated systems, where the polymerization starts as soon as the two (or more) monomers are brought into contact, just before the point of coating. This could eliminate, or at least greatly reduce the need for very energy consuming steps, and also reduce the size of the process. However, there are a lot of problems associated with such systems, the main one being that reactive polymer mixtures build viscosity rapidly. Moreover, the presence of solid surfaces causes shear flow, leading to varying extents of reaction and thus high viscosity gradients across any cross-section. In the case of crosslinking materials this leads to the formation of a layer of gelled polymer near the die walls, which causes a lack of dimensional stability for the extruded product and ultimately causes die plugging. This work intends to show that under certain conditions this problem can be avoided.

–OH
Mw~540
LF-168 (MDI)
ICI Rubicon
TONE-0305
UC
Polyol

tube < 0.8 mm give enough shear to keep from gelling.
– totally clean when run.

A simple, two component crosslinking polyurethane system, consisting of uretonomine modified MDI and a caprolactone based triol, was used. Using RIM-type impingement mixing and high pressure positive displacement pumps, these reactants were dispensed continuously through cylindrical dies. Using a "large diameter" die the pressure drop increases rapidly initially because of the rising viscosity and the progressive gel buildup. After a while the pressure seems to be approaching a plateau value, indicating that a steady state might indeed be possible. Stopping the reaction at different times and measuring the amount of buildup at different locations along the die shows that after a while the system seems to reach some critical diameter below which there is no more noticeable buildup. This critical diameter is reached first near the outlet of the die. The gradual pressure rise at later time is thus the planarization of this buildup, i.e. making the diameter uniform by building up toward the entrance. In view of these results, it seemed reasonable to start with a die of smaller diameter than the critical value. In this case a steady state is achieved immediately, with the final pressure being less than the one predicted by the assumption of undisturbed parabolic velocity profile with no slip at the wall. This indicates that the steady state might be due to a slip velocity at the wall that allows the residence time there to be less than the gel time of the material. The shear stress at which this was observed was approximately 10^4 Pa, which is significantly smaller than the critical stress at which slip is usually reported to occur for polyethylene. Similar behavior was observed for two other polyurethane systems, above wall shear stress of 0.8×10^4 and 1.4×10^4 Pa respectively.

high MW of polyol gives lower pressure rise

low MW
⇓
higher critical stress.

Lipshitz
+
Castro
+
Macosko

mechanism for unknown
– molecular migration
– catalyst aided lubrication
– stress aided depolymerization
↳ stress prevents –OH + NCO rxn.

An extension of this work is currently being investigated. It deals with the other limiting case, where the residence time in the die is more than the gel time of the material. In this case the hope is to continuously extrude a solid crosslinked profile. Very fast reacting systems, such as polyureas are used in this work. Preliminary experiments so far have proven that the process is feasible, but that it is very sensitive. Two different operating windows are thought to be possible; but more work is under way to elucidate the exact mechanism(s) responsible.

1/9 POLYMER CROSSLINKING IN PROCESSING OPERATIONS THROUGH CONTROLLED CHEMICAL REACTIONS : POLYVINYLCHLORIDE AND POLYETHYLENE

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The nucleophilic substitution of the chlorine atoms of polyvinylchloride with metal mercaptides obeys a SN_2 mechanism with steric control by the configurations according to which the reactivity of iso triads is greater than the reactivity of hetero triads. Such a reaction keeps its stereoselectivity in the condensed state and may be utilized to crosslink PVC in processing operations. For this purpose dimercaptan as crosslinking reactants have been synthesized through the coupling of O-mercaptobenzoic acid with α-ω diols and their alkaline and alkaline earth have been prepared. The efficiency of these crosslinking-agents in terms of induction time before change of viscosity, crosslinking speed and insoluble rate in tetrahydrofuran has been studied with the aid of Haake plasticorder equipped with an internal mixer.

A well-known route to crosslink polyethylene is the Sioplas process which is based upon radical grafting of vinyltrimethoxysilane before it can be further utilized to cause crosslinking through hydrolysis in the presence of water and dibutyltin dilaurate as a catalyst. Melt rheology is a powerfull tool to follow and characterize the formation of the chemical network which is consequential to the hydrolysis of methoxy-silane groups either by the traces of water in the polymer matrix after the grafting step (secondary reaction) or to the voluntary hydrolysis for the crosslinking step in the solid-state. The Si-O-Si bonds which are responsible for crosslinking have been located around crystallites with the aid of X-Ray scattering.

1/10

DEVELOPMENT OF THE SPHERICAL ULTRAFINE POLYMETHYL METHACRYLATE POWDER AND ITS APPLICATIONS FOR SURFACE MODIFICATION

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We have developed the spherical ultrafine uniform polymethylmethacrylate (PMMA) particles in the size range of 0.15 to 2 μm. These particles have been available for surface modification of various powder particles, such as toner, ceramics, organic powder, plastic powder, in powder/powder mixing system. PMMA monodisperse latexes of diameters larger than 0.5 μm have been prepared by emulsion polymerization with water-soluble initiators and a polymeric stabilizer, in conjunction with modified graft copolymers as costabilizer. In order to utilize PMMA particles as fine powders, latexes have been dried, and the dried powders have been crushed to single particle by a jet mill.

The effect of contact charging on adhesion of these PMMA particles to larger iron particle surfaces was studied by using blow-off charge measuring technique and a very large amount of charge was observed. On the other hand, by SEM observation and experimentation of mixing the PMMA with various powder particles, we found that the PMMA particles form a uniform layer on the powder particle surfaces and they easily produce the plastic films by mechanochemical method.

In this lecture, we would like to report on the production technique of ultrafine PMMA powders and a new technology for surface modification by mechanochemical method in powder/powder system.

1/11

THE FLOW OF GROWING VISCOSITY LIQUID IN TUBE UNDER THE FRONTAL POLYMERIZATION

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The flow of reactionable liquid in circular tube (the model of polymerization tube reactor) is under consideration in present paper. The viscosity is growing in the course of chemical reaction. The problem has been solved in two variants.

In first variant the process development in the case the heat ignition in the stream volume to take place has been considered. The polymerization process develops so that the reaction front is perpendicular to the reagent stream. High temperature state is unstable. Accumulation of high viscous products on the reactor walls leads to the acceleration of the motion in axial zone. As a result the high temperature front moves to the outlet and the process turn into low temperature stationary state. The present computational analysis is in a qualitively agreement with the experimental data by independent authors.

Second variant of the problem solution has been the search of the stable stationary high temperature state. It has been proposed that the viscosity grows jump-likely from initial to final value. Such assumption has been allowed to solve the problem in quadratures. The high temperature state is stationary when polymerization front presents the strongly stretched conic surface nearly parallel to the reactor walls. In present investigation the position and the form of the polymerization front and the pressure drop - flow rate dependence have been analysed. It has been shown that the main hydrodynamic features of such process are determined by the ratio of the final and the initial viscosities of the reactionable liquid.

2/1 COMPOUNDING, MIXING AND DEVOLATILIZATION

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In the production of polymer compounds (polymer blends and composites, respectively) by means of mixers for melts, the result of mixing is equally affected by both the technological conditions and the material characteristics of the components. It is shown that in the preparation of polymer blends the compatibility of the components and their rheological characteristics play a dominating role in the formation of the morphology during the mixing process. The viscosity and elasticity ratio of the component melts, in connection with the ratio of local strain and surface tension of the disperse phase, determines the amount of deformation of the disperse particles and the resulting type of morphology of the system. An a priori estimation of the degree of homogeneity and thermodynamic stability of the mixtures obtained can be achieved by assessment of the components with respect to their thermodynamic compatibility on the basis of the free mixing enthalpy, and calculation of the mixing effect of the mixer with the help of the characteristics of the deformative mixing effect.
The mixing effect is determined for various mixers by calculating the flow and the total deformation of the melt. Correlations between the mixing effect and the mixing quality of these mixers are presented and compared, and conclusions are drawn concerning preferable applications.

A process model for diffusion-controlled devolatilization is presented by the example of the twin screw extruder with counter-rotating engaged screws; it is based on calculated flow processes and concentration changes in the vacuum vent zone.
The model describes the achievable final concentration of volatile constituents depending on constructional and technological process parameters, including the rheological and thermodynamic material behaviour. Using a newly developed wedge-shaped part mounted on the calender, intensification of the devolatilization process has been proven theoretically by a process model and by experimental investigations.

2/2 NEW METHODS OF QUALITY ASSURANCE IN PLASTICS COMPOUNDING

Dipl.-Ing. Heinz Herrmann, Dipl.-Ing. Klaus Kapfer and
Dipl.-Ing. Hans-Jürgen Nettelnbreker
Werner & Pfleiderer GmbH, P.O. Box 301220
D-7000 Stuttgart 30, West Germany

Improvement and assurance of quality means:

- production of the compounded polymer within narrow, well defined quality tolerances on a high level and
- reduction of off-grade material and scrap.

In polymer compounding the following disturbance inputs can occur:

- long term fluctuations of product properties of feed materials (e.g. average molecular weight, particle size, volatile content, stock temperature)
- influences of discharge equipment operating discontinuously, such as periodical pressure changes at the downstream end when filtering the polymer melt.

All strategies to improve the constance of the compound properties have to take these disturbance factors into consideration.

Therefore it is necessary, to equip the compounding machine with a powerful measuring and control system, which enables the system to

- continuously measure all quality determining operating conditions and product properties
- automatically supervise all machine functions and operating parameters
- maintain the required outputs at their setpoints by using suitable control elements.

Suitable control strategies for the quality assurance will be demonstrated using four process examples.

- pressure control when filtering polymer melts
- viscosity control when viscbreaking Polypropylen with peroxide
- maximizing of throughput considering torque and quality limits
- product specific preselection of stock temperature at the end of the melting section.

2/3 MODELLING OF FLOW IN MODULAR INTERMESHING COROTATING TWIN SCREW EXTRUDERS AND PRELIMINARY EXPERIMENTAL STUDIES

Witold Szydlowski and James L. White
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Intermeshing corotating twin screw extruders are in general modular systems including left hand and right handed screw elements and kneading discs as well as sometimes other elements. Screw elements are used for dumping kneading disc elements disperse mixtures. We have developed models of flow in kneading disc and screw elements. The FAN method of Tadmor and Gutfinger is applied to predict pressure fields and flow patterns in these elements. The influence of kneading disc design on performance is discussed. Preliminary experimental studies of distributions of frozen plastic with markers in a Werner-Pfleiderer ZSK-30 are reported.

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The Open Shear Rolling Extruder for Processing of High Viscous Materials

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The shear rolling mill COMET CMS is an open twin screw extruder for homogenising, melting and dispersing.
It is used for plasticising, masticating and compounding of plastics, caoutchouc and ceramics.
Furthermore, products of medium and high viscosity, also with a high portion of filler, conventionally being processed on batch kneading machines, planetary mixers and extruders, are continously homogenised and dispersed on the shear rolling mill COMET CMS. Operating temperatures can be set from 20°C to 230°C.
Two horizontal shearing rolls operate counterrotating and are transporting the product from the left infeed side to the right delivery side.
The transport of the product is effected by the shearing grooves on the roll. In process are only about 1 - 2,5 kg of the product. Nip pressure, friction, temperature and high shearing rate are the factors for an excellent dispersion and homogenisation of the product. They are adjustable individually. The shearing grooves have a product specific geometry finding its expression in groove width, groove depth, angle of climb and number of shearing grooves. The shearing rolls are self-cleaning and permit a rapid change of product.
For a continuous product delivery on the right side of the machine supplements like strip cutting device and a pelletizer are available.
Shear rolling mills are in operation with shearing roll diameters of 120,165 and 200 mm, shearing roll lengths from 750 to 1500 mm and with a maximum capacity of 200 kg/h.
With the shear rolling mill COMET CMS often process operations can be solved which cannot - or only with difficulties - be handled with other machines.

2/5

Foam - Enhanced Devolatilization of Polymer Melts in Rolling Pools: Further Contributions Toward Understanding the Process

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A systematic, experimental study was conducted on the elementary process of devolatilization (DV) and the various parameters affecting it, using specially designed devices, which are devoid of the flow complexities present in industrial equipment and which permit independent control of all pertinent parameters.

The devices simulate a flow configuration present in all rotating machinery used in DV, viz. the rotating melt pool. Parameters studied include residence time, feed composition deformation rate, pressure (vacuum) level, melt viscosity, vapor pressure of volatile contaminant and addition of inert substances for DV enhancement. All feed and product contaminant levels were analyzed using gas chromatography.

2/6 DESIGN AIDS FOR VENTED SINGLE SCREWS

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In a previous publication /1/, a comprehensive computation model for the flow of polymer melts in single screw channels was reported on: The flow equations are solved without making geometrical simplifications like unwinding the channel or neglecting the adherence to the flight faces, and the pseudoplastic non-isothermal flow behavior is fully accounted for. The main results have been cast in the form of a universal screw characteristic system which describes the screw performance with respect to throughput, pressure build-up, power consumption and mixing (in terms of total strain and residence time) dependent on the screw geometry and the power law exponent.

The present work deals with a two-stage single screw devolatilization extruder (DE) for which a largely applicable set of design diagrams is derived from said model.

In the DE's second stage, the length of the metering zone can be calculated and, moreover, be minimized by optimizing the channel depth for prescribed die restriction and mass throughput.
If, in addition to the usual rheological and thermodynamical data, information on the melt's foaming behavior is available, the exposed melt surface can be predicted, so the proper design of the deep-flighted (partly filled) portion of the 2nd stage is also feasible.
In the plastication stage (1st stage of the DE) a barrier screw section can advantageously be employed to enable a forward degassing (which complements the normal backward degassing of the 2nd stage). Here the melt channel(s) can be designed along the same lines.
The method likewise applies to vented injection molding machines.
Basing such predictions on geometrically simplified flow calculations would lead to faulty or at least uneconomical designs (e.g. with melt escape from the vent, or inadequate exposed melt surface etc.) as will be shown using examples from practice as well as laboratory scale experiments.

Ref.: /1/ H. Kühnle, J. Polym. Eng. 6 (1986) 51 - 77

2/7

ANALYSIS OF THE HIGH-MASS TRANSFER RATE REGIME OF EXTRUSION DEVOLATILIZATION

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The mass transfer efficiency of the bubble-growth controlled devolatilization process has been analyzed using a 20mm counter-rotating non-intermeshing extruder. The rheology of the initially 50/50 w/w polystyrene/ethylbenzene solution has been characterized at the processing temperatures using a novel pressurized capillary viscometer.

The data has been interpreted using a theoretical cell model. It has been suggested that during the initial stages of devolatilization of supersaturated, relatively dilute, solutions, the local mass transfer rates within the foaming medium are not affected appreciably by the externally imposed deformation due to the screw rotation. The screw speed affects, however, the volume available for devolatilization. This concept has been further supported by comparing the extrusion experiments with model devolatilization measurements carried out in a visualization batch apparatus.

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2/8 DYNAMICS OF AGGLOMERATE SIZE DISTRIBUTION IN LINEAR SHEAR FLOW FIELDS

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A dispersive mixing model was developed and analyzed for the case when separation of the fragments following rupture of agglomerates primarily determines the dynamics of the mixing process. The model incorporates the effects of van der Waals forces within agglomerates and hydrodynamic interactions between fragments as they are convected apart from each other by the applied shear field. The essential features of the model are illustrated by examining the effect of shear on the breakage of parent agglomerates and their first five generations of fragments for a particular test case. In addition the dynamics of the agglomerate size distribution, produced by linear shear flow fields in gaps of various aspect ratios was analyzed for two types of initial conditions. These results provide insight into the design of high shear zones in actual mixing equipment.

2/9 LAMINAR SHEAR MIXING IN PLASTICATING EXTRUDERS

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The state of the art in extruder screw design in respect to mixing homogeneity is marked by a highly emperically foundated experience. So there is a necessity to have theoretical foundations which lead to calculabe prediction of the achievable mixing result.

A first step is a quantifying measuring method allowing to give a correlation between mixing results and the theory of laminar shear flow.

The experimentally fitted mixing theory leads to the prediction of achievable mixing results depending on screw geometry, material and process data. This way a complete concept of calculation can be performed including the mixing aspect of the extrudate homogeneity.

2/10 STATIC MIXERS FOR THE PROCESSING OF THERMOPLASTICS

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A perfectly homogeneous polymer melt upstream of the die is one of the most important prerequisites for the extrusion or injection moulding of high quality products. But melts leaving the extrusion section have very often strong radial temperature gradients and a non-uniform pigment and/or additive distribution, a consequence of an inadequate mixing performance of screws. Extrudates and moulded parts showing a non-uniform wall thickness, distortion, surface stucturing, colour streaks, spots, etc. are the result.

By installation of a SMX static mixer in the flow channel between the screw tip and the die inhomogeneities within the melt are evened out. The mixing is effected by mixing elements arranged in series inside a pipe. Their stationary arranged guide plates divide and recombine the flow in a geometric sequence.

With the relative standard deviation σ/σ_0 the mixing performance of such mixers can be indicated. For thermoplastic processing in most applications a mixer with 4 SMX mixing elements (relative mixer length L/D = 4) creating a $\sigma/\sigma_0 = 0{,}2$ is sufficient. The latter means that an inhomogeneity is reduced by factor 5, which in case of temperature homogeneization is further increased by the effect of the thermal conductivity.

With a diagram using the throughput ($\dot{V}$) and the flow curve of the polymer ($\eta = f\ (\dot{\gamma})$) the optimum mixer size can be selected and its pressure drop estimated in advance. Typical pressure drop with the melt blender SSM-X in extrusion is 30 - 60 bar and 100 - 200 bar with the mixing head SMK-X in injection moulding (pressure drop occurse only during the injection phase). In extrusion the mixer diameter is equal to 0,5 - 1 screw diameter and to 0,2 - 0,4 screw diameter in injection moulding.

Due to the geometrical mixing principle, which is ruling out random mixing, the specific energy demand is 0,001 - 0,002 kWh/kg (extruder: 0,1 - 0,3 kWh/kg) only. Due to the low energy input the temperature rise caused by pressure drop is small, approx. 1° C per 20 bar pressure drop.

Due to the very low shear forces in the mixer the range of application is confined to distributive mixing. Static mixers are not suited for dispersive mixing e.g. breaking-up of agglomerates or melting-up of unmolten granulates.

Practical applications show that these mixers can be applied for nearly all thermoplastics with exception of rigid PVC. They provide many benefits to operators of extruders and injection moulding machines, e.g. quality improvements, cost savings by reduced consumption of polymer or dyestuff/masterbatch, lower reject rates, stabilization of entire production process, amortization of mixer within a short time by the savings achieved.

2/11

NOVEL MELT MIXING DEVICE & PROCESS

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The growth of polymers requiring additives and the more recent developments in the area of reactive blends created an increasing demand for an efficient and versatile mixing device and process. The economic advantage of accomplishing blending and product extrusion in a single operation further adds to this demand and the need for judicious mixer selection and design. This paper describes a mechanical device which is both, an efficient mixer and heat exchanger. Typically, such a mixer is used as an adjunct to existing extruders. Mechanical performance characteristics are quantified in terms of power, enthalpy etc. to aid in the selection and design of the mixer to specific end use requirements. Data on blending quality include physical properties, relaxation modulus, Tg/Tm and microscopic slides for various types of blends of common interest. An attempt is made at correlating these results with known theories of mixing.

Finally, the need for an analytical approach to mixing polymers is discussed terms of phase diagrams which illustrate the diverse mixing requirements as well as the need for tailoring mixing intensity to specific blending characteristics.

3/1

CONVENTIONAL AND NEW MODES OF DEFORMATION IN POLYMER MELT RHEOMETRY

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The processing behaviour of polymers is closely connected with the rheological behaviour of polymer melts. Polymer melt rheology was started by engineers who needed flow curves for the solution of practical problems and by chemists who performed linear viscoelastic measurements and looked for structure - properties relationships. Today, commercial instruments are available for such conventional tests. However, a critical review shows that conventional testing can only deliver a very incomplete picture which narrows our way of thinking. In the future, not only improvement of the conventional test equipment is required, but in addition we need new modes of testing in order to obtain a more general picture concerning the material behaviour.

Polymer melts are rubberlike elastic liquids. Therefore, they are extremely nonlinear, the "true" constitutive equation is not yet formulated, each theoretical prediction is a speculation and describes only part of the reality. As an example, the prediction of the behaviour in simple elongational flow from the known behaviour in simple shear flow makes remarkable errors, when the transient viscosity functions are considered: We find softening or thinning in shear but hardening in elongation. Moreover, conceptual doubts arise whether these two test modes are adequate for such a comparison, because they are defined with concepts adequate for Newtonian liquids. When tests are performed with the same history of the principal component of the stretch tensor, the behaviour in shear and in elongation is the same!

Another difference between speculation and reality comes from the fact that shear flow measurements are mostly performed in unidirectional tests. This leads to the conclusion that the rheological behaviour is and remains isotropic during flow. But the macromolecules get oriented and, therefore, the behaviour must change from isotropic into deformation-induced anisotropic. Conventional methods do not notice this transition because the flow lines are straight. But during processing the direction of the velocity field is changed several times for a material particle under consideration, and what are the consequences for the relevant rheological properties? A newly designed multidirectional shear rheometer will answer this question.

Finally, the development of a new elongational rheometer is described for the investigation of the melt behaviour under multiaxial elongational flows of different deformation modes including the change of the principal axes of the strain rate tensor during the deformation period.

3/2 THE RELATION BETWEEN THE STRESS-TENSOR, THE DEFORMATION TENSOR AND THE ORIENTATION OF CHAIN-LIKE MOLECULES.

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One of the side effects of polymer processing is the orientation of molecules during the deformation process. Many attempts have been made to describe the rate of orientation in the melt or product in terms of birefringerence and stress-tensor by means of the stress-optical-law..

In this paper a model is presented to calculate the molecular orientation from the transient-network equations first presented by Lodge [1].

Let $\psi_1(q,t)d^3q$ be the number of network-segments, consisting of i freely jointed rigid links, that have their end-to-end vector q in the volume element d^3q in the configuration space. The balance equation, which gives the time dependence of ψ is [2]

$$\frac{\delta\psi_i}{\delta t} = -\frac{\delta}{\delta \underline{q}} \cdot (\psi_i \dot{\underline{q}}) + k_i - h_i\psi_i$$

where k_i and $h_i\psi_i$ represents the formation and annihilation of the segments. We use the orientation and annihilation function given by Jongschaap [3]. By solving this equation one can get a measure of the molecular orientation due to the deformation process. Calculations show no simple relationship between the molecular orientation and the deformation tensor nor the stress tensor.

[1] A.S. Lodge, Trans. Faraday Soc.52 (1956) 120

[2] M. Yamamoto, J.Phys.Soc.Japan 11 (1956) 413

[3] R.J.J. Jongschaap, J.Non Newtonian Fluid Mech.8 (1981) 183

3/3 VISCOSITY OF ENTANGLED POLYMER MELTS

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Applying Graessley's theories (entanglement network model) about the viscosity of linear polydisperse polymer systems the viscosity of raw elastomers (trans-polypenteneamere) and thermoplastic melts (polycarbonate) was calculated using the molecular weight distribution as determinde by gel permeation chromatography. As result a relation between the normalized viscosity η/η_o and the product of the longest relaxation time λ and the shear rate $\dot{\gamma}$ was obtained.

For low shear rates (to evaluate the zero shear viscosity η_o) a cone and plate rheometer and for intermediate and high shear rates a capillary rheometer were used for the measurements of viscosity. By shifting the experimentally determined dubble logarithmic plot of the normalized viscosity η/η_o versus the shear rate along the shear rate axis until it fits best with the calculated plot, the longest relaxation time λ was evaluated. This relaxation time is very important for the predicition of the processibility of polymers in various processes.

Using the mathematical term of a two parametric (number average molecular weight M_n and weight average molecular weight M_w) logarithmic normal molecular weight distribution (MWD) we can estimate the influence of the MWD (molecular weight M_w and polydispersity M_w/M_n for a uni-modal MWD and number, position and width of the maxima for a multi-modal MWD) upon η/η_o and λ. The results of these model calculations supply useful instructions about the processibility of polymers under development in various processes such as milling, extruding, injection moulding or coating.

3/4 MELT FLOW INDEX - RHEOMETRY AND QUALITY CONTROL

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The Melt Flow Index (MFI) is a number with the dimension of a mass rate to characterize the very complex flow behaviour of polymers. Testing device and procedure are standardized so that many plastic manufacturers use MFI as a kind of viscosity number to describe the flow behaviour of their products on one hand and on the other hand as a quality control.

Using MFI-apparatus as a rheometer, then the viscosity calculated from MFI-value is only accurate enough for Newtonian fluids. In the case of pseudoplastic materials however measurements and calculations show that MFI is no linear function of the viscosity η and their relationship depends very strong from the measuring range within the viscosity function $\eta(\dot{\gamma})$ itself. At low loadings apparent (η(MFI)) and true viscosity ($\eta(\dot{\gamma})$) are closer together than at high loadings. Even at constant loading the MFI-values vary with the filling height of the test fluid in the MFI-apparatus. With decreasing filling height MFI can increase about some hundred percents. The relations between MFI and viscosity become still more complicated if the test fluid has significant elastic properties.–The use of a MFI-apparatus as a rheometer is not ingenious, if the flow function of the test fluid is completely unknown.

The MFI can be applied with greater confidence in the field of quality control. The correlation between MFI and viscosity is independent of the magnitude of the MFI-value, if fluids have "similar" viscosity functions. Viscosity functions are similar, if the reduced viscosity functions $\eta/\eta_o = f(\dot{\gamma}\ \eta_o)$ are equal. (Homologous polymer series have similar viscosity functions over a limited range of polymerization degrees.) From this similarity follows that a change of the MFI-value has a proportional change of the viscosity function as consequence. If there is a "viscoelastic similarity", what means that additional to the viscosity function also the functions of the normal stress coefficient $\Theta(\dot{\gamma})$ are similar, then the MFI-value represents at constant loading also a constant ratio between viscous and elastic properties. Because of the small ratio L/D of the test die the elastic contribution in the MFI-value can be significant.

The MFI-measurement is in the first approach a stress controlled test. In the range of pseudoplastic flow behaviour, the stress controlled test is much more sensitiv against changes of the average molecular weight $\bar{M}$, than a test at constant shear rate. The relative change of the MFI-value with changing $\bar{M}$ is for viscous similar materials independent of the loading.

3/5 MELT FRACTURE AND SHARSKIN INSTABILITIES IN ORIFICE DIES

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Although much work has been done in the field of melt fracture, controversy still exists regarding the site of initiation and mechanism of the instabilities.

Flow visualisation of melt fracture type instabilities was performed both upstream and downstream of orifice dies through which various linear or branched silicone fluids flowed. The effect of slip at the wall was investigated.

Measurements of the pressure drop and flow rate across the orifices have been used, together with viscometric functions of the fluids, to calculate the stress levels, Weissenberg numbers, and the ratio of the energy dissipated in the flow of a viscoelastic fluid to that which would be dissipated in the flow of an inelastic viscous shear-thinning fluid with the same viscosity and at the same rate of flow .

For very viscous silicones, cracks appeared on the surface of the extrudate, whose length and width increased as the pressure increased. These cracks penetrate very deeply into the extrudate and the size of these cracks (width and length) is maximum at the level of the exit of the die where the tension stresses on the surface of the extrudate are maximum. The size of these cracks decreases as the cracks are carried along the extrudate and degenerate into a roughness of the extrudate far downstream of the orifice. It is made clear that sharskin, the phenomenon at hand, must be studied very near the die exit where the cracks are initiated, and that it is common to extrudates of very viscous materials.

Observation of the extrusion of moderately viscous silicones showed that no sharkskin could be observed whatever the upstream pressure for both the linear and branched oils. There is a big advantage in studying the instability of the flow which appears clearly and is well isolated since there is no sharkskin.

Moreover it is suggested that melt fracture instabilities origin can be studied experimentally for any fluid, using submerged orifice dies.

Flow visualization upstream of a venturi shaped and a cylindrical profile orifice die at the onset of melt fracture has revealed interesting pulsations at the onset of melt fracture for all the silicone fluids studied whether the fluid be branched or not. Because of their amplitude and frequency, these pulsations can be easily overlooked when they appear.

The evolution of the pulsations observed upstream of the orifice die was followed and was related to the pulsations observed downstream.

The more and more distorted appearance of the extrudate was explained as being due to an increase in the amplitude of the non axisymmetrical pulsations leading to retractions observed upstream of the orifice die above a certain upstream pressure.

3/6 THE BEHAVIOUR OF RIGID VERSUS FLEXIBLE MOLECULE SOLUTIONS IN DIE ENTRY FLOWS

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The steady shear viscosity, η, first normal stress different, N_1, storage modulus, G', and the dynamic viscosity, η', are measured for a series of viscous solutions of flexible and rigid molecules in viscous solvents. The flexible molecule solutions, constructed by dissolving polyisobutylene in polybutene, and the rigid molecule solutions, constructed by dissolving xanthan gums in corn syrup, are both constant viscosity fluids but with different N_1 characteristics. The flexible molecule solutions show the expected quadratic behaviour of N_1 with shear rate, while the rigid molecule solutions exhibit a linear N_1 shear rate dependent.

The kinematics of the two solutions in die entry flows are very different. While the flexible molecule solution shows the characteristic large corner vortex which grows with flow rate or Weissenberg number, the rigid rod molecule solution exhibits a large corner vortex (relative to Newtonian behaviour) which does not grow with flow rate. The difference in the kinematics of the two solutions in entry flow is illustrated with a motion picture film and explained in terms of the different elongational characteristics of the two solutions.

3/7

A STUDY OF VISCOELASTIC FLUID FLOWING THROUGH A CONICAL DIE

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Practical extrusion processes often involve geometrically complex dies, such as conical die, etc. When a viscoelastic fluid is flowing through the conical die, it may be considered to have a strong stretching flow component. As for explaining such a kind of flow, researchers has been working in this area but no satisfatory result has been derived yet.

Assuming that the viscoelastic fluid flowing through the cone is a pure stretching flow, a Finger's strain tensor was provided for describing a viscoelastic fluid flowing through a cone:

$$C_t^{-1} = \begin{bmatrix} \left(1+\frac{3}{4}tg\theta\frac{S_R}{De}\right)^{\frac{4}{3}} & 0 & 0 \\ 0 & \left(1+\frac{3}{4}tg\theta\frac{S_R}{De}\right)^{-\frac{2}{3}} & 0 \\ 0 & 0 & \left(1+\frac{3}{4}tg\theta\frac{S_R}{De}\right)^{-\frac{2}{3}} \end{bmatrix}$$

where C_t^{-1} ----- Finger's strain tensor;

θ ----- the half angle of the cone;

S_R ----- the recoverable shear strain;

De ----- Deborah number.

The above theorectical method can be used to predict the flowing pressure drop and extrusion swell. The experiments showed that the calculated values were coincident with the experimental data.

3/8

EFFECT OF CONTRACTION RATIO ON THE VISCOELASTIC FLOW TRANSITIONS IN AN AXISYMMETRIC SUDDEN CONTRACTION

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The flow of a viscoelastic fluid through an axisymmetric contraction has been studied experimentally. At low flow rates, or low values of the Deborah number (De), the fluid has long been known to exhibit Newtonian flow behavior, with Moffatt eddies forming in the corner of the contraction. Boger (J. Non-Newtonian Fluid Mech., 5 (1979), 353-368) has shown that at high values of De large symmetric vortices develop in the corners and these become asymmetric with further increase in De. Laser Doppler Velocimetry (LDV) experiments have recently been performed by Muller (J. Non-Newtonian Fluid Mech., 20 (1986), 51-92) for intermediate Deborah number flow through a 4:1 contraction; this work reported new, three-dimensional, time-periodic vortices in a small region near the lip of the contraction.

The purpose of this paper is to investigate the effect of the contraction ratio on the development of these time-periodic flows. Experiments are performed with a 2-color, 4-beam LDV system to measure velocities in both a 4:1 and an 8:1 contraction. The viscoelastic fluid is 6% polyisobutylene dissolved in tetradecane. Higher De values are obtained relative to Muller's work, thus allowing a more complete mapping of the flow transitions involving the lip and the corner vortices.

3/9 FLOW INDUCED CRYSTALLIZZATION OF HDPE OBSERVED BY CAPILLARY RHEOMETRY

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The occurrence of enhanced crystallization of polymers due to flow has attracted the attention of several workers in recent years. Crystallization actually taking place above the rest thermodinamic temperature has been considered only sparingly, however. The latter possibility has been here explored by means of a very simple experiment, i.e., by measuring the presure drop due to flow of the polymer in a capillary at progressively lower temperatures. For HDPE it is found that the pressure drop increases negligibly over a range of temperatures and then abruptly grows without bounds at some temperature which, in all our experiments, is always significantly above the thermodynamic value. It is believed that this phenomenon results from flow induced crystallization.

A standard piston driven capillary rheometer, electrically heated, was used in the experiments. Capillary dies of either 1.0 or 1.5 mm diameter were used with lengths ranging from 5 to 60 mm. Uniformity of temperature (to within 1°C) throughout the reservoir and capillary was ascertained in preliminary experiments with a thermocouple. A typical run started with the molten polymer at 180°C in the full reservoir (1 cm in diameter). Then, at each subsequent drop in temperature the polymer was held stationary for at least 30' to ensure good uniformity at the new temperature. At each flow rate the steady state force driving the piston, as mentioned above, was found to increase very little by progressively decreasing the temperature to rise suddenly to the machine limits (about 700Kg) at the crytical temperature T_c. In all cases, T_c was larger than T_m by several degrees, were T_m was determined independently by standard differential scanning calorimetry under both heating and cooling conditions at several rates. Whereas T_m was about 127°C, T_c ranged from 130°C as much as to 150°C, depending on flow rate and capillary geometry. The value of T_c increased not only with increasing the flow rate , as expected, but also with increasing the capillary length (for a fixed diameter) thus indicating a significant influence of the residence time spent at the given shear rate. A quantitative interpretation of these results based on existing theories of flow induced crystallization did not prouve a simple tasc. A striking simple correlation was found, however, which appears to link linearly T_c and $\ln(P)$, where P is the observed pressure drop before the sudden rise takes place (i.e. at a temperature somewhat higher than critical).

3/10 DYNAMIC MEASUREMENTS ON LIQUID-CRYSTALLINE SOLUTIONS OF POLY(p-PHENYLENE-2,6-BENZOBISTHIAZOLE)

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The rheological properties of polyphosphoric acid solutions of poly(p-phenylene-2,6-benzobisthiazole) (PBT) are reported as the third paper in a series of articles dealing with dynamic measurements on polymer liquid crystals. It is known that high-strength and high-modulus fibers are made from the liquid-crystalline solutions of PBT in polyphosphoric acid. Two samples, PBT-20 and PBT-23, were used whose inherent viscosities were 11.2 and 4.72 dL/g, respectively. The 6.0 wt% solution of PBT-20 at 80°C consists of minute crystalline grains and exhibits green-yellow opalescence and can readily be spun into fine filaments using water as a coagulant. The dynamic properties of the solution are very different from those of the usual isotropic polymer liquids. The logarithmic plots of G' and G" against frequency (10^{-2} to 10^{2} radian·sec^{-1}) show the curves with small slopes, while η' changes from the order of magnitude of 10^{4} to 10^{2} Pa.sec, without showing the Newtonian region where η' is constant independent of frequency. However, the viscoelastic behavior of liquid-crystalline solutions of PBT seems to be nearly linear. The wave of torque or shear stress generated by the sinusoidally alternating strain maintains the undeformed sinusoidal form and is out of phase with strain. When the solution is heated up to 105°C, isotropic phase becomes predominant, and the curves of G' and G" decline rapidly with decrease in frequency. The curve of η', on the other hand, becomes horizontal in the region of low frequencies, as is the case with Newtonian liquids. The 6.0 wt% solution of PBT-23 at 15° and 24°C show the dynamic properties similar to those of PBT-20 at 80°C, but the solution of PBT-23 at 80°C exhibits radically different dynamic properties indicating the Newtonian behavior at low frequencies. Thus, the temperature of phase transition depends on the molecular weight of PBT. The 1.7, 0.8, 0.5, and 0.3 wt% solutions of PBT-23 were studied dynamically. Every solution in the state of mesophase shows the dynamic properties characteristic of liquid crystal. The plot of steady-flow viscosity against temperature suggests that the solutions are in the state of nematic mesophase. With increase in temperature the solutions change into isotropic solutions. It is shown that the temperature of phase transition decreases with decrease in concentration. It is interesting to see that the dilute solution of PBT-23 whose concentration is as small as 0.3 wt% is liquid-crystalline at room temperature, demonstrating the stiffness of molecule. The microscopic structure of PBT fibers and films is interpreted in terms of the structure and rheological properties of solution.

3/11

NON-LINEAR VISCOELASTICITY OF ABS POLYMERS IN THE MOLTEN STATE

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The multi-phase polymeric materials, polymer alloys, have been widely used and the knowledge of the properties has become important. ABS polymer is very interesting polymer system to investigate the rheological properties of two-phase polymeric materials by several reasons; (1) the rubber particles are well(individually) dispersed in molten polymeric phase and no structure of particles is formed in the system, (2) the rubber particles are never broken by the stress field experimentally applied and the system must remain the original structure during measurements, and (3) the rigidity of rubber particles is almost the same as the rubbery plateau modulus of the continuous phase.

In this study, linear and non-linear viscoelastic properties of ABS polymer systems were measured in the molten state to investigate the effects of rubber-particle content and molecular weight of the matrix polymer on the rheological properties measured in this study are dynamic viscoelastic functions G' and G", stress relaxation moduli under single- and double-step strains in both linear and non-linear regimes and extensional viscosity functions.

Linear viscoelasticity of the materials has shown an extremely long-time relaxation mechanism associated with the rubber particles. Experimental results for the relaxation modulus under large strains have revealed the striking fact that the non-linear characteristics appear only in entanglement relaxation of the matrix polymer and not in the long-time relaxation due to the particles. The two relaxation mechanisms, entanglement and particle relaxations, have been separated by the double-step stress relaxation experiments. Elongational viscosity functions are also affected by the existence of particles.

From the linear and non-linear viscoelastic behavior of the well-dispersed particle-polymer melt systems, the relaxation mechanism of the system has been discussed. It is concluded that the long-time relaxation associated with the particles can be attributed to the translational motion of the particles back to the equilibrium positions. The theory predicts the characteristic time and the intensity of the relaxation, and can also be applicable to the other similar systems.

3/12

RHEOLOGICAL AND DIELECTRIC PROPERTIES OF SHORT FIBER-POLYMER SUSPENSIONS

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The motion of fibers in a viscoelastic matrix is studied through the time-dependent dielectric properties of the suspension. The effect of particle orientation on the permittivity of the composite is independently determined in a specially constructed cell and compared with theory. A Sliding Cylinder Rheometer is modified to allow for dielectric measurements during transient flow tests, allowing simultaneous observation of rheological properties and fiber motion. Methods for Stokesian dynamics simulations of fiber suspensions are also being explored to describe multi-fiber hydrodynamic interaction in shear flow.

3/13 APPLICATION OF A BLENDING RULE FOR THE DYNAMIC VISCOSITY OF POLYMER MELTS

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A semiempirical blending rule for the components of the dynamic shear viscosity of polymer melts is known to be valid for some polystyrene melts (Montfort et al., Rheol. acta 18 (1979), 623). This rule reads: $\overset{*}{\eta}_b^a = w_1 \overset{*}{\eta}_1^a + w_2 \overset{*}{\eta}_2^b$; with $a = 1/3,4$, w_1, w_2: weight fractions of the components ($w_1 + w_2 = 1$), $\overset{*}{\eta}_1$, $\overset{*}{\eta}_2$, $\overset{*}{\eta}_b$ dynamic viscosities of the components and the blend for a given frequency ω, the viscosities being in complex notation.

An examination of the rule using literature data and own ones for melts of unbranched polymers like PS, HDPE, polybutadiene yields: All experimental results including those for the components of the dynamic viscosity are well described. In some cases however thermal degradation of the polymer and sensitivity problems of the apparatus have to be taken into account, especially if the blend contains high molecular weight components.

An application to data known for blends of star-branched polybutadiene totally fails. This is expected from the assumptions made in the derivation of the rule.

Quantitative results for melts of linear polymers are:

1. The admixture of high molecular weight components to a melt with a low steady state compliance J_e^o considerably increases J_e^o.

2. The admixture of low molecular weight components reduces the viscosity in a different manner as plasticizers will do.

3. A polymer with a narrow molecular weight distribution not only has a low J_e^o, but also has a relatively sharp transition in going from the range with constant viscosity to the one with decreasing viscosity.

4/1 STRUCTURE DEVELOPMENT DURING PROCESSING

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The properties of polymeric materials are largely determined by structure that is developed during liquid-state processing. Substantial progress has been made in recent years in prediction of such structure development, but there are areas in which serious questions remain unresolved. We will briefly examine those areas of structure development that appear to be well understood quantitatively or qualitatively, and will identify the areas in which major fundamental questions remain unresolved. We will then present recent results in two of these latter areas: structure development in thermotropic liquid crystal polymers, and failure of adhesion at a polymer melt/metal interface. With regard to the former topic, we will show how mechanical and magneto-rheometry, combined with spectroscopy, can elucidate information about the phase behavior and response of the fluid state in the liquid crystalline systems. With regard to the failure of adhesion, we will review some recent theoretical and experimental results that point to the need for a new understanding of the nature of the structure of the melt near a solid surface and the appropriate boundary conditions for use in continuum theories.

Free surface
fiber spinning
Break-up of Viscoelastic jet (essentially solved)
Blown film (thin sheet, SS + transient)
~~transient~~
pressure / ~~film diameter~~ is a bad control coupling
(measured) air flow

diameter / pressure.

use chopped glass fibers in marking contraction flows.

not understood
high stress fields
heterogeneous fluids e.g. LC

melt/surface adhesion not well understood
└ flow stability
– High De
– Failure + Fatigue

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USE OF THE FINITE ELEMENT METHOD TO INTERPRET VISCOUS AND VISCOELASTIC EFFECTS IN BLADE COATING

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Coating thickness data and finite element simulations are presented for the blade coating of a series of Newtonian and non-Newtonian fluids. Experiments using non-Newtonian fluids with almost identical viscosity-shear rate behavior, but varying normal stress coefficients, make it possible to isolate nonlinear viscosity effects from "elastic" phenomena. Finite element simulations, which assume purely viscous behavior (four parameter Bird-Carreau model), are in good agreement with data for Newtonian and inelastic non-Newtonian fluids.

Fluid rheology is found to have a significant impact on coating thickness in a blade coater. Viscoelastic liquids, characterized by their viscosity (shear thinning) and normal stress (elastic) behavior in steady shear flow, exhibit both an increase and decrease in coating thickness relative to Newtonian liquids, depending on the relative contribution of shear thinning and elastic effects. Nonlinear viscosity causes an increase in coating thickness (flatter velocity profile), relative to Newtonian fluids. This increase is observed experimentally and predicted using finite element simulations for purely viscous fluids. However, as the normal stress coefficient of a relatively inelastic carboxymethylcellulose (CMC) solution is increased, by adding very small amounts of high molecular weight polyacrylamide (Separan AP-273), the coating thickness is reduced (no attempt has yet been made to include elasticity into the finite element simulations). In addition, a Boger fluid, with a nearly constant shear viscosity but a large normal stress coefficient, coats much thinner than a Newtonian fluid. Of particular interest, is the observation that the coating thickness for the highly elastic Boger fluid (i.e., corn syrup with polyacrylamide) appears to be independent of blade geometry, in contrast to Newtonian results which show a significant dependence on blade angle and width.

4/3

INTERFACE SHAPE IN COEXTRUSION

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The problem of determining the interface shape in the coextrusion of two fluids of different viscosity through long dies of arbitrary cross section was examined. The principle of minimum viscous dissipation for a given flowrate in the equivalent form of maximization of flowrate for a given pressure gradient subject to a flowrate ratio constraint was used. A combined optimization/finite element procedure was employed to allow simultaneous prediction of the interface shape and the velocity field. The preferential configuration is shown to be the one with the less viscous fluid wetting the walls and encapsulating the more viscous fluid which is found at the core.

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RECENT ADVANCES IN THE FINITE ELEMENT MODELLING OF VISCOELASTIC FLUID FLOW

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The finite element simulation of viscoelastic fluid flow problems is of a major importance in the modelling of polymer processing. One of the most critical findings of previous studies is certainly the loss of convergence of the numerical methods beyond a certain Weissemberg number threshold value in the presence of geometric singularity. The present study addresses specifically this high Weissemberg number problem. Instead of using the classical "mixed" method stress-velocity-pressure to model viscoelastic fluid flow, we have devised two new numerical strategies which consist of the solution of a series of Stokes-type flow coupled to a "local" solution of the stress equation. This local solution is based either on the use of the method of characteristics, or on the use of the Lesaint-Raviart method. This new methodology is applied to the solution of the flow of a Maxwell fluid and a Phan-Tien-Tanner fluid in a sudden contraction. Results are in a qualitative agreement with experimental data of viscoelastic fluid flow.

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A SURVEY OF RECENT DEVELOPMENTS IN THE NUMERICAL SIMULATION OF VISCOELASTIC FLOWS

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In this talk, we summarize a recent survey of numerical methods for solving viscoelastic flows in complex geometries.† We draw a global picture of the spectrum of available numerical techniques, the organizing thread being the two main approaches of handling the fluid memory: the coupled approach, in which the viscoelastic constitutive model and the conservation laws are solved simultaneously, and the decoupled approach, in which the computation of the viscoelastic stresses is done separately from that of the flow kinematics. These two different methodologies have been used with both differential and integral models, and in conjunction with various discretization methods. A number of successful simulations are described briefly. Finally, we discuss some of the outstanding numerical, mathematical, and modeling problems.

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†R. Keunings, "Simulation of Viscoelastic Fluid Flow," to appear as a chapter of the textbook "Fundamentals of Computer Modeling for Polymer Processing," C.L. Tucker III, editor, Carl Hanser Verlag, 1987.

write to Roland for it.

4/6

DYNAMIC MODELLING OF A SINGLE SCREW EXTRUDER

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A phenomenological dynamic model has been developed for a single-screw plasticating extruder (1" diameter, L/D equal to 20). The model is based on a macroscopic heat transfer balance on each of the five heating zones of the barrel. For positive or negative step changes on the electrical power of the heating barrel zones, the unsteady-state model can predict the time evolution of the barrel temperature profile and the polymer temperature and pression profiles in the screw channel. Barrel - polymer heat transfer coefficients and polymer temperature in the channel (non-directly measurable parameters of the model) are estimated from successive applications of the steady-state model. The predictions of the model are in good agreement with the experimental data obtained for a low density polyethylene and polystyrene.

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AN ACCUMULATOR DEVICE TO COMPENSATE FOR SHORT-TERM CYCLIC OUTPUT VARIATION IN A CONTINUOUS PROCESS

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Variation in continuous polymer processes can be characterized in terms of drift and short-term irregular cyclic variations. In most cases, drift can be practically eliminated by conventional process control, and cyclic variation can be reduced by optimizing operating conditions or equipment design. The remaining cyclic variation, for example, in output rate can still cause significant dimensional variation when the product is conveyed downstream at a steady rate.

To reduce this variation, two mechanical devices known as accumulators were designed to increase the flow path length or material inventory between the extruder and conveyor during the high output portion of the cycle and to decrease it during the low output portion. The path length is changed by means of a movable roller subject to an external force. When the output is high and the line tension low, the external force moves the roller away from the conveyor, thereby accumulating the excess material. When the output is low, the high line tension overcomes the external force so that the accumulator reverses direction and gives up stored material.

With the "pivot" accumulator design, an externally counterbalanced roller moved back and forth along an arc at the end of lever arms. In an experimental test, a variable extruder output rate was obtained by changing screw speed ± 11% every 15 sec in the form of a square wave. The "pivot" accumulator reduced thickness variation from ± 9.0% (three standard deviations) to ± 1.8%.

The "linear" accumulator design involved a roller which was mounted on linear bearings and moved back and forth in a plane. Transducers mounted on the shaft measured the in-plane component of the force on the roller resulting from tension in the extrudate. This measured force was maintained constant by a magnetic clutch which manipulated the external force on the roller. This more sophisticated control system reduced sensitivity to static and dynamic friction and inertia. Since tension in the extrudate could drift because of property changes, the force set point on the roller could be adjusted as needed to keep the roller off mechanical stops. A guide roll mounted outside the transducers maintained the extrudate at a fixed wrap angle around the roller. The guide roll insured the relation between line tension and the associated force on the roller was independent of roller position.

Testing of this device on an extrusion line showed the expected correlation between dimensions, tension and roller position. The "linear" accumulator reduced variations in the extrudate thickness and width by factors ranging from 1.8 to 2.0.

4/8

STATE-VARIABLE TEMPERATURE CONTROLLER FOR EXTRUDERS

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Increased demands on product quality and efficiency in extrusion processing coupled with more knowledge about the extrusion process and with the rapid decline in the cost of computational power have proved strong motivation in developing more efficient temperature control strategies. Up to now the main trend has been to use DDC-systems which are adjusted for a particular operating point. The temperature controlled elements in extruders are dependent on an operating point in their performance; this is a result of their constructional form, of variations in melt consistency and melt throughput together with external disturbances.

It is therefore necessary to make provision for these special conditions by the development of higher performance control concepts. For this purpose a state-variable controller to control the cylinder wall temperatures was developed and tested in practice.

The discrete-time process model presupposes a process step response which is a sigmoid shaped curve and which is typical for many industrial processes, not only in the temperature range. It matches the first n-1 points of the step response curve and is subsequently fitted with an exponential rise from the n-th point to the steady state value with a decaying factor p.

The input-output relation can be described by the following equations:

$$\underline{x}(k+1) = \underline{A}\,\underline{x}(k) + \underline{b}\,u(k), \quad y(k) = \underline{c}^T \cdot \underline{x}(k),$$

with:

$$\underline{A} = \begin{bmatrix} 0 & 1 & \dots & 0 \\ 0 & & & \\ \vdots & & & 1 \\ 0 & & & p \end{bmatrix}, \quad \underline{b} = \begin{bmatrix} g_1 \\ g_2 \\ \vdots \\ g_n \end{bmatrix}, \quad \underline{c}^T = [1\ 0\ \dots\ 0]\ .$$

A feedback controller is implemented on the basis of this state model. Since it is not possible to measure the complete state vector $\underline{x}$ an observer is used. An I-action is added in order to prevent a steady-state control error. The control algorithm is designed on the basis of the pole-assignment method.

Investigations on developing a self-tuning concept were carried out and showed that an automatic identification of the decaying factor p during the heating phase is possible. The control results obtained show that an industrial application of the state variable method is possible in this case.

4/9

A CRITERION FOR ESTIMATION OF POLYMER TEMPERATURE FLUCTUATION IN A SINGLE SCREW EXTRUSION PROCESS

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The criterion for estimation of the polymer temperature fluctuation in the single screw extrusion process has been presented*. This criterion enables to predict the temperature fluctuation if the extrusion conditions are known. Unlike previous methods this criterion takes into consideration the effect of the polymer melting course on the temperature fluctuation (in the case of complete polymer melting in the screw channel). The criterion has been verified experimentally.

The hypothesis has been submitted that identical temperature fluctuation amplitude may be obtained under various extrusion conditions if similarity of polymer flow in the screw channel is maintained.

In the first stage, the polymer flow in the screw metering zone (assumed as filled with fully molten polymer) has been considered. For the flow in this zone the similarity number best correlating with the temperature fluctuation amplitude has been assigned. For this purpose the equations of motion and energy governing the material flow in the metering zone have been cast into dimensionless form. It has been assumed that the processed polymer is an incompressible viscoelastic fluid described by the second order model (Rivlin-Ericksen). In result the similarity numbers of Strouhal, Euler, Reynolds, Fourier, Graetz, Brinkman and a quotient of the Deborah-Reynolds numbers as well as a product of the Brinkman-Deborah numbers have been obtained. The Fourier number has been found to correlate best with the temperature fluctuation amplitude.

It has been taken into consideration that in the real extrusion process the metering zone is not equivalent to a region of occurrence of the polymer in molten state only. Accordingly the region of molten polymer has been investigated. In this region a certain infinitesimal volume has been separated. For this volume, a Fourier number has been defined. Adding the values obtained in the infinitesimal volumes the criterion for the whole region of molten polymer has been obtained as follows:

$$K_J = \int_{L'}^{L} \frac{k}{\rho \cdot c_p} \cdot \frac{dz}{V_{mz} \cdot H^2}$$

where the values k(thermal conductivity), (density), c (specific heat), V (average velocity of melt), H(depth of screw channel) are functions of the position in down channel direction(z) and where L', L are the limits of the integration (from the beginning of the polymer melting to the end of the screw channel length).

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*The work concerns the plasticating extrusion of thermoplastic materials (without venting) with the use of conventional screws.

4/10 FLOW PATTERNS IN THE MELTING ZONE OF A SINGLE-SCREW EXTRUDER

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A broad range of polymers obey the Maddock melting mechanism as determined by flow visualization experiments. Graphic illustrations of flow, melting and mixing are obtained by stopping the extruder and removing the screw. However, mathematical models based on this mechanism, either with the constant solid bed velocity assumption or with the freely deformable solid bed approximation, while reasonably successful in predicting axial melting profiles, fail to predict axial pressure profiles.

In order to obtain a thorough description of the kinematics and dynamics of the melting zone of a single-screw extruder, flow visualization experiments were performed with linear polycarbonate resin. A 47 ton hydraulic screw extractor was used to pull a 24 L/D screw from a 63.5mm diameter extruder without recourse barrel heating.

Cross sectional cuts in the transverse channel direction of the unwrapped polymer from the screw revealed that polycarbonate also follows the general description of the Maddock melting mechanism. Moreover, a strong recirculating flow in the melt pool leading to an overall recirculating flow pattern encapsulating the solid bed was observed. Cross sectional cuts in the down channel direction showed considerable solid bed deformation near the barrel surface. At the early stages of melting a sharp flow/no flow interface is seen to exist between the melt film and the solid bed. This interface loses its definition towards the latter stages of melting as individual pellets undergo a gross shearing deformation.

Since the extractions were done without recourse to barrel heating, flow patterns as seen by streaklines of pigment were preserved on both screw and barrel sides of the unwrapped polymer. The flow patterns on the barrel side showed that these streaks did not change direction as they crossed from over the solid bed to over the melt pool, casting doubt on the validity of the method employing streak angles as a means of calculating solid bed velocities. A new method of calculating solid bed velocities that uses the pigment streak directions underneath the melt pool on the screw surface side is proposed. Implications of this method as well as the above experimental observations in calculating axial pressure profiles is discussed.

4/11

EXTRUSION CHARACTERISTICS OF POWER LAW FLUIDS IN SCREW PUMPS

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The output of power law fluids as a function of pressure gradient is considerably different from that of Newtonian fluids. Unfortunately, no analytical expressions are available that accurately describe the output as a function of pressure gradient over a wide range of helix angles and power law index values. In this paper, output data will be presented in graphical form that will allow analysis of output over a wide range of helix angles and power law indices. Furthermore, data will be presented that will allow determination of the helix angle at which the output is optimized as a function of the power law index and the pressure gradient.

The energy consumption in screw pumps is strongly affected by the degree of non-Newtonian behavior of the fluid being extruded. It is shown that the energy efficiency in the screw channel is highest for Newtonian fluids and reduces as the fluid becomes more non-Newtonian. The total energy efficiency is considerably less than the energy efficiency in the channel because a substantial amount of energy is consumed also in the flight clearance. This amount is large for relatively Newtonian fluids, as much as 50 percent of the total energy consumption, and reduces as the polymer is more strongly non-Newtonian. As a result, the overall energy efficiency is optimum for a power law index value of about 0.5.

It is shown that the total energy consumption is minimized at a specific value of the dimensionless axial pressure gradient. This value allows calculation of the optimum channel depth through a simple expression. The optimum helix angle can be expressed as a simple linear function of the power law index. The total energy consumption for power law fluids can be written in a closed form expression with an accuracy of 3 percent or better. Once the optimum channel depth and helix angle have been determined, the most efficient way to further reduce the energy consumption is to reduce the flight width and increase the flight clearance.

4/12 FLOW INDUCED TORQUE IN A BARREL SCREW SYSTEM

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To study the energy dissipation in the different zones of an extruder a special barrel has been designed where local torques Tq can be measured at the beginning of the conveying, resp. the transition and the metering zone. Experiments carried out for a commercial polyethylene and a polyvinyl chloride at different processing conditions show that in some cases negative Tq in the metering zone may occur. A very basic analytical treatment of the flow situation in the metering zone shows that for a given drag flow Tq is dependent on the pressure gradient and particularly on its sign. Tq is decreasing for decreasing positive pressure gradient until there is pure drag flow. It is further decreasing for increasing negative pressure gradient until zero and may become even negative. A comparison of theoretical and experimental results for the metering zone shows good quantitative agreement though the main aim of the paper is to provide a better general understanding of the complex situations inside of an extruder.

4/13 "STATISTICAL EVALUATION OF PROCESS PARAMETERS IN A COUNTER ROTATING TWIN SCREW EXTRUDER: EFFECTS ON MIXING"

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A counter-rotating intermeshing twin screw extruder was used to compound a formulation of 20% (by weight) magnesium hydroxide in polypropylene. Two processing variables (feed rate and screw speed) as well as one machine variable (exit diameter of the die) were varied in a 2^3 factorial experiment in order to determine which of the three factors had significant effects on the quality of the final mixture. Physical properties and the morphology of tensile bars prepared from the various extrudates were used to evaluate the effects of the aforementioned factors.

It was found that extrusion conditions of low feed rate and high screw speed produced the mixture which had the highest ultimate tensile elongation at break. The morphology of the fracture surfaces of these samples also indicated significant break down of agglomerates had occurred. For extrusion conditions of high feed rate and low screw speed, the opposite effect was observed.

The residence time distribution was determined using a radioactive tracer technique. The results indicate feed rate has a significant effect on the average residence time.

4/14

ON THE MODELLING OF COROTATING TWIN SCREW EXTRUDERS

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Analogous to the treatment of a single screw extruder as a pump for viscous fluids (1922 , 1928), a model is developed for a (hot meld fed) corotating twin screw extruder. Typical for this kind of extruders is the variety in screw geometry and the fact that the screws are only locally filled.
From the pump characteristics (resulting from combined drag-, pressure - and leakage flows) for each screw element and from the prescibed, metered throughput the local pressure gradients can be calculated.
The sign of the pressure gradient and its magnitude provide the information necessary for the determination of those places where the screws are completely filled, because local pressure consumption (negative pressure gradient) must be preceeded by local pressure buildup. With the local shear stresses at the wall, calculated from the velocity gradients, and the surface area where the stresses are active, which are known now, the energy and consequently the specific energy can be calculated, depending on screw geometry and processing conditions.
This simple newtonian model is improved to allow the use of a shear thinning, temperature dependent viscosity with the aid of a local overall heat balance.
Results from model calculations are compared with experimental data and they show remarkably good agreement for specific energy and temperature rise (deviations smaller than 5 %) provided that a screw speed and wall temperature dependent heat transfer coefficient is used.
The same analyses, with some necessary adaptations, is also applicable to the Buss-cokneader. The first results from theory and experiments will be presented.

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4/15 MODEL FORMULATION FOR MATERIAL FEEDING IN TWIN-SCREW EXTRUDERS

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Assuming that the solid moves in consequence of wall friction and friction of the material, transport equation have been established by means of a force and momentum balance on the volume element.

These equations serve as a basis for describing

- the material feeding, i. e. transition of the polymer from the feed hopper, or the feeding device, into the filling region of screws and
- the transport and compression of the solid polymer, i. e. the movement of the feed towards the plasticating zone, with simultaneous decrease of porosity.

Depending on the geometry of the screws and on technological and material parameters, the model may give information on

- degree of filling
- compression
- pressure build up
- throughput of solids transport zone
- power consumption.

The process model is proven to be suited for the design of the solids transport zone.

5/1 NUMERICAL SIMULATION OF TRANSIENT MOLD FILLING

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A finite element algorithm has been developed for the simulation of mold filling in injection molding. Velocities, pressure and the coefficients of the free surface parametrization are determined simultaneously through a u-v-p-h formulation of the Navier-Stokes system. A second order predictor-corrector method is used to integrate the equations in time. Problems considered include: startup flow of a fluid initially at rest, cessation of flow when a flow front hits a solid wall and collision of two flow fronts to form a weld line. Special emphasis is placed on the fountain effect involved in all cases, the evolution of the free surface and the deformation history experienced by the fluid. Current efforts focus on the molecular orientation patterns developed during mold filling and their prediction.

5/2 NUMERICAL SIMULATION OF MOLD FILLING WITH POLYMERS

by A.LATROBE, H.BUNG, M.E DELALANDE

The prediction of the flow field and the temperature field during mold injection is of crucial importance for the plastics industry. Two different approaches are presented here : a 1D semi-analytical approach, and a 3D finite Element Method. The problem to be solved is a separate two phase flow model, values of interest are front progression versus time, temperature and pressure values. In the first section of this paper, equations and the rheological law are presented. In the second section, the two numerical models mentioned previously are developed. In the third and last section, results of the two models are compared and each time it is attempted to give the field of application.

Finally, a prospective view for application of these methods to mold injection of other materials is presented.

Used MOLDFLOW approach - has paper. Similar to Tadmor approach.

5/3 INJECTION MOLDING OF REINFORCED THERMOSETS : FIBER ORIENTATION OBSERVATIONS AND FLOW CALCULATION

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Injection molding of fiber reinforced thermosets is a process which is now developing to realize parts for mass production.The optimisation of part final properties implies the understanding of the mechanisms that govern the fiber orientation and the modelisation of the filling stage of the mold.

The orientation of long glass fibers (about 20 mm) has been studied. Observations have been made in several molds : a disk shape mold, a plaque mold with constant width, a plaque mold with different widths connected by divergent and convergent zones. These observations show that the fibers (which are constituted of about two hundred filaments of 15 µm diameter) can be split and broken into fimaments, both being more or less buckled. Whatever the mold shape is, there is a small layer (about 5 % of the thickness) near the surface without fibers, but with filaments which are mostly oriented parallel to the flow direction. In the disk, except this thin layer, the fibers are mostly oriented perpendicular to the flow direction but the filaments present an intermediate layer, just under the first skin layer, where the orientation seems to be isotropic. In the plaque the initial orientation of filaments and fibers, near the gate, is just like in the disk. Away from the entrance, this orientation disappears and an orientation mostly parallel to the flow direction takes place. When a more complex geometry with variable width is used, succesive radial and parallel orientations are observed which can be qualitatively related to the shear and elongational rate during the flow.

The filling stage of the molds has been studied both experimentaly and theoreticaly. The pressure at several locations in the mold and the screw displacement were recorded. The influence of the flow rate and of the mold temperature is shown. These experiments point out that the cross-linking can occur during the filling stage (for instance at low flow rates). The calculation takes into account a viscosity law which is not only a function of temperature and shear rate but also of time. Polyester resin can react very fast. The rheological kinetic curves have been determined and theoretical constitutive equation has been deduced. At each time step, the unsteady mechanical and thermal equations are solved, using finite difference method. Because of the time dependence of the viscosity, it is necessary to follow each particle of fluid on its trajectory to determine its viscosity evolution between two time steps. The fountain effect, near the flow front is taken into account in a simplified way. The numerical results are in good agreement with experimental measurements.

5/4

MANIFESTATION OF THE EFFECTS OF FOUNTAIN FLOW AND PACKING IN REAL INJECTION MOLDING SYSTEMS

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Computer simulation and experimental data will be used to illustrate the effects of fountain flow and packing in the injection molding of crystallizing thermoplastics systems. The predictions of computer simulation will be compared to experimental results.

Use Newton, Power-law + White-Metzner constitutive models. Use MAC model. ~~for~~ Allow variable flow-rate in nozzle - calculate pressure throughout runner + molds. Pressure profiles good. Calculate temp. profiles in delivery runners, and pressure distributions. Allow non-isothermal effects + crystallization kinetics (Nakamura model) In non-isothermal the fountain flow markers are pushed away from wall. Showed Coyle/Blake/Macosko work. In non-isothermal another V is formed? — based on Blake's "mushroom"

Shrinkage from Menges. During packing the V's are compressed to wall and ~~st~~ moved a bit downstream

5/5

A VISUAL INVESTIGATION ON FLOW BEHAVIOR ARROUND INSERTS IN CAVITY OF INJECTION FILLING PROCESS

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This paper presents the visual investigation results on the flow behavior arround the cylidrical and square inserts in flow paths for better understanding and prediction on the flow analysis injection filling process.

The experiments were carried out such as two methods; experiment A is the visualisation test of PAA(polyacrylamide) water solutions by using of the special designed apparatus with tranparent molds, other is experiment B which used the transparent mold of injection molding machine by HDPE melt.

Before the visualization tests,the viscosities of PAA water solutions and HDPE melt were measured by the cone-plate viscometer and INSTRON CAPILLARY RHEOMETER ,respectively.

The velosities were changed by the screw revolutions of the pump(Exp. A) and molding machine(Exp. B).

In order to visualize flow pattern clealy, a small amount of cut hair was mixed as a flow marker in the Exp. A, and in the Exp. B was used a polarized right analysis method, and those flow patterns were recorded by VTR system.

Generally,it is recognized reasonably that the stagnations were observed not only rear part but also front part of the inserts.

The stagnation was developed extremely at the front zone of the inserts than rear zone and this was emphsized in the case of square insert and also were found in several conditions the generation of the secondary flow in those front stagnated zone.

The air bubbles set up at the center of rear wall of inserts in high velocity regions ,which may cause the extreme generation of the weldline,and may be recognized not occurrence of Karman's eddies in the rear zone.in this experimental regions.

It is concluded that those results show the flow pattern of the nom-Newtonian fluid are extremely different from those of Newtonian fluid where unsteady flow with eddies are usually occured.

5/6 ANALYSIS OF BIREFRINGENCE IN THE INJECTION MOLDED DISKS

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Recently, injection molded products of circular and thin disk-shape as substrates for optical recording media such as compact disks are being widely produced industrially. The molded products for this purpose requires low degree of birefringence. Birefringence itself is the interesting information. Because,as well known,the formation of it results from molecular orientation of polymer and residual stress in the molded products,the degree of molecular orientation and/or the distribution of residual stress can be estimated from it.

In this report, the birefringence resulting from two factors, i.e. molecular orientation and residual stress, was analyzed in conjection with injection molding operating conditions. To estimate the contribution of these two factors to total birefringence separately, the residual stress was released by two methods: first, the molded disk was cut at radial direction, second, it was annealed below the glass transition temperature (Tg) of the material. The material mainly used was polycarbonate of bisphenol-A which is transparent and has high degree of birefringence when it is oriented and/or stressed.

The in-plane(Δn_{12}) and cross-plane(Δn_{13}) birefringence of polycarbonate disks were determined and Δn_{13} was found to be one order higher than Δn_{12}. The low degree of Δn_{12} can be obtained by cancelling the effect of molecular orientation and residual stress, whereas Δn_{13} is mainly determined by molecular orientation and is not affected by residual stress substantially. The molding conditions affect both molecular orientation and residual stress. More specifically, the holding and the cooling process affect the residual stress, whereas the molecular orientation mostly occures during the filling process although the filling condition used in this work did not change the degree of it substantially. Compared with the distribution of the birefringence in the rectangular molded products, the result that the Δn_{12} birefingence induced by molecular orientation in the molded disk is high around the gate and decreases linearly at the flow direction is considered to result from the radial flow.

5/7

PREDICTION OF VISCOSITY AND MOLECULAR ORIENTATION IN INJECTION MOULDING

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Arguably the main problems in injection moulding reside in post-moulding distortion, manifested as shrinkage, warping and sinking. A major contribution to these problems is the existence of non-equilibrium conformations or shapes of the polymer chains in the post-mould state. As is well-known, the degree of this non-equilibrium condition various throughout the moulding, usually being greatest in the wall regions closest to the gate. This variation arises essentially from the many large differences in strain rate experienced by a chain flowing into and within a mould, coupled with the fact that production rates of cooling do not, in general, allow chains time to fully relax while still in the fluid state.

During the injection process, the conformation of the chains, particularly their degree of entanglement, determines, with the temperature, the local viscosity. Both viscosity and conformation change with time and from point to point. In fact chain shape (and therefore viscosity) is the product of local conditions inherited from upstream. Mathematical models of injection moulding, however, customarily treat viscosity, where it is not taken as constant, as an empirical function of the local variables usually a principal strain rate ($|\dot{r}|$) and temperature.

By contrast the approach adopted by this paper is to employ a formulation which treats chain conformation and viscosity as dependent variables to be calculated within the computation along with the usual microscopic variables, namely bulk velocities $\{\underline{u}\}$ and temperature (T). The chain shape is characterised by variables $\{\underline{s}\}$ whose local rates of change $\{\dot{\underline{s}}\}$ are functions of the shape variables themselves $\{\underline{s}\}$, the velocity gradients $\{\delta\underline{u}/\delta\underline{x}\}$ and temperature. The chain shape $\{\underline{s}\}$ in a finite region of the mould at any instant is then obtained as the resultant of the local rate of change $\{\dot{\underline{s}}\}$ and values of $\{\underline{s}\}$ convected into the region from upstream. The local viscosity and elasticity are then obtained as functions $\eta(\underline{s}, T)$, $E(\underline{s}, T)$ respectively. In this way we both obtain a prediction of molecular orientation (through $\underline{s}$) and account directly for the viscosity and elasticity memory.

The results of this formulation are presented as simulations of three-dimensional injection mouldings of a variety of basic shapes. The simulation model is part of a design system which includes a graphical interpreter of mould cavity detail. Velocities, temperatures, pressure and molecular orientation are displayed by the post-processor as colour-graphic contours at various stages of mould-filling.

5/8 Optimizing the application of melting cores in injection molding

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Hollow parts with complicated geometry can be injection molded using cores out of metallic alloys with low melting points. In the series production of big components a number of problems arise, which influence the quality and costs of the product. The most important problems in injection molding, which result from mechanical and thermal strengthening of the cores can be minimized using finite element methods for numerical simulation of the filling process and the heat transfer. The melting of the cores through high frequency induction in a hot liquid allows an efficient application of this technique for big components and large series with negligible metall loss and a non-polluting cleaning process. The main development steps are demonstrated on the optimization of the processing conditions for air inlet manifolds for motor vehicles.

5/9 PVC-POWDER-SLUSH FOR CAR-DASH-BOARDS

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Thermoformed PVC films on dash-boards in cars may crack when exposed to extreme temperature conditions. An alternative use is a stressless skin which can be produced by PVC slush-moulding technique.

This technology of moulding or rotational moulding of PVC plastisols is quite old. Wellknown are garden-dwarfs and toy-balls made by rotational moulding. Recently PVC dry blends are in use preferably instead of PVC plastisols; i. e. PVC powder-slush.

PVC skins made by slush-moulding have a number of advantages in comparison with usual thermoformed PVC films: no cracks can occur, a softer touch is possible, the range of surface design is wider.

5/10

FINITE ELEMENT CONTROL VOLUME SIMULATION OF NON-PLANAR COMPRESSION MOLD

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Simulating the compression mold filling process before a mold is actually constructed can eliminate some of the expense and time consumed in the early stages of the part and mold design. Due to the moving boundary nature of the problem, most of the effort in such a simulation goes into mesh generation during filling. The control volume approach which uses a fixed finite element mesh can significantly simplify this problem especially when dealing with complicated three-dimensional parts. This paper presents the implementation of the control volume approach in a simulation of compression molding in thin non-planar mold cavities. The cavity geometry is represented by a mesh of shell-type finite elements. The simulation automatically divides the part into nodal control volumes which are used to keep track of the charge geometry during filling. Equations of momentum and continuity, simplified by the assumption that the charge is thin, are solved for each time step during the simulation. The solution is then used to calculate the flow rates between neighboring control volumes and advance the free flow fronts. Results are compared to several experiments, including the filling of three-dimensional automotive body panels. Results from the simulation were also compared to the flow patterns of multi-thickness charge configurations. The simulation accurately predicted the flow pattern of thin non-Newtonian, non-isothermal charges such as sheet molding compound and clearly showed the limitations that exist with the thin charge approximation. The control volume approach offers the ability to model the mold filling of most parts including complicated non-planar shell type geometries with variable thickness.

5/11 INJECTION WELDING OF POLYAMIDES

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There are many reasons why one would want to join different materials with each other. They can be for a construction reason or based on applicational necessity.

Design considerations for example led to the combination of polymers with different colours or of transparent parts combined with opaque parts. But material engineers and designers are realizing more and more the possibilities that they can achieve by combining flexible elements made out of an elastomeric polymer together with a rigid engineering plastic in one piece.

Many techniques are known for combining different materials, e.g. usage of adhesives or welding techniques like ultra sonic, frictional, high-frequency welding and so on. Most of these techniques are labor-intensive or require special handling like pre-treatment with primers or specific design of the joint line.

The injection welding technique (IWT) on the contrary, can be a relatively simple process and tends to become more widely used especially in its modern form of co-injection.

IWT has been known for many years. Its principle is the joining of different polymers, of which at least one is in a molten state, in an injection mould. Under the influence of heat and pressure the polymers are welded together.

To achieve the optimal adhesion between the parts to be welded, the best suited materials have to be chosen and the correct injection moulding parameters have to be used as well as the optimization of the joint line.

In this speech the correct usage of IWT with semicristalline, amorphous and elastomeric polyamides will be discussed.

Polyamides are available in a wide variety of versions, from those of very flexible to those of high rigidity, either in their amorphous form or as carbon or glassfibre reinforced versions.

All polyamides are common in that they have in their molecular structure the amide group. This chemical configuration is able to build up strong hydrogen bonds, which allows us to injection weld many different grades with another.

This speech deals with optimal polyamide combinations, the correct moulding technique and the relevant design rules.

The differences of the achievable adhesion strength between the insert technique and co-injection will be discussed.

Finally I will show some possible application.

6/1

EVOLUTION OF RHEOLOGY DURING CHEMICAL GELATION

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Very little has been known about the transient states of network polymers during the crosslinking reaction. Measurements could be readily taken during early stages or near completion of the reaction. Intermediate states near the gel point were passed by too quickly to allow detailed physical characterization. Chambon and Winter (1) therefore developped a method for conserving intermediate states of a crosslinking polydimethylsiloxane (PDMS). Stopping the reaction did not disturb the preceding network formation process. The continuous crosslinking reaction was thus represented by a discrete set of stable samples with increasing extent of reaction. Rheological measurements on these stable samples showed clearly how the gel point was approached and passed during network formation. The linear viscoelastic behavior <u>at the gel point</u> was found to follow a surprisingly simple constitutive relation (2)

$$\tau(t) = S \int_{-\infty}^{t} (t - t')^{-n} \, \mathring{\gamma}(t') \, dt'$$

where τ and $\mathring{\gamma}$ are the stress and the rate of deformation. Stress relaxation of the gel follows a power law with an exponent

$$n \begin{array}{ll} = 1/2 & \text{stoichiometrically balanced} \\ > 1/2 & \text{stoichiometrically imbalanced} \end{array}$$

which depends on the stoichiometry of the polymer system. The gel strength S depends on the molecular parameters of the network. For completeness, it should be mentioned that the constitutive equation can easily be rewritten for finite viscoelasticity (2).

Uses theory from Muthukumar

The networks under investigation were all formed by endlinking reaction. They were studied much above the glass transition, except for one sample which indicated that closeness to glass transition may mask the rheology of the gel. Physical entanglements are assumed to be of no importance in this study since the molecular weight of the prepolymers was chosen below the entanglement limit.

Acknowledgement

Financial support from the Center for UMass Industry Research in Polymers (CUMIRP) and from NSF (Equipment Grant CPE 8203273) is gratefully acknowledged.

References

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6/2

DYNAMICS OF MIXING-INITIATED FOAM GROWTH

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Crosslinked polymeric foams, such as polyurethane foams, are formed as a result of complex interactions between polymerization kinetics, diffusion of a multitude of chemical species including gases, heat transfer and flow. The time-dependent foam structure, resulted from such interactions, affects the processing properties of the foaming system exhibited along the reaction path as well as the material properties of the finished foam.

A mathematical model and some supporting experiments, including foaming flow characterization measurements, will be discussed for cases of foam growth initiated by mixing of two monomers that undergo an exothermic crosslinking reaction that provides the thermal energy to induce supersaturation of a physical blowing agent originally in solution or alternatively a gaseous by-product acting as a chemical blowing agent.

A unit cell approach is used to account for the interaction between closely spaced bubbles. A key feature of this problem is the drastic increase in molecular weight during the reaction. The combination of the high viscosity and low diffusivity near the gel point can result in non-equilibrium structures in the foam.

The role of various factors such as non-ideal thermodynamics, the concentration- and temperature-dependence of the transport properties and the nucleation density as well as of some selected processing parameters e.g. the reactant and blowing agent concentrations and initial temperature are examined.

The theoretical results are applicable to examinations of the foam stability during processing and optimization of properties of the cured foam including the density and thermal conductivity as a function of the chemical formulation and processing conditions.

6/3

COMPUTER MONITORED INJECTION MOULDING OF UREA FORMALDEHYDE: ON-LINE SHEAR AND ELASTIC FLOW CHARACTERISATION

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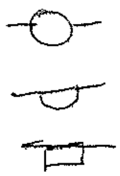
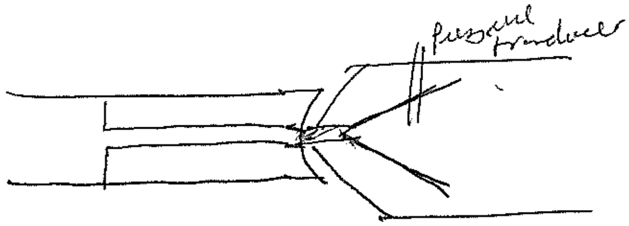
Extensive flow testing on commercial grades of urea formaldehyde (UF) has been undertaken on an instrumented thermoset injection moulding machine. A variety of on-line rheometers were investigated: these included the injection machine nozzle, split die capillaries of various cross sectional geometries, a cylindrical mould block rheometer and an instrumented test tool. Results are presented which indicate the relatively high pressure losses in the flow of UF in typical process geometries due to elongational contributions. Simple predictions based on the flow characterisations prove to fit experimental data - the computer monitored pressure/time profiles - well.

channel in-line rheometers
used similar type geometries
not used





6/4 A CONTRIBUTION TO THE SILANE GRAFTING AND CROSSLINKING PROCESS OF POLYETHYLENES.

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From within the framework of a broadly based research project, initial results are given concerning the silane grafting and crosslinking of high density polyethylenes and possibilities for combining this technique with conventional shaping technologies such as extrusion (profiles, films), injection moulding and compression moulding are considered. For this purpose, the processes occuring during the individual reaction steps are analysed in depth and, as far as possible, quantified conformal to the processing time in order to attain a concept for process monitoring and/or control.
Studies concerning the graft polymerization and crosslinking process were done for Ziegler and Phillips polyethylene grades which were previously characterized with regard to structure and rheological behaviour. The grafting process was carried out in a laboratory scale using a Brabender Plastic-order for various types of peroxide (DHBP, DCUP, DIPP) and various peroxide and organosilane contents. Changes in the structure of the samples were analysed and the attainable gel content due to the subsequent crosslinking process was determined. Using this data concerning the reactivity of the investigated recipes, a sample preparation procedure meeting practical requirements was applied using a twin screw extruder and an on-line rheometer system in order to accomplish a means of material characterization conforming to processing time. Studies were carried out on these samples for various crosslinking times and at various measurement temperatures using a mechanical spectrometer. These dynamic measurements (tensile modulus resp.$G'(\omega)$, $G''(\omega)$ lead to a deeper understanding of the relationships between grafting conditions, crosslinking history and attainable end-product properties of silane crosslinked high sensity polyethylenes.

6/5

IMIDIFICATION REACTION BY REACTIVE EXTRUSION

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Copolymers of ethylene an maleic anhydride are characterized by their potential reactivity and the good thermal behaviour in adhesive formulations. However these products are sensitive to moisture and need anhydrous storage conditions. In order to generalize the use of these kind of adhesives, it seemed interesting to perform a chemical modification of the cyclic anhydride group leading to a stable imide cycle. Various equilibrated reactions are to be taken into account successively, by reaction of gaseous ammonia on the solid or molten polymers. The basic reactions were studied by FTIR and this fundamental approach was helpful for the choice of reactive processing conditions. Using two different processes, it was possible to convert 50 to 80% of the anhydride groups to cyclic imides, by extrusion in a single screw equipment. These results and the characteristics of the products will be presented.

6/6 COUPLING OF REACTIVE POLYSTYRENE AND POLYETHYLENE IN MELTS

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Polystyrene(OPS) having oxazoline groups and polyethylene (CPE) having carboxyl groups, were melt blended in a Rheomix mixer, and the effects of composition, temperature, time, and shear rate on torque, thermal transitions, solubility and phase structure of the blends were investigated. Differential scanning calorimetery (DSC) was used to determine thermal transitions and heat of fusion (ΔH) characteristics of these blends, and their microstructure was examined under a scanning electron microscope (SEM). The results are compared with the corresponding melt blends of the nonreactive polymers and dry mixed blends of the reactive polymers. It was found that with small but increasing amounts of CPE in the blend, torque, solubility and ΔH are affected, but not substantially. However, when the CPE amount in the blend reaches 40% (wt), a major change in these properties occur. For instance, the differences between the maximum and minimum torque ($T_{max} - T_{min}$) values for 10, 20, 30, 40% blends are 48,155,219 and 510 m•g respectively, showing a considerable increase in the later case. Similarly the 10% CPE blend was found to be completely soluble in toluene at room temperature whereas the 40% CPE blend was almost insoluble. Also, the difference in thermograms of dry and melt blended reactive polymers of this composition was noticeable. This suggests that a 40% CPE blend composition corresponds to maximum reactivity between the two polymers and a further increase in CPE content amounts to a simple excess of this polymer. SEM micrographs of reactive polymer blends also reveal fine microstructure compared to the corresponding unreactive polymer blend.

6/7 REACTIVE POLYMER COMPOUNDING

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New parameters can be realized by compounding and coreacting of different organic polymer in the melt, which could not be reached until now with the known homo- and multipolymers. Most of the polymers are not mutually miscible because of thermodynamic reasons and the "physical incompatibility" does in many cases not allow a finaly dispersed distribution of the polymers into one another. A sufficient interaction at the interfaces are of high importance for a finaly dispersed distribution of the one polymer in the so called matrix polymer. Blends of high modulus thermotropic polymer materials with elastomers are of special practical interest to get high impact resistance thermoplastics as well as also thermoplastic elastomers. We investigate polymer blends of polyamide-6 (PA-6) and of ethylene vinylacetat copolymers (EVA) or of thermoplastic polyurethanes (TPU) with and without a radical reaction (RR) during the melt mixing process at a temperature of about 245 °C in a twin-screw extruder ZSK 30 of the firm Werner and Pfleiderer. We aimed at a chemical reaction between elastomer and thermoplastic matrix to encrease the interaction at the interface.
The TEM representations demonstrate that under equal compounding conditions with RR the particle size reduction of the elastomers is distinctly recognizable.
In contrast to the PA-6/EVA/RR the areas of fracture of the PA-6/TPU/RR blends are not any more keenly delimited. The small particle size of the PA-6/TPU/RR-blends corresponds with an increase of the notched impact strength (a_n) by addition of 10 % TPU and directs to a higher interaction of PA-6 with TPU and RR. The results correspond with the statements of Wu /1/ but an attainment of the critical partical distance can not yet be expected at these concentrations.
The increase of the toughness of the composite material is connected with a decrease of the properties stifferes and strength.

/1/ S. Wu, Polymer <u>26</u>, 11(1985), 1855 - 1863

6/8 TERNARY SYSTEM OF PVC, UNSATURATED POLYESTER AND STYRENE MONOMER FOR REACTIVE POLYMER PROCESSING.

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Compounds of P.V.C and Saturated polyesters are well established commercially. Basically, these are P.V.C compositions containing a polymeric plasticizer.

As result of our work, we have developed compositions containing P.V.C and certain unsaturated polyesters. These are ternary systems, comprising mixture of P.V.C., on unsaturated polyester resin and styrene monomer.

The resulting compound may be processed by conventional means, such as injection molding or extrusion.

Injection molding temperatures are lowered by about 30°C as compared to unplasticized P.V.C. without adversly affecting the physical properties as compared to unplasticized P.V.C.

The objects obtained have a very smooth and shiny surface and it appears that the outer surface of the objects contain an increased proportion of the polyester phase, forming a barrier, that may be advantageous on protecting surface degradation.

6/9

INTERACTIONS OF PROCESSING, MORPHOLOGY AND MECHANICAL PROPERTIES OF POLYURETHANE-POLYESTER IPN

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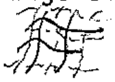
To improve the performance properties of the polyurethane-RIM products, which are considered inappropriate for structural applications due to their high thermal expansion coefficient and low rigidity, there have been many investigations on developing new RIM resins such as nylon, epoxy and polyester, or on reinforcing externally the existing materials by compounding with various reinforcing agents (ie., reinforced RIM or RRIM). There is, however, another approach of material modification by using an internal reinforcement to enhance the physical properties of existing resins. This is done by introducing a second reactive system into the RIM process to make up the deficiencies of the existing material. This approach is essentially an application of interpenetrating polymer network (IPN) to the RIM process.

In this work, we study the interactions of processing, morphology and mechanical properties of a polyurethane-polyester IPN. Processes tried include a slow one, transfer molding (i.e., reaction time - 1 hour), and a fast one, reaction injection molding (i.e., reaction time - 1 minute). Sample morphology is measured by transmission electron microscopy, and product mechanical properties are measured by dynamical mechanical analysis and tensile test. Results show that morphology and mechanical properties depend strongly on compound composition and processing conditions such as relative reaction rates of constituent polymers, molding temperature and extent of mixing. TGM pictures indicate that both polyurethane and polyester appear in the continuous and dispersed phases due to polymer chain interpenetration and grafting. Processing conditions and compound composition determine the phase structure which, in turn, set the physical properties. At a given compound composition, varying processing conditions may cause phase inversion and result in a drastical change of physical properties.

IPN 

PU MDI UCP 2?0
143L DIOL UC 800
Triol UC P310

Polyester slow

Vary components to vary rxn rate.
PU tends to form the continuous phase because it reacts faster.
IPN is very sensitive to mold temperature.
RIM (for same IPN formulation) get better dispersion compared to transfer molding.

use polyester polyol / polyester → polystyrene phases out quickly

unsaturated polyester
MDI
styrene
} commercial IPN

6/10 KINETICS OF THE REACTION OF WATER AND TOLULENE DIISOCYANATE

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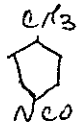
The reaction of TDI with polyols, amines, and water has been used extensively in commercial products including foam, sealents, coatings and RIM. In many of the products the water isocyanate reaction is very important. Most of the literature on this reaction is base on P-tolulene isocyanate. We will show that the kinetics of the TDI reaction can not be very effectively predicted using this model compound. We will report the results of a series of experiments in which the uncatalyzed reaction of TDI and water to produce carbon dioxide was investigated. The results of these experiments were very surprising when compared with previous literature analysis. The reaction is autocatalyic with the reaction catalyzed by the urea produced by the 4-4 reaction product. The activation energy decreased from 23000 to 6300 during the first five percent of the reaction. Also, there is strong evidence that a stable product, perhaps an anhydride, is formed and accounts for about 50 percent of the reaction product when the reaction is carried out below 80 degrees C. We develop and report a model which will fit the loss of isocyanste and generation of carbon dioxide for this system over the temperature ranges investigated.

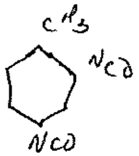
Sees bimodal peaks in $\frac{dT}{dt}$ for rxn, and in CO_2 evolution.

$RNCO + H_2O \rightarrow CO_2 + R-\underset{H}{N}-\overset{O}{C}\underset{H}{N}R$

most data

toluene / ~~disocyanate~~ phenyl disocyanate





2,4 toluene diisocyanate → better conversion

non-catalyzed systems.

rate constants — $E = 6000$ cal/mole

should have $E = 20,000$ cal/mole

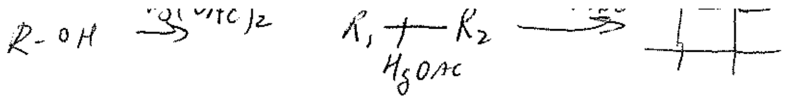
low viscosity so it can't be diffusion controlled

assume 2nd order

get a $\frac{dx}{dt}$ that it is autocatalytic rxn.

should be

Rossby model → doesn't explain data



Can put catalyst in
B side (wrong side)
A/B incompatible — have
catalyst search A phase
can delay rxn time — ba
keep same cure time.

6/11

PHASE LOCALISED CATALYSIS IN REACTION PROCESSING

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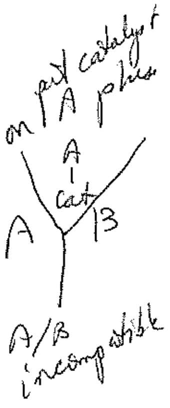
Reaction processing offers new opportunities in processing and materials' development. These make demands of chemical reactions which invite new approaches to reaction control. For reactions in bulk polymers, accessibility becomes the key to control. Enhancing or reducing this accessiblibity offers a unique route to achieving the fullest promise of reaction processing.

This paper describes one approach to achieving this control by attention to reaction catalysts. In a series of curing studies catalysts were bound directly to specific polymer backbones, and such polymer-supported catalysts were seen to match the activity of equivalent low-molecular weight catalysts. This activity was maintained even after crosslinking or when the catalyst itself is the site of a crosslink. In single-phase systems the benefits of macromolecular catalysis can include the optimisation of rates and improvements in product properties.

It may be viewed that macromolecular catalysis guarantees the availability of a catalyst within a given polymer phase. The concept can be extended to two-phase systems in which specific compatibility effects can be usefully exploited. It is shown to be possible to retain catalyst species, and hence progress a given reaction, exclusively within a single phase. Additionally the controlled transfer of active species between phases can delay the onset of cure and offers a new dimension in reaction control.



6/12 ION AGGREGATION IN THICKENED POLYESTER RESINS - S.A.X.S. STUDY ON MODELS.

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The addition of MgO to styrene solutions of carboxyl group containing unsaturated polyesters leads to compounds with very high viscosities. This "thickening reaction", which is the basis of the "sheet molding compound " (SMC) process, is not wholly understood because a reliable reaction mechanism has not yet been established. Mechanisms reported in literature involve either the formation of polymeric neutral magnesium salts of polyester or a crosslinking due to the formation of coordinate bonding between ester groups in the chains or hydroxyl end groups, and magnesium carboxylate groups. As these two mechanisms did not fit some of our previous results, we proposed a mechanism involving, as in ionomers, the formation and the aggregation of magnesium carboxylates in ionic domains .

Small Angle X-ray Scattering (SAXS) studies of magnesium eicosanoate, ω,ω'-dimagnesium carboxylato-poly(1,2-ethylene adipate), ω,ω'-dimagnesium carboxylato-poly(2-hexyl-1,2-ethylene adipate) and their swollen samples in various solvents are in accordance with the above mechanism. From the comparison of these results to those obtained for a MgO neutralized commercial unsaturated polyester/styrene resin it is concluded that the formation of aggregates is the key phenomenon of the thickening reaction of polyester resins.

6/13 A NEW MICROWAVE APPLICATOR FOR THE CONTINUOUS VULCANISATION OF RUBBER

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The aim of this paper is to give more details of the microwave preheater. The microwave applicator is a consisting part of the continuous vulcanization system, and includes an extruder, a microwave preheating section and a hot air section. The main characteristics of the applicator are : the low reflection loss for a wide range of rubber profile cross-section, the air support system and the quality of the product.

The applicator consists of a multimode cavity with a homogeneous power distribution at the product area. The microwave energy is coupled into the cavity by means of two symmetrically spaced antennas. The construction of these antennas is based on the concept of the leaky wave antenna which gives a uniform coupling of microwave power along the product.

The leaky wave antenna is constructed as a tapered and slotted rectangular wave-guide on its smallest side. A special feature of the applicator is the air support. The air support is so provided that the extrusions are transported through the applicator without touching anything.

No conveyor belt is used so that subvulcanization and deformation of the profile is avoided.

The hot air is guided through a thin groove between four glass plates.

The air support system is used as well in the microwave section as is the the hot air section and the cooling section.

The advantages of the concept are :

- homogeneous vulcanization of the extrusion in absence of contact with the conveyor belt.
- the leaky wave antenna gives a low reflection loss for a wide range of profile cross-sections and the coupling between the two opposite antennas is neglegable.

The microwave preheater is extensively tested in a production line for the treatment of different rubbers, such as EPDM, EPT and SBR. The profile cross-sections varied from full and hollow tubes to more complicated sections for the automobile industry.

Finally we presented a new microwave applicator for the continuous vulcanization of extrudates in the rubber industry. Due to the characteristics of the microwave applicator and the air support the vulcanization gives improved performances.

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P.J. Luypaert, P. Reusens, G. Frère, "Microwave Applicator for the Continuous Vulcanization", Symposium of the International Microwave Power Institute 1985.

7/1 EXAMPLE OF A F.M.S. (FLEXIBLE MANUFACTURING STATION) FOR THERMOPLAST-RUBBER ARTICLES

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Developmental basis and experiences with this on the fair in Düsseldorf, 4 - 13 Nov. 1986, first time exposed development as an example of futuristic fabrication in plastics, will be given.

This conception to a futuristic production of plastic articles is not only an example of a new kind of fabrication methods, it is as well about the first time that CIM (computer integrated manufacturing) following rules in article-mold design and machine adjustment have been used. It integrates two different kinds of artificial intelligence implemented in the computer control of the injection molding machines and some material novelties like direct powder rubber melting and a new to rubber self adhesiv thermoplastic polymer.

Consequently it will be shown in this lecture the basics of the used software packages for thermoplastic and rubber materials and the practical experience with those partly commercial programs. Later on it will be given the design principles of this combination of commercial machines consisting of 2 computer controlled commercial injection molding machines, one computer controlled 6 axes robot and the developed multifunctional molds and robot tools for demolding, transfer and assembling of articles. Especially the principles of the software for the closed loop adapted control for production of wastless and flashless thermoplast rubber articles and the datalink of this 3 machines the mold-changing units and the robot will be given.

Finally are discussed the experiences and the aspects of such methods.

7/2 A NEW CONCEPT FOR PROCESSABILITY CHARACTERIZATION OF RAW RUBBER

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By means of a simple 5 minute measurement of torque, integral torque and mass temperature in a Brabender laboratory mixer during a shearing process on raw rubbers (batches and compounds as well), various information about processability as well as molecular characteristics of the polymer is obtained. Our method can also be used for quality testing of those materials. A particular advantage we see in the capability of the apparatus used to serve both as torque rheometer and as a miniaturized internal mixer. Deformations and deformation rates are realistic concerning the processing practice under factory conditions. Scale up experiments are possible. The most serious problem of precision and uniformity of the procedure has to be solved by a new feeding technique. The achieved coefficients of variation range between 0,3 % and 2,5 % depending on the property considered.
Raw rubber specimens of about 70 cm^3 are cut directly from bales in a special manner. Thus the specimen does not undergo any shear history prior to the measurement. Specifically, the specimen is sheared for 5 minutes at constant rotor speed of 120 min^{-1} and apparatus temperature of 70°C. The shear process runs prevailingly adiabatically. The whole measurement including specimen preparation, feeding, measuring and computer evaluation can be performed within 10 to 15 minutes. The method avoids the disadvantages of complicated and time consuming specimen preparation, unrealistic small deformations or deformation rates, poor discrimination power or one point measurement typical for other methods to measure raw rubbers.

One 5 minute measurement yields torque and mass temperature as functions of time. That mass temperature curve gives insight into the shear heating property of a material - which is important to the mixing process. The shape of the initial peak of the torque curve delivers valuable semiquantitative information about high molecular portions in the material. The torque-mass temperature relationship is subjected to an Arrhenius evaluation beginning with values 1,5 minutes after the start of the measurement. The slope of the Arrhenius straight line refers to the elastic properties of the material. The meaning of the ordinate intercept is still not sufficiently clear. Torque values related to mass temperatures of about 90 - 140°C at constant shear rate of approximate 100 s^{-1} give a realistic viscosity measure for processing operations. The integral torque delivers an energy consumption characteristic of the over all process which is informative to the work input during mixing operations.

7/3 INFLUENCE OF THE MACROSTRUCTURE ON RHEOLOGY AND PROCESSIBILITY OF POLYBUTADIENES

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Polybutadiene samples were polymerized with Lithumbutyl to yield polymers with the same microstructure but big differences in macrostructure. Samples with different molecular weigth averages and distributions were obtained as well as samples with different degrees of long-chain branching.

The influence on rheology and processibility of these macrostructure features are demonstrated.

The polymers are characterized by GPC and rheological testing (complex viscosity in rotational rheometer in ERD-mode, complex modulus in Roelig-test; viscosity and elasticity with their shear rate dependences in the new Defo-test and Mooney viscosity and Mooney relaxation).

In order to assess the processibility of the polymers a carbon black test compound is mixed under computer controled conditions in a modern laboratory mixer equipped with additional sensors to better characterize the mixing process in its different steps. The compounds are tested in several rheological tests, including the capillary rheometer and the Brabender extruder.

714 RHEOVULKAMETER - FOR FAST AND EASY TESTING PROCESSABILITY OF RUBBER COMPOUNDS

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Nowadays many rubber compounds will be processed by extrusion and/or injection moulding. In the course of these processes the compounds will be subjected to high shear rates. Hence in order to optimize the processing conditions and also to guarantee a constant quality of the compounds it is necessary to test the processability of the compounds in the shear rate range of practical processing. Processability of rubber compounds is predominantly determined by the viscosity that is balanced by two effects: the viscosity of these materials decreases drastically with increasing shear rate (pseudoplasticity) but increases markedly with the onset and development of curing. Hence there is need for adequate testing equipment to measure easily and fast the processability of rubber compounds under conditions of practical processing by taking care of these effects.

This can be done with the RHEOVULKAMETER. One mode of operation is to use it like a capillary rheometer, where the compound to be tested will be injected into free space at temperatures low enough to prevent curing. By variing the pressure and measuring the output, the viscosity function $\eta = \eta(\dot{\gamma})$ in the shear rate range of practical processing can be determined. Another mode of operation is to use the RHEOVULKAMETER as an injection moulding tester, by injecting into a hot mould. This test will give a combined information about the flowability (viscosity) of a compound and its variation with the onset and development of curing.

After a short introduction of the instrument experimental results on different rubber compounds will be presented and discussed. Part of these results will be compared with the results of the high pressure capillary rheometer RHEOGRAPH 2001 and with the results of the rotorless curemeter ELASTOGRAPH 67.85 to demonstrate that the RHEOVULKAMETER will give informations about both: flowing (RHEO-) and curing (VULKAMETER) of the compound.

7/5

CONTROL OF PLASTICATION DURING MIXING PROCESS

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The mixing process has many purposes. They are plastication, dispersion of fillers and chemicals, blending of polymers, etc. Especially in rubber industry, the plastication is important in the subsequent processes. Usually good dispersion does not cause any trouble, but either excessive or less plastication often causes many troubles in the subsequent processes. Therefore control of plastication during mixing process is very important.

There mainly exists two types of mixing control processes. One type of control is done by setting up an object value for each parameter, such as temperature, time and power, and by monitoring the parameter during mixing. When it reaches the set up value the mixing sequence will go to the next step. In this case, the machine conditions will not be changed. Another way uses a typical profile of any given parameter during mixing as a reference. The parameter value of the mixing process is monitored and compared with the reference continuously. If any deviation is found, feedback will be given to the machine to change accordingly the running condition such as rotor speed, ram pressure, and temperature of tempared water. It needs heavily equipped machine. For the plastication control former method woul be adopted. Usually these control methods do not take account of the chemical reaction. For the plastication control, however, chemical reaction can not be neglected.

In this study attempts were made to take the effect of chemical reaction into account. Suppose that correlation between plastication and temperature obeys the Arrenius equation. The extent of chemical reaction Th can be expressed as

$$Th=\int k(t)dt= k_0\int \exp\{-Ea/RT(t)\}dT$$

$$k(t)=k_0 \exp\{-Ea/RT(t)\}$$

Th: The extent of chemical reaction
Ea: activation energy
R : gas constant
k_0: constant
$k(t)$: reaction rate at time t
$T(t)$: material temperature at time t

Suppose that the plastication is proportional to the mechanical energy input, W[KWH/Kg]. As an approximation the total effect of plastication could be expressed by the sum of the chemical and the mechanical plastications. The total effect P can be expressed as

$$P=C_1 W + C_2 Th$$

C_1 and C_2 are constants, and depend on the material. By monitoring temperature and the power input, total effect P can be calculated. Setting up such a computor control system, mixing tests were carried out, using laboratory O-OC B/M and Brabender plasticorder. The materials tested were NR and NR /carbonblack composites. Comparing with the ordinary parameter (time, temperature, power) methods, the new parameter method was found to give more stable plastication even though the mixing conditions such as tempared water temperature, material temperature and rotor speed were varied.

7/6

A DISPERSIVE MIXING TESTING APPARATUS

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The Dispersion process of agglomerated solids, such as carbon-black, into rubber and plastics is still not understood to a satisfactory extent. Such dispersive mixing is commonly carried out in roll mills, internal mixers and continuous intensive mixers. Dispersive mixing is accomplished by repeated passage of the mixtures, through converging-tight clearance high stress regions, of the mixers. The key design and operational variables are the geometry of this region, the stress history of the fluid element, and the passage distributions function. A laboratory apparatus was designed and built to enable systematic study of the effect of these variables on mixing. The apparatus, and experimental results are described. Results verify that the number of passages is a dominant variable in dispersive mixing, and proves the utility of the apparatus to study the dispersive mixing process.

7/7 PROCESS ANALYSIS OF A LABORATORY INTERNAL MIXER

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In spite of many investigations in the field of internal mixing there is a lack of thermodynamic analyses and this means that its influence on the mixing result is fully unknown. Therefore a 1.5 l laboratory machine, which had been made available to the IKV, was equipped with measurement devices to take this fact into account. In addition to the installation of appropriate sensors a measuring system was developed, which can be used not only under laboratory conditions, but also under production conditions. The existing hardware and software used for recording the measured values, has been expanded to include "evaluation software" which presents many options for graphic presentation and mathematical manipulation (integration, differentiation...). Further examinations deal with methods for the characterization of the mixing result, which take practical conditions into account. Microtoming for example appears to be too expensive and too time consuming and produces too few usable results. We therefore believe that only two possibilities for characterization can be considered

- measurement of the electrical resistance
- characterization of the visco-elastic behaviour with the help of the torsion-vulcameter.

The IKV has developed additional measurement devices for both. In intial experiments, the flow processes were made visible inside the machine using a yellow compound. To achieve good contrast, a blue pigment was put into the premasticated material instead of carbon black. The water temperatures of the chamber and the rotors and the mixing time were varied. Because the upper part of the machine can be opened, we received instant shots of the mixing state at various positions in the mixer. They show that the thermal boundary conditions strongly influence the take-in behaviour of the material between the rotors as well as at the beginning of a visco-elastic flow. Pictures of cuts of the region in front of the rotor wing, and between the rotors, indicate that it seems to be impossible to achieve reasonable computer simulations of the flow in an internal mixer, in a similar way to the method used for simulating the flow in extruder screws. In the mixing chamber a random distribution of material sections takes place, in which visco-elastic flow occurs. Within this visco-elastic flow, unsheared material can be found, which can more or less only be deformed elastically. Investigations with natural rubber and carbon black mixtures also show the strong influence of the thermal boundary conditions on the incorporation of the carbon black and the take-in behaviour of the machine. These effects can be seen not only in the ram movement, but also in the curve of power consumption over time. In experiments with both the laboratory internal mixer and production machines, extreme preoperation effects can be seen in the thermodynamic condition of the machine, which are reflected in the changes of the wall temperature. The larger the machine is, the more pronounced these effects become.

7/8

MILLING BEHAVIOR OF COMPOUNDED AND FIBER REINFORCED ELASTOMERS

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The experimental verification of a mathematical model proposed to explain the occurrence of bagging and roll preference phenomena on two-roll differential rubber mills is presented. Black compounds of natural rubber, EPDM rubber and blends of natural rubber and chlorobutyl rubber were reinforced with short cellulose fibers to impart a wide variation in stock stiffness. Unreinforced compounds are also represented. Evaluation of the terms in the model requires the characterization and correlation of property data on viscosity, modulus, and roll adhesion.

It is shown that separation of the stock from the roll surface can initiate either at the top or bottom of the roll. A study of the forces acting on stocks just separated from the roll then leads to recommendations on stock properties and mill characteristics to avoid bagging. In many cases these conditions are at variance with the requirements for slow roll preference. By studying behavior on mills varying in diameter from 6" to 28" the criteria for scale-up are indicated.

7/9 BASIC STUDIES OF EXTRUSION OF RUBBER COMPOUNDS

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Researches on extrusion of rubber compounds are described. We have studied the screw extrusion characteristics including the extrusion rate-pressure rise-screw speed characteristics, the distribution of rubber in the screw (determined by screw pulling experiments) and transverse flow patterns. Starvation in rubber screw extruders is a common situation and we describe factors determining it and behavior associated with it. Results for several different extruders are compared.

7/10

TEMPERATURE DEVELOPMENT IN A RUBBER PROCESSING PIN BARREL EXTRUDER

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One of the remarkable features of the pin barrel extruder is its high output at low temperature and good mechanical and thermal homogeneity. The dependency of the output-pressure characteristic of the system screw-die, of the thermal homogeneity, of the die swell and of the mechanical properties of the vulcanized extrudate on the most important process parameters was investigated with a 60/14D pin barrel extruder. The test facility, its instrumentation and the test program are described.

The experimental results regarding the thermal homogeneity are discussed in detail. The radial temperature profiles were measured at the wall of the pins, at the screw tip and for the first time in the cross-section of the extrudate right at the outlet of the die. For the latter one a thermographic system was used. This system produces a thermal picture of an object by detecting its emitted infrared radiation. The experiments were carried out with SBR-, EPDM- and NR-compounds.

A comparison of the temperature profile at the screw tip with those at the pins shows the good homogeneization effect of these. At the screw tip the shape of the profile is influenced mainly by the programmed heating of screw and barrel. The mean temperature and the thermal homogeneity however depend on the programmed heating as well as on the screw speed and the pressure. The evaluation of the thermograms reveals, that the shape of the temperature profile in the cross-section of the extrudate corresponds to that one at the screw tip. The thermal inhomogeneity however is strongly decreased on the way from the screw tip to the die. The intensity of this homogeneity improvement is determined by screw speed and pressure.

7/11 THE EXTRUSION OF TIRE PROFILES FREE OF TENSION AND WITHOUT AIR BUBBLES (with elimination of the shrinkage section)

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- increased capacity at the builders
- higher capacity at the presses through shorter cycles-times
- smallest tolerances and raw-material savings through tensionfree profiles without bubbles

All may be reached quickly through newest technology.

However the rubberindustry - and here especially the tire-industry - should more accept the fact and take into consideration, that the extrusion doesn't begin only at the extruder. The first link in the production-chain is also here the regular and right produced compound.

The other hand, also the best extruder is only a simple link in the production-chain and not even the most important, if its the discussion of tire-profiles.

The basis of our studies is ouf course the coldfeed-extruder. Today are, apart the PIN-type extruder especially the BLEND-EXTRUDER as qualified machines with the great capacity - required by the tire-industry - available. However, during many years was the tire-industry thrown on warmfeed-extruders. But conditional on the less pressure build-up of the warmfeed-extruder the design of the extruderhead and of the dieplate had been the whole time limited.

However, a die of 3/8" resp. of about 10 mm thickness isn't enough for to reach sharp profile-edges and profiles without tension. It has to be changed here to 2 1/2" resp. 60 mm thickness.

As long as the profiles discharges the extruder-head with tension, it can also not be done without shrinkage section.

But why correcting the mistake afterwards, when it can be easily eliminated, as far as the tireindustry will be ready to forget for one time the conservative thinking?

Air-bubbles in an extruder profile are - against the opinion widely held - also on pressing in the mould eliminated only for a smallest part. However compressed air can the abrasion not put up resistance and force. Shorter running-kilometres resp. less durability of the tire are the result.

Against the opinion still widely held, that air-bubbles are a result of the compound-ingredients, are these in this connection only of a secundary importance.

Everybody knows, that condensation the product of a corresponding temperature-difference is. This knowledge should be used in the production. Small air-bubbles in a tread profiles <u>are primary the production of condensation</u> through to high temperature-difference in the compound cross-section.

Humidity condenses to water. Water evaporates on reaching of the boiling point. Steam expands. The result in tire-profiles - and not only there - is showed with air-bubbles.

A blend-part at the end of the extruder, new developped for the rubber-industry, setted-in as at the blend-extruder, can solve the problem. (Video 4 min. about temperature-blending).

7/12 MILL PROCESSABILITY, RHEOLOGY AND STRUCTURE DIFFERENCES OF POLYACRYLATE ELASTOMERS

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Two commercial polyacrylate elastomers, one having epoxide (EP) crosslinking sites and the other ethylidene norbornene (ENB) were selected. It was demonstrated that the former was more difficult to mill-process than the latter. The viscoelastic properties measured at very small strain in shear oscillation indicated that the ENB polymer was more branched than the EP polymer. The gel determination by filtration confirmed this. The tensile stress-strain measurements were conducted at four different deformation rates. These data were treated according to the strain-time correspondence principle to see if this principle applies to the data of these samples. The data of EP polymer did not form a master curve, thus, the above principle is not applicable; at the larger deformation the strain-hardening tendencies were observed. This indicates that the EP polymer has a rather extensive long branching, a type of which usually results from a chain transfer reaction.

The data of ENB polymer on the other hand form a master-curve; that is, the strain-time correspondence principle is applicable, in spite of the presence of the large amount of gel. Only such a gel-contain sample known to obey the principle is that containing micro-gel. The micro-gel in this case is polymer-latex particle crosslinked during emulsion polymerization with a difunctional comonomer.

Thus, in this work polymer rheology was effectively used to find a major difference in the polymer chain structure. In this way it was shown that the results of polymerization may be related to the mill processability.

7/13

RUBBER /THERMOPLASTIC BLENDS: THERMAL AND VISCOELASTIC PROPERTIES

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Using a differential scanning calorimeter and mechanical spectrometer the thermal and viscoelastic properties of blends of various polyisoprene rubbers (hevea rubber (nr), guayule rubber (gr) and synthetic polyisoprene (ir)) with high density polyethylene (hdpe) were studied.

Temperature of fusion of blends was lower than that of hdpe, with a minimum at about 30% rubber content. Heat of fusion of blends (as well as cristallinity) were higher than that of hdpe, within 10 to 50% rubber content. Free energy of mix was negative for blends (in molten state) within 15 to 65% rubber content. Magnitude of these three deviations was greater for gr blends, then for nr of ir blends.

In general complex viscosity decreases with frequency, temperature and polyethylene content in the blend. The values of complex viscosity are similar for the three systems, at low rubber content (10 and 30%). At higher rubber content, however, the value of complex viscosity is about the same for the nr and ir blends, but it is lower for the gr blend (influences from the different rubbers). Storage and loss modulus increase with frequency and decrease with temperature and polyethylene content. Tan δ equals one at higher rubber content in the blends.

7/14

POLYBLEND OF POLYSTYRENE AND POLYACRYLATE RUBBER MODIFIED BY POLYSTYRENE MACROMER AND BUTYL ACRYLATE GRAFT COPOLYMER

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The compatibility of polymers and the physical and mechanical properties of polyblend could be improved by adding graft copolymer[1]. Well-defined graft copolymers composed of polystyrene (PS) brances and poly (butyl acrylate) as backbone were prepared by macromer technique[2] and their microstructures were also characterized, as shown in table 1, to study their application as a compatible agent for the polyblend of PS and polyacrylate rubber. It can be seen in table 2 that impact and tensile strength of such a polyblend contained 3 wt % graft copolymer increased up to about 8-fold and 2-fold respectively by contrast to the reference specimen, so it could be used as HIPS. Fig.1 shows that the added graft copolymers have improved the compatibility between PS and polyacrylate rubber obviously. Further details are being studied.

Table 1 Characterization of graft coplymers

sample	PS macromer		Mn	composition	Tg(℃)		no. of
No.	Mn	Mw/Mn	total	of st(wt%)	Tg1	Tg2	branches
5-20-2	5900	1.06	193000	22.2	-44	/	8
5-20-4	14900	1.12	244000	23.4	-30	62	4

Table 2 Properties of polyblends

sample	composition of polyblend (%)			tensile strength	impact strength
No.	PS	polyacrylate rubber	graft copolymer (a)	(MPa)	(MPa)
5-9-1	100	0	0	34.6	0.35
6-5-7	80	20	0	10.1	0.12
6-5-5	78	19	3	30.3	1.10

(a) Mn total=244000, reference to table 1

Fig.1 Scanning electron micrographs of fracture surface of polyblends(x2000): A) added 3 wt% graft copolymer; B) have not added graft copolymer.

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7/15

Morphology and Properties of HDPE/Butyl Rubber Blends

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The relationship between properties and compositions of HDPE/butyl rubber blends was studied. With the increase of butyl rubber content, the environmental stress crack resistance, impact strength and elongation of the polyblends are increased, while the modulus and yield strength are decreased.

The morphological structures of the polyblends were identified with SEM, TEM, DSC, WAXD, IR and DMS. The results show that the crystal lattice of HDPE in the polyblends is the same as that of HDPE, the degree of crystallization keeps unchanged until the content of butyl rubber exceeds 70%, the thickness of crystalline lamella decreases with the increase of butyl rubber content. IR and DMS show that there might be a special interaction between HDPE and butyl rubber, HDPE always forms a continuous phase even if the content of butyl rubber is as high as 90%.

The phase separation takes place even in their melt state as viewed from the reological properties and crystalline dynamics of the HDPE/butyl rubber blends. A morphological model was proposed based on the above experimental results.

8/1 A COMPARISON OF MATHEMATICAL MODELING WITH ON-LINE EXPERIMENTAL MEASUREMENTS OF DYNAMICS AND STRUCTURE DEVELOPMENT DURING HIGH SPEED MELT SPINNING OF SYNTHETIC FILAMENTS

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A brief overview of the dynamics and structure development during melt spinning of synthetic filaments is presented with emphasis on on-line measurement techniques and process simulation.

A specific mathematical model is described for the calculation of temperature, diameter, birefringence, and crystallinity variations as a function of distance from the spinneret. The predictions of the model are compared to experimental temperature, diameter, and birefringence profiles measured on running spinlines of several polymers.

A detailed comparison of model predictions with experiment is presented for polyamide 6, and the sources of differences are examined. An analytical treatment designed to use experimental measurements to obtain improved input parameters for the model is described, and its application to polyamide 6 is presented.

8/2

MAXWELL VISCOELASTICITY IN DYNAMIC MELT SPINNING MODEL

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Upper convected Maxwell constitutive equations developed by Fisher and Denn for the fluid geometry of thin filament were tested numerically and analytically in the simulation of steady state and transient melt spinning. Following are novel results obtained. I) One of the most significant features of Maxwell fluid filaments and spinlines as opposed to Newtonian ones was the instantaneous extension and contraction exhibited by Maxwell in response to a sudden increase or decrease in the tensile force acting on the filament. After a stepwise increase in tensile force the elongational stain shows a stepwise discontinuos increase followed by a monotonical and gradual climb well reflecting the spring and dash-pot nature of the Maxwell model. II) The above instantaneous deformation governs the upstream end boundary condition of continuous melt spinning model. The thin filament analogy of the flow within the spinneret hole is a prestressing of the filament. As the filament emerges from the spinneret it exhibits an instantaneous contraction due to a sudden decrease in tension. This is a prediction of die swell as discussed by Nam and Bogue. Maxwell spinline is known to exhibit an infinite tensile force at a finite draw down ratio if the cross-sectional area at the upstream end is assumed to remain constant. However, when the takeup speed is increased without changing the flow within the spinneret the upstream end cross-area must decrease with incresing draw down ratio since die swell decreases with increasing tension. Thanks to the decreasing up-end cross-area the spinline tension never reaches infinity and the so called unattainnable region in Maxwell spinning does not exist. In order to realise the above infinitely large spinline tension a very artificial provision must be made on the flow within the spinneret hole. An increase in takeup speed results in an increased spinline tension which in turn tends to decrease the filament cross-area at spinneret exit due to elastic extension. To counteract this effect the flow within the spinneret must be changed in such a way to increase the preloading of filament. Thus an infinitely large filament tension must accompany an infinitely strong preloading within the spinneret. III) Instantaneous deformation of Maxwell fluid filament obeys the classical equation of rubber-like elastic body. IV) Stability limits of spinline were in good agreement with the previous results by Fischer and Denn.

8/3 INFLUENCE OF THE MOLECULAR WEIGHT IN THE POLYPROPYLENE SPINNING

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Polypropylene with controlled molecular weight have been prepared by thermal degradation of a commercial polymer previously peroxidized with the aid of air-ozone in a fluidized bed. The wide angle X-Rays diffraction has shown that a smectic phase may appear in the as-spun fibers. Its presence depends upon the spinning temperature, the average molecular weight, the high molecular weight fraction and the melt drawdown ratio. For high fluidity polypropylene (melt index higher than 50) the smectic phase appears at as low a temperature 200°C. At this temperature if the melt drawdown ratio raises the smectic phase is converted into oriented monoclinic form. These results are correlated with melt elongational behavior of polypropylene at constant rate of deformation which undergoes also the influence of the high molecular weight fraction. All the previous results are discussed in terms of rate of deformation with respect to relaxation rate of macromolecular chains.

8/4

STUDIES ON THE HIGH SPEED SPINNING OF PET. THE DYNAMIC ANALYSIS OF SPINNING LINE AT THE SPEED OF 3600 M/MIN

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It has been observed that the preoriented yarn (POY) began to orient and crystallize near the area of sharp structural change through the measurements of stress, optical birefringence and density at the speed of 3600 m/min. The investigated relationship between optical birefringence (Δn) and stress (σ) of spinning line proposed by Hamana is, to some extent, deviating from that. That paper gives an empirical formulation as $\Delta k = 13.18 \times 10^{-3} + 6.32 \times 10^{-10}$ with a deviation within 4%. It also provides a predicting method for controlling the change of PET structure of spinning line. Our tests have shown that the less the denier of POY single yarn, the greater the stress and crystallinity during the fiber formation, and that stress induced effects of the crystallization kinetics of PET high speed spinning are greater than that of the cooling rate.

8/5 PHYSICAL STRUCTURE IN RELATION TO PROCESS CONDITIONS AND PROPERTIES OF POLY(ETHYLENE TEREPHTHALATE) YARNS.

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The physical structure of a semi-crystalline polymer such as poly(ethylene terephthalate) can be described adequately by a two-phase model, consisting of alternating amorphous and crystalline regions. Using a combination of measuring techniques, a fairly good idea of the parameters involved in such a structure can be obtained. As measuring techniques X-ray diffraction, density via gradient column, pulse propagation, (interference) microscopy and infrared spectroscopy are in use in our laboratory. Combination of the quantitative information of these techniques results in a physical yarn structure in terms of crystallinity, crystal sizes and crystalline orientation. The amorphous domains are characterized in terms of their size, the orientation distribution, an estimate of the amount of folds and the ratio of trans and gauche conformers.

Such a two-phase structure is controlled primarily by the conditions at which the yarn is produced. This physical structure in its turn determines the thermal and mechanical properties of the yarn. Therefore, knowledge of the molecular arrangements in yarns is very helpful, both with respect to process control and process development.

In the lecture, attention will be given to the measuring techniques, in particular to the way they have been adapted for our purposes. Furthermore, examples will be discussed of relations between process conditions, physical structure and properties of yarns.

8/6 GELSPINNING of FLEXIBLE MACROMOLECULES

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In the past ten years,great progress has been made in the development and production of high-strength/high-modulus organic fibres.One of the prime prerequisites for obtaining high-modulus fibrous structures:"chains extended and oriented parallel to the fibre-axis" is met relatively easily in the case of intrinsically rigid chain molecules.Well-known high-performance fibres based on (rather) rigid chains are the aromatic polyamides notably PPTA (poly-p-phenyleneterephthalamide) marketd under trade names of Kevlar/DuPont and Twaron/AKZO.

Flexible/regular macromolecules such as polyethylene,polypropylene and the polyesters/amides tend to fold during crystallization/solidification and consequently in conventional spinning procedures folded-chain type crystals will be present in the as-spun yarns. The transformation of these folded-chain type crystals into chain-extended structures is the main goal in order to exploit the intrinsic properties of the polymer chain with respect to stiffness and strength.

In the case of flexible macromolecules,polyethylene has been studied extensively.The gelspinning process,invented in the late seventies at DSM-Research,proved to be most versatile in producing high-performance chain-extended polyethylene structures.

The various routes, models and theories for chain-extension of flexible macromolecules will be reviewed as well as future prospects concerning applications of chain-extended flexible polymers in textiles and composites.

8/7 Drawing and Heating Effect on the Mophology of Gel Spinning PE Filament

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One of the most hopeful processes to obtain ultra-high strength filament is the gel spinning-ultrahigh draw process, in which, it still does not clarify whether & when extended chain crystallites are formed.

Here, ultra high molecular weight (Mw=1500000) PE and solvent decalin are adoped to make spinning dope with concentration 2-3%, then to obtain PE gel filament. The structural variations during drawing and heating are studied by means of SEM, TMA, WAXS and DSC.

The caves on the filament surface mainly disappear and the degree of orientation trends to be saturated when draw ratio proceeds over 10. The continuous increases of filament strength and modulus are due to the increase of crystallinity and the improvement of evenness during stretching.

DSC curve shows that second melt peak starts to appear during draw ratio near 20, it means the initiation of extended chain crystallization. Second melt point Tm_2 (150-152.5°C) is about 6°C higher than the first one Tm_1(145°C).The higher the draw ratio, the more the crystlline fraction of folded transfering to extended chain. That is the special mechanism of ultra high drawing.

Thermal relaxation of drawn filament keeps the strength constant, but causes multi-melting behavior with two new melt peaks appearing between Tm_1 and Tm_2 . It is supposed to be concerned with the size and perfection of the crystallites reformed.

8/8 Coagulation Studies for Cellulose in the Ammonia/Ammonium Thiocyanate (NH_3/NH_4SCN) Direct Solvent System

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An extensive study of coagulation of cellulose from cellulose/ammonia/ammonium thiocyanate solutions is presented. The effect of major variables upon the coagulation process for cellulose solutions is reported. Microscopic observations of the moving boundary associated with coagulation were performed on gelled cellulose solutions to determine the coagulation rate as a function of molecular volumes of coagulant, bath temperatures, bath compositions and cellulose concentrations. The data were analyzed by means of a one-dimensional linear diffusion model based on Fick's law, thereby depicting the mechanism of the coagulation process, and obtaining the diffusion coefficients of mobile components involved in the coagulation.

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8/9 TWO-STAGE DRAWING OF ULTRA-HIGH MOLECULAR WEIGHT POLYETHYLENE REACTOR POWDERS

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Recently, a great progress has been made in preparation of high modulus and strength fibers and films by uniaxial drawing of ultrahigh molecular weight (UHMW) flexible chain polymers. We have shown that solid-state coextrusion followed by tensile drawing of UHMW-PE and UHMW-PP single crystal mats, grown from dilute solutions, produce superdrawn films with tensile moduli approaching the lowest theoretical value reported for the crystal for each of the two polymers.

In this study, the two-stage drawing technique has been successfully applied for ultradrawing UHMW-PE reactor powder of commercial grades. Compacted powder films, prepared below the ambient melting point of the initial powder, was solid-state coextruded with high density polyethylene to a low extrusion draw ratio of 6, followed by tensile drawing at elevated temperatures of 120-135°C. The drawability for the second-stage tensile drawing and the uniformity of the resultant films were sensitively affected by the drawing temperatures and rates, and also by the reactor powder used. The maximum draw ratio, thus achieved, was 85 with the corresponding tensile moduli of up to 132 GPa, under the experimental conditions emplyed in this work. Although the sample fracture usually proceeded by a repetitive partial rupture at the edge of cramp, the observed tensile strength were 1.6-1.8 GPa at draw ratios of 70-80. The drawability and the maximum achievable tensile properties are remarkably higher than for those achieved for drawing melt-crystallized UHMW-PE, yet they are significantly lower than for superdrawing of UHMW-PE single crystal mats. It is also noted that the efficiency of draw, as evaluated by the tensile modulus vs draw ratio, is also slightly lower than that observed for drawing of single crystals formed from the same UHMW-PE. These facts indicate that the coherency of the crystalline particles as well as their morphology has important influence on the drawability and the efficiency of draw. The x-ray diffraction and DSC measurements suggest the characteristic morphology of UHMW-PE reactor powders and the morphological changes occurring during deformation.

8/10 TRANSIENT ELONGATIONAL VISCOSITIES AND DRAWABILITY OF POLYMER MELTS.

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Laboratory experiments like uniaxial stretching after extrusion and isothermal homogeneous drawing in extensional rheometers both allow some predictions on differences of the drawability in tubular film blowing of LDPE melts. Multiaxial elongation tests will be commented. The shape of the die is shown to significantly influence the subsequent stretching behaviour. This effect can be attributed to preorientations during extrusion.

There exist interesting correlations between the shape of the elongational viscosity versus strain rate, transient tensile stresses as a function of temperature and stretch rate, and entrance pressure losses.

In addition new experimental results on the influence of molar mass distribution on the stress-strain behaviour will be presented. A linear polystyrene (M_w = 200 000) showing no strain-hardening does not yield any maximum of elongational viscosity if blended with another linear polystyrene of M_w = 1 000 000.

8/11 ELONGATIONAL FLOW OF HIGH DENSITY POLYETHYLENE SAMPLES AND BUBBLE INSTABILITY IN FILM BLOWING

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In assisting product development there is ample opportunity to compare the processing behaviour with laboratory data. Similar and different grades of HDPE - and for some of our own products, many lots - were investigated. Bubble stability of the samples in film blowing on a commercial production line is related to rheological properties in elongation. Strain hardening behaviour enhances stability as it is well known. The influence of even small differences can be shown, but in these cases the absolute value of the viscosity, the strain rate hardening behaviour and the activation energy of flow also become important. The processing behaviour can be improved by shear modification. The experimental results are discussed confirming the pulsations to be a kind of draw resonance.

8/12 TEM, WAXS AND LASER DOPPLER ANEMOMETRY STUDIES OF HIGHLY ORIENTED LDPE-FILM

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Blown film extrusion is the most widely used converting technique for LDPE. In the past 5 years several major improvements have been developed e.g. Long Stalk extrusion and recently the HaMLeT technique. Long Stalk and HaMLeT both use orientation effects to improve film properties, but in a completely different way. Long Stalk avoids uniaxial orientation in a macroscopicly unbalanced film i.e. high draw ratios in machine direction (combined with low blow up ratio) by shaping the bubble in such a way that the effective orientation in both directions is the same (large die gaps, consequently thick films, combined with a high frost line provide a mushroom like shape of the bubble. Therefore most of the orientation in the machine direction takes place at relatively high temperatures, consequently part of the molecular orientation in this direction will relax, while the orientation in perpendicular direction is performed at relatively low temperatures.)
The aim of HaMLeT processing is to maximize uniaxial orientation and minimize relaxation. This is realized by using high draw ratios, therefore also large die gaps, now combined with a low frost line, low temperatures and special grades which can be processed at low temperatures.
HaMLeT films have improved properties. The tensile moduli in both directions are almost the same. The average modulus of a LDPE film (density = 921 kg/m^3) produced under standard conditions is roughly 200 N/mm^2, while the average modulus of a HaMLeT film with the same density is about 300 N/mm^2 (which is as high as a normal grade of density 935 kg/m^3, the highest possible density for LDPE grades). The modulus of HaMLeT films with a density of 935 kg/m^3 is about 400 N/mm^2 which is unique for LDPE film. Optical properties, puncture resistance and tear strength at low deformation speeds are as good as (or better than) normal LDPE films.

In order to find an explanation for the improved moduli, the effects of this new converting technique are studied. Detailed information of stretching and stretching rates in both directions during the film blowing process is obtained with use of a laser doppler anemometer. The resulting orientation in and morfology of the films is investigated with TEM and WAXS techniques.

8/13 ISOTHERMAL AND NON-ISOTHERMAL MODELS FOR FILM EXTRUSION

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Film extrusion is an important activity in polymer industry. In this process, the polymer is extruded through a slit die, slightly stretched in air and cooled on a chill roll. This primary film is then stretched longitudinally and transversally. This work is devoted to the study of polyethylene terephthalate extrusion. As the obtained films are used to produce audio or video tapes, a good thickness regularity is of prime importance. We have studied the primary film manufacturing process at both experimental and theoretical levels, since it appears that the thickness fluctuations of the final film greatly depends on this process stage.

EXPERIMENTAL STUDY

These experiments were carried out with a laser anemometer at the Rhône Poulenc Films Company. These measurements give the evolution of velocities in the stretching direction and in the transverse direction. Besides, they allow us to determine the profile of the film between the die and the roll.

THEORETICAL STUDY

Both isothermal and non-isothermal models have been developed. The most important assumptions are :

- the polymer is supposed to be incompressible and newtonian,
- the process is stationary,
- the chosen velocity field implies that the film section remains rectangular during the path in air,
- surface tension forces and forces resulting from friction with air are neglected, but gravity and inertia forces can be taken into account,
- the curvature of the film between the die and the roll is taken into account. The lateral necking can also be taken into account.
- the temperature profile is supposed to be uniform throughout the width of the film ; the viscous dissipation and the heat conduction in the flow direction are neglected,

The mechanical resolution is performed writing the kinematic in curvilinear coordinates and the equilibrium equation in a local cartesian system. An iterative scheme is used in order to adjust the stretching force, the trajectory of the film and the contact point on the roll.

The temperature field computation is along the stretching direction and in the thickness performed using a local heat transfer coefficient which is determined taking into account convective and radiative heat transfer phenomena. The connection between thermal and mechanical resolutions is achieved by introducing the temperature dependence of the viscosity.

All these computations are performed using finite difference numerical methods.

RESULTS AND PERSPECTIVES

Experimental and numerical results for the film profile and the velocity evolution between the die and the roll contact are in a very good agreement. Further developments are in progress using viscoelastic constitutive equations and taking into account non-stationary phenomena.

8/14

PROCESSABILITY OF T-DIE FILM EXTRUSION

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The melt behavior of T-die extrusion between the die exit and chill roll was predicted by using theoretical equations and numerical analysis under various process conditions.

As a result of the theoretical analysis, the take-up stress increased in a linear manner with viscosity, and the activation energy affected the velocity profile and take-up stress. The resins, of which the viscosity decreases with increasing elongational rate, were deformed near the roll. LDPE having long chain branches was easily deformed near the die exit as compared with other resins. By comparison of the theoretical results with the experimental ones under various process conditions, good agreements were obtained in the melt behaviors.

Processability was also discussed by using the theoretical analysis. Instability was evaluated by dimensionless deformation rate and draw down ratio. Film failure was estimated by maximum stretching stress at the roll touch. Cooling air blowed off from an air knife which much influences processability made dimensionless deformation rate at the roll touch smaller, and it made stability better.

8/15

MECHANICAL PROPERTIES OF UNIAXIALLY AND BIAXIALLY ROLLED POLYMER SHEETS

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Scope of this study was to develop a sheet rolling process to produce stampable thick polymer sheets of general-purpose plastic materials, such as polyethylene and polypropylene, with large tensile strength, Young's modulus and small anisotropy of these properties. Effects of rolling at temperature just below the melting point on tensile strength and Young's modulus in uniaxial and biaxial rollings has been investigated by using a laboratory mill.

Elongation of about 20 along the rolling direction(L-axis) in uniaxial rolling was attained by applying forward and backward tensions during rolling. It was found that the mechanical properties along L-axis were improved substantially as the elongation was increased. But the mechanical properties perpendicular to the rolling direction(C-axis) remained almost unchanged, which resulted in strong anisotropy of the rolled polymer sheets. To avoid this anisotropy we introduced biaxial rolling or so-called "cross rolling" technique, where a sheet was turned in the plane by the angle of 90 degrees between the first step and the second step rollings.

Experiments showed that such biaxial rolling was effective to improve the anisotropies of tensile strength and Young's modulus, especially for polypropylene, while the improvement was not very large for polyethylene. From the above results, polypropylene was intensively examined concerning to the effects of combination of L and C elongations. The elongation at the second step rolling strongly increased tensile strength along the rolling direction, but radically decreased that along the lateral direction. The elongation at the first step rolling emphasized the above mentioned effect of the second step rolling.

Direct second step rolling process without cooling after the first step rolling was more efficient in improving the tensile strength along both L- and C- directions than colling-and-reheating process. The optimum condition to give the same value of tensile strengths along both directions was obtained, and the tensile strength was improved as the elongation at the first step rolling was large. These behaviors were discussed in relation to measured volume fraction of crystalline phase and molecular chain orientation.

Hot press forming experiments were conducted with biaxially rolled sheets to evaluate their formability. Since polyethylene was not improved in its anisotropy by biaxial rolling, it showed poor formability. On the other hand, polypropylene exhibited very good formability because of its better isotropy.

A study was also made on basic rolling characteristics, such as elastic recovery, mean deformation resistance, width spread and rolling load. These data are usefull for designing commercial rolling mills and other equipments for producing stampable rolled sheets.

9/1

Concepts of Polymer Crystallization under Varying Processing Conditions

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Using two industrial polypropylenes as model substances of suitable time constants (with respect to melt rheology and crystallization), the authors readily succeeded in separating two types of crystallization phenomena. In both cases crystallized layers are formed at the quenching wall. In the case of a melt which is in equilibrium, when its (lateral) quench is induced, a crystallized layer starts growing from the wall in a continuous fashion. If, on the other hand, the state of the melt is influenced by preshearing in a duct of rectangular cross-section (slit die), the thickness of the finally formed layer is predetermined by the flow history. In this respect it must be emphasized that the mere state of molecular orientation, as created by previous flow, is insufficient for an explanation of this phenomenon. This conclusion is drawn on the basis of flow birefringence, as measured near the end of the duct. It is corroborated also by other experiences: there is a well defined minimum shear rate for the formation of a shear induced layer. This layer shows a sharp boundary with respect to the core. The discussion of these phenomena includes theoretical considerations with respect to moving boundary value problems and nucleation concepts.

9/2 DEVELOPMENT OF CRYSTALLIZATION IN POLYMER PROCESSING

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Crystallization of polymers in industrial processes is highly dependent on mechanical (flow), thermal (cooling rate, thermal gradient) and geometrical (walls of processing devices) conditions. A classical way to treat this problem is :

- to develop a thermomechanical model of the process to determine strain-rates, stresses and temperatures,
- to analyze the structures and morphologies in polymer specimens processed in various conditions.

This approach has been applied in our laboratory to several processes (injection molding, cast-film extrusion, film blowing ...) and makes it possible to derive correlations between processing conditions and microstructure. Typical results will be given as examples. So, it has been shown that :

- Flow increases the number of crystalline nuclei and induces an anisotropic growth of lamellar crystals. For an increasing flow intensity, the following morphologies are likely to be observed : spherulites, spherulites deformed into ellipsoids, sheaves, cylindrites (Keller's models), fibrillar crystals.
- An important surface nucleation promotes transcristallinity.
- Thermal gradients are responsible for the deformation of spherulites into teardrop-shaped entities.

These correlations allow a first interpretation of the influence of processing parameters on microstructure but, obviously, such an approach cannot predict how the polymer will crystallize in a given process. A predictive approach requires the development of crystallization models taking into account the actual conditions encountered by the polymer in the process. Several aspects have been already considered in our laboratory :

- Influence of surface nucleation : a model based either on Evans' (isothermal case) or on Ozawa's theory (anisothermal case) shows the effects of surface nucleation on the overall crystallization kinetics. Besides, computer simulation is used to visualize the formation of transcrystalline regions.
- Influence of cooling : the combination of thermal equations and Ozawa's model makes it possible to calculate the crystallization kinetics for any cooling condition.
- Influence of flow : the orientation of macromolecules in the molten polymer is deduced either from the dumbbell model or from the rubber elasticity theory. The consecutive change in entropy is then introduced into the crystallization model to calculate the influence of flow on crystalline nucleation.

Work is in progress to apply these results to some processes, e.g. fiber spinning. This step requires a complete coupling with an thermomechanical model of the process.

9/3 RATE CONTROLLED NON-ISOTHERMAL CRYSTALLIZATION OF POLYMERS

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The crystallization process due to quenching of polymer melts is studied. The kinetics of non-isothermal crystallization, taking into account both formation and growth of nuclei, is formulated in terms of rate-equations. Depending on whether Avrami's or Tobin's models of impingement are applied, sets of, respectively, (m + 1) and (m + 2) first-order differential equations are obtained, where m is the number of spatial dimensions of growth. The number of rate equations reduces to one if the activation of nuclei is much faster than their growth. Avrami's well-known formula is re-obtained from isothermal limiting cases.

In contrast to the classical front model (the Stefan problem) and its more recent modification (by Janeschitz-Kriegl et al.), the present approach is capable of describing semicrystalline layers of variable degrees of crystallinity.

For applications to non-isothermal crystallization problems, the set of rate equations and the energy equation are to be solved simultaneously.

As an example of a transient problem, the quenching of a slab of finite thickness is considered. The initial temperature of the slab, T_i, is assumed to be larger than the equilibrium melting temperature, T_M. For times $t > 0$, one or both surfaces are kept at a constant temperature well below the melting point. The process is governed by a dimensionless parameter R defined as the ratio of the characteristic time of heat diffusion to the characteristic time of the crystallization kinetics. Crystallization takes place in a progressive zone if R is less than, or of the order of, one. If, on the other hand, $R \gg 1$, large gradients of the degree of crystallinity are predicted. For $R \to \infty$, the well-known Stefan solution is re-obtained as a limiting case. The numerical results are compared with experimental data of Janeschitz-Kriegl et al..

Another application concerns the continuous solidification of a rod moving through a cooling region at constant speed. Through the cooling, the rod temperature is reduced from above the melting point to below the glass transition point. Under certain conditions, a continuous crystallization zone is followed by a stationary front with a finite jump in the degree of crystallinity. The described process is suggested as a means of determining crystallization kinetics data from experiments.

9/4 ORIENTATION AND CRYSTALLIZATION DURING STRETCHING OF POLYESTER FILMS

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Strain induced crystallization differs from isothermal crystallization by its origin, its kinetics and the resulting morphology. Induced crystallization of poly(ethylene terephthalate) (PET) has been studied for a long time because its thermomechanical behavior is largely affected by this phenomenon.

The present work reports a study of the induced crystallization in PET and shows the relationship with the amorphous orientation generated in a PET film stretched above Tg at different constant strain rates. The results show the existence of a critical amorphous orientation for the beginning of crystallization. This critical orientation depends on the temperature of stretching but not on the strain rate. It is also shown that, during a stretching, the crystallinity of PET is completely determined by the temperature and the level of amorphous orientation in the sample, and it increases with both parameters.

The kinetics of induced crystallization is also studied during uniaxial stretching of amorphous PET films and annealing of oriented samples. The time scale of crystallization and the influence of orientation and temperature are determined for annealing of stretched films. During stretching, it is shown that crystallization obeys a "forced kinetics" controlled by the strain rate and affected by the stretching temperature.

The results are extended to more specific stretchings which correspond to industrial drawings in the bioriented film processing : stretching under constant load for the longitudinal stretching and stretching at constant drawing speed for the transverse stretching.

The large difference between these two kinds of stretching is the spectrum of strain rates which take low values at constant rate of elongation and high values under constant load. These different time scales explain the fact that under constant load, the crystallization is less completed. So, at a given degree of crystallinity and for the same stretching temperature, the amorphous orientation is much higher under constant load than at constant drawing speed.

9/5 STRUCTURE FORMATION IN CRYSTALLIZABLE BLEND FLOWS

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Flow induced crystallization of high density polyethylene and polypropylene has been studied in a two phase flow system using linear low density polyethylene as the carrier phase. Extensional stresses were generated under slow flow conditions by either of two methods: one involving flow past a stationary seed, the other involving a droplet deformation and bursting mechanism. In both cases, oriented, fibrillar crystallization of the high density phase was observed optically and correlated with calculations indicating the presence of flow-induced extensional gradients. Morphological, thermal, and birefringence data indicate that the crystalline fibers produced are oriented and superheatable, and consist of a multifibrillar substructure. For fibers produced by the droplet bursting process a semi-quantitative agreement was found between fiber melting point and birefringence based on the simplified analysis for the bursting induced extensional flow. Comparisons with capillary viscometry data are also made to show the effects of flow-induced crystallization on the blend rheological behavior.

9/6 INFLUENCE OF FLOW HISTORY ON POLYMER BLEND MORPHOLOGY

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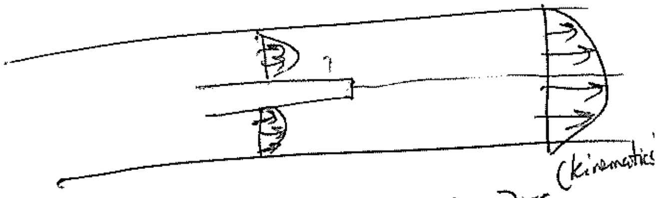
The morphology of blends of liquid crystalline copolyesters with engineering thermoplastics is dependent on a number of factors. These factors include the concentration of the liquid crystalline polymer (LCP), the viscosity ratio of the LCP to the engineering thermoplastic, and the deformation history. Once the concentration of LCP reached a critical limit, the LCP would exist as long thin fibrils under some conditions of extrusion. It was found that the fibrils formed when the L/D ratio of the capillary was less than 20. Otherwise the LCP phase existed as droplets. It is believed that the formation of fibrils is due to extensional flow at the die entry rather than shear flow in the land section. Shear flow tends to disperse and break up the fibrils as evidenced by the use of long capillaries and studies in a parallel plate rheometer. Migration of the lower viscosity LCP to the surface of the extrudate was also observed. Additional drawing steps lead to the enhancement of the physical properties of the blend as a result of increasing the orientation of the LCP fibrils.



in PES (kinematics)
+ another in PES (tracking)

9/7 ORIENTATION DEVELOPMENT IN PLANE WELDING FLOWS, MODELLING AND FLOW BIREFRINGENCE EXPERIMENTS

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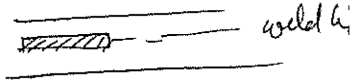
A numerical method is described for calculating the stress a viscoelastic melt exhibits in a flow, based on approximate kinematics. The method assumes that the kinematics are reasonably close to those of a shear-thinning fluid such as the Carreau model. The strain history of a given flow and the resulting stress are calculated via a tracking method from finite element kinematics. Full field flow birefringence experiments were done for low-density polyethylene and polystyrene flowing past a thin plate-divider in a 1.254 mm planar slit die. By digitally analyzing birefringence photographs of the flow field, the birefringence was measured over two dimensions. These birefringence results are in good agreement with birefringence fields calculated from the numerical simulations and the stress-optical law. The flow fields were most highly oriented in a region surrounding the weld interface just downstream of the plate-divider. This orientation relaxed farther downstream, with polystyrene relaxing faster than low density polyethylene.

Use approximate kinematics – power-law e.g. – get shearing.
Track material elements in that strain field. along path line.
Use strain of inelastic flow as approximate strain.
Use Carreau type eq'n – FEM on channel.
Parabolic up + downstream. (hard for elastic liquids)
Stretching from stagnation pt. to max downstream.
Tracking – given velocity field – want strain tensor. Get Finger strain tensor. Rotate tensor because it is on streamline coordinate system.
get $\underline{\underline{\tau}}$ and $\Delta n = C\left[(\tau_{xx}-\tau_{yy})^2 + 4\tau_{xy}^2\right]^{1/2}$ to compare to birefringence data. Max'm in stretching region



higher flow → higher molecular orientation.
higher temp → faster relaxation
big obstacle relative to channel smooth flow
Coarse FEM grid gives poor residual estimate. - Lubricating flow.
is OK for approximate kinematics.

9/8 ENTANGLEMENTS AS AN ELEMENT OF POLYMER TEXTURE

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Through differential thermal calorimetric analysis of acrylic fibers, we discovered that in the thermogram there are usually four endothermic peaks. The first peak was considered to be due to the amorphous region, the second peak was attributed to the swelling of the paracrystalline region, the third peak was thought to represent the dissolution of the paracrystalline region while the fourth peak was tentatively attributed to the entanglements. The lagging of dissolution behind swelling might be due also to the effects of entanglements and morphological structure. By further study we came to realize the influences of molecular weight on the last thermogram peak, thus strengthening our conviction that entanglement is an important element of the polymer texture, just like amorphicity, crystallinity, crystallite size and perfection and orientation are.

The energy required for the entangled macromolecular chain to reptate out can be shown experimentally to be proportional nearly to the first power of number average molecular weight if the calculation is done on the basis of one gram of polymer. Thus we are able to establish a new method of evaluating entanglement density in a polymer by DSC analysis of that polymer in the swollen state. This same job formerly can only be done through viscosity measurements. Our new method is based on energy considerations; it is more direct, more accurate and quicker and is particularly suitable for studying entanglements in polymers which are in the solid state. The job can be completed within a quarter of an hour.

Further study showed that entanglements can be modified by thermal treatments of the polymer at various temperatures and in various solvents. The degree of tightening and loosening of entanglements can be modified by mechanical treatments. These studies can be extended to polymers and fibers other than acrylics if suitable solvents and temperatures are employed. Consequently, study of entanglements possesses a general character and might exert far-reaching influences on polymer research.

9/9 STRUCTURE DEVELOPMENT DURING MOLDING OF THE THERMOTROPIC COPOLYESTER XYDAR®

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X-ray methods have been used to investigate the structure of a thermotropic copolyester which is the basis for the XYDAR® family of resins, and to follow the development of orientation and molecular ordering during molding. The copolyester is prepared from p-hydroxy benzoic acid (HBA), terephthalic acid (TPA) and biphenol (BP). X-ray data from as-drawn fibers of copolymers with four different HBA/TPA/BP composition ratios show a series of aperiodic meridional intensity maxima. These maxima, which are in different positions for each composition, indicate that the copolymers have completely random monomer sequences. Nevertheless, there is evidence for three-dimensional crystallinity, with the chains packed in an orthorhombic pseudohexagonal structure. Annealing above 300°C has no effect on the sequence distribution but leads to changes in the chain packing. The annealed specimens contain two polymorphic orthorhombic structures, one of which is similar to the pseudohexagonal structure present in the as-drawn specimens.

The copolymer with HBA/TPA/BP mole ratio of 50/25/25 can be injection molded at about 400°C. Molded plaques are found to consist of at least seven layers perpendicular to the thin dimension. The molecules enter the mold (full edge gate) with their long axes perpendicular to the fill direction, and this orientation is maintained along the center line of the core. However, the molecular orientation in the skin layer is changed by 90° and is parallel to the fill direction, due to fountain flow effects. Analysis of the X-ray patterns shows a high degree of molecular orientation in the skin and core layers, comparable to that in melt spun fibers. The X-ray pattern for the core is very similar to that for the annealed fibers, and this region of the molded plaque contains the same two orthorhombic crystalline forms. In contrast the data for the skin layer are similar to those for the as-drawn fibers, and indicate that only the one pseudohexagonal structure is present. These differences probably occur due to the much more rapid cooling at the surface of the mold.

XYDAR® is a trademark of Dartco Manufacturing Inc.

9/10 MICROPROCESSING - PREPARATION OF LANGMUIR BLODGETT MONOLAYER AND MULTILAYER FILMS

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Over the past several years considerable interest has developed in the preparation of Langmuir Blodgett monolayer and multilayer films, both prior to and subsequent to polymerization. These films are expected to find applications in sensors, gas barriers, membranes and electronics. In this paper we will discuss the development of a processing window for the production of monolayer and multilayer films. Temperature,residence time, surface pressure, dipping speed, chemical stability, creep and the nature of the monolayer's water substrate are some of the variables we have considered. The effect of surface pressure annealing (akin to work hardenning in bulk materials) of monolayers prior to deposition will be described.

9/11 Lattice Deformation and Meso-phase Structure in Poly(ethylene terephthalate) Drawn by Solid State Coextrusion

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Roger S. Porter
(University of Massachusetts, USA)

Interest remains intense in the development of polymers of high modulus and strength. Poly(ethylene terephthalate) (PET) prepared by solid state extrusion is certainly a candidate. The development of crystalline and meso-phase structure by solid state extrusion at 50° to 90°c has been studied for PET. The initial PET film for draw was isotropic and amorphous. The unit cell parameters of stress-induced crystallites in extrudates have been determined as a function of extrusion draw ratio, EDR, and extrusion temperature, ET, above its Tg, at 70° to 90°c. The X-ray diffraction spectra have the (010), ($\bar{1}$10), and (100) peaks, three peaks can be resolved. The higher the ET, the longer the c axis, the shorter the a,b axes and the smaller the unit cell volume.The higher the EDR, the longer the c axis. In comparison with the conventional lattice parameters obtained by Bunn and Fisher, the highest elongation of c axis is near 10%. The internal stresses and lattice moduli have also been evaluated and compared with those of conventional values. All these imply that the lattice of stress-induced crystallites are far from the closest packing state.

WAXD patterns of PET extruded at 50°c (below its Tg) exhibites very small and/or imperfect crystallites, so that the (010), ($\bar{1}$10), and (100) peaks are not resolved. They appear as those of typical meso-phase materials. Between the coextrudates made below and above its Tg a major difference appears. The distance between macromolecular chains range from 3.2-5.4 A°. Its average value is 4 A°, approching to the interplaner distance 3.4 A° of (100) crystal face on which benzene rings lie. The oritation factor, density, crystallinity, stress-strain curve and modulus of meso-phase PET have been determined. The WAXD curve simulating function of meso-phase can be adopted for crystalline peak separation of PET WAXD curve to obtain the absolute crystallinities, the contents of meso-phase and amorphous region.

9/12 PRODUCTION OF HIGHLY ORIENTED POLYMERS BY DIE-DRAWING

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Early attempts to achieve orientation and so improve the mechanical and physical properties of polymer products was centred initially on the solid forming of billets using the hydrostatic extrusion process. Extrusion output speeds were found to be limited and die-drawing was shown to be a more viable method of producing rod, tube and sheet products of substantial size.

This paper shows that with die-drawing, orientation occurs within the die zone due to deformation forces as well as downstream of the die exit where tensile drawing forces contribute significantly to orientation, Production speeds are seen to be dependent on polymer properties including the strain hardening characteristic and strain rate sensitivity of the material as well as on die design and temperature of drawing. Production speeds achieved vary from a few cm/min for particular grades of polyethylene to several m/min for polypropylene.

The mechanical properties of a wide range of drawn polymers are discussed; the elastic modulus of a particular grade of polyethylene is seen to increase with draw ratio, reaching 60 GPa at a draw ratio of about 25. Molecular weight has an effect on properties; low molecular weight polyethylene produces high modulus products at low production speeds whilst intermediate molecular weight materials give an acceptable compromise between product properties and production rate. Improved mechanical strength has been achieved in biaxially orientated tubes where biaxiality is produced by drawing tubular billets over a mandrel and so achieving orientation in the hoop and axial directions. Thermal conductivity increases significantly in the draw direction and axial drawn polyethylene rod is found to have a thermal conductivity 20 times its isotropic value at high draw ratios.

9/13 PROCESSING CHARACTERISTICS AND STRUCTURE DEVELOPMENT IN COLD ROLLING POLY ETHER ETHER KETONE

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Poly ether ether ketone (PEEK) is a high temperature thermoplastic which can be obtained in amorphous form or in semi-crystalline form depending on the thermal-deformation history. In this paper, we report our results on cold rolling characteristics of semi-crystalline PEEK sheets. The results indicate that the crystalline structure is progressively destroyed as the roll reduction is increased. The morphology and orientation developed in cold-rolling is analyzed using wide-angle x-ray pole figures, small angle x-ray scattering and differential scanning calorimetry techniques. The mechanical properties are discussed as a function of direction in the film plane and process conditions.

10/1

NEW TECHNOLOGIES FOR THERMOPLASTIC MORPHOLOGY DEVELOPMENT

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This presentation will cover recent developments throughout the world on new compositions and new processes. Emphasis follows from personal interests in the areas of polymer characterization, physics and rheology with concentration on the physical and mechanical properties of polymers, particularly high modulus fibers and their composites. Both flexible chain and rod-like liquid crystal systems will be discussed. Examples will be shown of new polymeric materials, and the processes for their generation.

Features will be illustrated with the phase diagram developed for poly(bisphenol E-isophthalate-co-naphthanate) in a parasubstituted phenyl ester of terephthalic acid, di- p-methylbenzoate terephthalate. This binary system exhibits miscibility in a nematic phase and does not form cocrystals. The crystal to nematic phase transition has been characterized by the temperature and heat of transition data and by the Flory-Huggins theory for the melting point depression of a polymer-diluent system. Studies were made at 20 mol% co-naphthalate (N20).

The phase behavior was examined at high copolyester content with three different moelcular weights of BPE/I/N20. These blends were subsequently transesterified in the solid state at 220°C and the change in phase transitions are reported. The phase behavior and transesterification were characterized by DSC, TGA, polarized light microscopy, x-ray diffraction, and dilute solution viscometry. The thermodynamic criteria for the melting point depression and the kinetics of transesterification are also reported for the utilization of this new processing technique.

Our studies of morphology development of flexible chain polymers also continue. Solid-state (co)extrusion of a single crystal morphology of high density polyethylene, superdrawing of ultrahigh molecular weight polyethylene (UHMW-PE) and of polypropylene (UHMW-PP) has been achieved by solid-state coextrusion and tensile drawing of the single crystal mats precipitated from dilute solutions (0.05-0.2 wt-%). These techniques produced ultraoriented films with draw ratios (DR) 240 for UHMW-PE and 40 for UHMW-PP. Even higher DR were achieved by a combination of solid-state coextrusion followed by tensile drawing at controlled rates and temperatures. The maximum DR attained for the mats by this drawing combination was ~ 350 for UHMW-PE and ~ 80 for UHMW-PP. Such superdrawn films exhibit tensile moduli and strength ≤ 220 GPa and ≤ 5.6 GPa, respectively, for the former, and ≤ 34 GPa and ≤ 2.2 GPa, respectively, for the latter polymer. These moduli approach an yet uncertain theoretical maximum modulus reported for the crystal for each of the two polymers. Drawing results on yet other polymers and blends have been demonstrated.

10/2 SELF-REINFORCEMENT OF THERMOPLASTICS IN INJECTION MOULDING

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Reinforcement of thermoplastics is not only performed with glass or carbon fibers but there exists a trend to self-reinforcement of semi-crystalline thermoplastics. States of orientation and conditions of crystallisation change as a function of the most important parameters of injection moulding, especially geometrical conditions of melt flow, melt temperature and holding pressure. By variation of these processing parameters the correponding morphological changes can be controlled and the macroscopic mould properties considerable improved, Tensile strengths of 140 N/mm² for HDPE are higher by more than a factor of 4 compared with the normally processed material, Young's modulus with 7500 N/mm² by more than a factor of 6 corresponding to an ultimate elongation of 15 %.

The reinforcement is due to the shish-kebab structure which is responsible for the improvement of thermal and mechanical properties. The growth of shish-kebab structures with an extended chain crystal axis and the radially lamellar structure, originated by flow induced crystallization, depends on the orientation of the macromolekules in the melt. A high degree of orientation is obtained by an elongational flow in the cavity which is, because of wall friction, combined with the shear flow.

Rheological measurements in the cavity showed, that there is a dependence on melt viscosity together with the pressure for the reinforcement of the Polyethylene bars.

The aim of further investigations presented here is to achieve self-reinforcement with other semi-crystalline thermoplastic polymers. Successful experiments made with Polypropylene, shows an improvement in mechanical properties up to 2800 N/mm² for Young's modulus and 73 N/mm² for tensile strength. It is more than a factor of 2 compared with the basic properties of this material.

Some examples for technical constructions show the self-reinforcement in practice.

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10/3 HIGH-MODULUS/HIGH-STRENGTH POLYETHYLENE FIBER PREPARED BY THE MELT-DRAW ORIENTATION METHOD

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Pre-oriented filament was prepared by spinning the mixture of relatively high fraction of ultra high molecular weight polyethylene and low molecular weight polyethylene wax under the draft condition. After then, this pre-oriented filament was stretched in the heated medium which extracted low molecular weight polyethylene wax at the same time.

In spite of the crystallized state from the molten mixture of high fraction of ultra high molecular weight polyethylene, this pre-oriented filament showed superior drawability. Modulus and strength were both increased with the increase of draw ratio. These tensile properties of the obtained fiber were equivalent to those of conventional gel span fiber. By x-ray analysis, it was found that the pre-oriented filament crystallized under the draft condition was in high c-axis orientation and was constituted from the ordered long period structure extended along the filament axis. The intensity of small angle x-ray scattering was decreased with the increase of the draft ratio but the long period did not change. On the other hand, the long period was not observed for the stretched fiber. This suggested that the fiber was based on the extended chain structure.

It was considered that molecular chains in the pre-oriented filament were extended along the thread line under the draft condition. And in the process of the crystallization, molecules were transformed into lamellar structure with a small number of molecular entanglement. It is concluded that the drawability of the pre-oriented filament and the high modulus and high strength of the fiber gifted from such drawability would result from the such lamellar structure.

10/4

ULTRA HIGH MOLECULAR WEIGHT POLYETHYLENE PRODUCTS FROM PSEUDO-GEL PRECURSORS

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Ultra high molecular weight polyethylene (UHMWPE) has been processed into high modulus and strength fibers by dissolving in some suitable solvent, spinning and subsequently quenching the spun fiber, removing the solvent and stretching to some high draw ratio. Whereas the effects of the processing and preparation conditions on the mechanical properties of the spun-drawn fibers have been investigated to a considerable extent, the viscoelastic behavior of the UHMWPE pseudo-gel precursors has been examined only recently by rheological and rheo-optical studies which indicate that these systems are not true gels and that their dynamic moduli G' and G" are frequency and temperature dependent. The UHMWPE pseudo-gels have a crystalline structure which varies significantly with the conditions of their preparation as can be ascertained by the thermal behavior of the crystalline morphologies which are obtained after solvent extraction. These semicrystalline morphologies exhibit remarkable deformability and can be drawn by solid state forming processes into high modulus and strength products.

10/5

"PULTRUDED THERMOPLASTICS - MANUFACTURE AND PRODUCT PROPERTIES"

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Pultruded thermoplastics are currently emerging as a significant group of injection moldable polymers exhibiting the properties of the base resin plus the extremely high impact strengths and high flexural moduli usually associated with structural composites. This is due to the advent of novel processes for manufacture, which can be described as "pultrusion compounding". In these processes rovings of reinforcing material containing large numbers of individual filaments are manipulated so that the individual filaments may be completely "wet out" by the base resin. The complete "wet out" of the filaments by the base resin is unique to pultrusion compounding and ensures high properties are attained. Fiber loadings up to 70% are possible. There are a number of ways to achieve this, and these will be presented in detail in the text. The coated rovings resulting from the pultrusion compounding process are then pelletized into pellets varying in lengths from 1/8" to 1 1/2". All of these pellet lengths are injection moldable, with a high percentage of the long fibers retained unbroken in the molded part. This is achieved on conventional reciprocating - screw injection molding machines by using slow speeds for plastication and injection. In fact, the pultrusion compounded materials, with a large reduction in the number of fiber ends compared with their extrusion compounded counterparts, flow easily into molds and can be used to obtain fine surface detail. During the mold filling process some interesting, and as yet unexplained, flow phenomena occur. Fibers are seen protruding from the "fountain flow" in all directions, loading to speculation that the fibers may reverse direction during the filling stage. Photographs of these phenomena will be included in the text. Part design and more particularly, mold design must be approached somewhat differently with these materials. Due to the physical size of the fibers it is not yet possible to make rheological measurements on the melt. This means that mold filling simulation computerized software packages cannot be utilized. So mold design is performed using traditional techniques. The key to successful design is to use abnormally large sprues, runners and gates. In addition the gate land length must be minimal. Using all of these new or modified processing techniques it is possible to achieve vast improvements in physical properties for current engineering resins, opening new markets to plastics as metal replacements.

10/6 INJECTION MOULDING OF HOSTALEN GUR 812

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Meinhard Gusik " "
Dr. Wolfgang Payer " "

Hostalen GUR is a ultra-high molecular weight polyethylene with an average mol mass of 4-6 $10^6 g \cdot mol^{-1}$. Owing to its very high melt viscosity the material is generally processed by pressure sintering or ram extrusion to sheets or profiles which are in turn machined to the finished product. So far with ultra-high molecular weight polyethylene it has not been possible to employ the injection moulding process which is particulary economical for the manufacture of complicated parts in large series.

Perfect parts can now be manufactured on injection moulding machines permitting injection pressures of more than 100 MPa by the selection of suitable processing parameters. The follow-up pressure time has to be optimised to avoid laminate structures caused by cooling. Moreover, an improvement in the flow behaviour of UHMW-PE is necessary.

10/7 RADIO-FREQUENCY ASSISTED PROCESSING OF UHMWPE

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Ultra high molecular weight polyethylene (UHMWPE) has many outstanding properties such as high impact strength (including at low temperatures) and excellent abrasion and chemical resistance. With a typical molecular weight in excess of 3.10^6 g/mole, viscosity of molten UHMWPE is so high that it cannot be processed by forming techniques which rely on the flow of molten polymer processes such as compression molding or ram extrusion have to be used. Recent years have seen the emergence of several new approaches to UHMWPE processing. Among them, the use of high speed kinetic energy mixer, forging and modified injection molding have shown promising results.

In this work another method of processing UHMWPE is described. It involves the use of radio frequency radiations. UHMWPE being transparent to RF waves a high dielectric loss additive has to be used for this method to be usable. In our case carbon black, was blended with UHMWPE powder at a concentration of 0.5% (wt). The size of carbon black primary particles is several orders of magnitude less than that of the UHMWPE. With a proper blending method each polymer particle is coated with carbon black. When subjected to RF excitation the heat softens the surface of UHMWPE particles and the material can be easily consolidated using adequate pressure. Large parts can then be molded in a few minutes. The typical residence time in the RF oven being only 2 min, the thermal history of the material processed using the RF heating / compression molding method described here compares favorably to other UHMWPE processes.

Using a frequency of 55 MHz, effect of processing parameters such as heating time, mold temperature, dwell time and molding pressure on material morphology and mechanical properties was investigated. The results obtained were compared to those obtained by conventional compression molding of UHMWPE powder.

10/8 POLYMER EXTRUSION THROUGH OSCILLATORY DIES

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Recent investigations have shown that by super imposing longitudinal oscillations upon a constant pressure gradient flow of a polymer solution through a straight pipe, extremely large changes occur. Transverse oscillations produce similar effects. Although the shear thinning properties of the polymer appear to be the dominating factor in such flow situations, elastic effects are also important, particularly for the stress distribution in the flow.

A novel application based on the above results is presented in the form of an oscillatory die at the exit of an extruder. Longitudinal and transverse vibrations are imposed on the die at a large variety of amplitudes and frequencies of oscillation. The effects of these vibrations upon the polymer result in very large increases of the mechanical properties of the finished product. For some polymers, the ultimate strength of extrudates increases by 150 %. Resistance to torsion is also greatly increased. Die swell is reduced and substantial increases in flow rate are also possible.

Results will be presented for a number of frequently used polymers suggesting the enormous possibility of the use of this method in industrial processes.

10/9

SOLID-PHASE FORMING AND COFORMING OF HIGH-PERFORMANCE THERMOPLASTICS

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Dow Solid-Phase Forming (SPF) is a unique fabrication process for manufacturing hollow articles from thermoplastic materials. In SPF, a polymeric blank is heated to slightly above its glass transition temperature (amorphous polymer) or below its melting point (semicrystalline polymer). Next, the heated blank is forged (squeezed) into a sheet-like preform which is cooled and clamped at its perimeter. The clamped preform is then shaped into a hollow part by standard pressure forming techniques, the clamped area providing the lip of the finished article.

SPF has many advantages over conventional thermoforming: it can be scrapless; parts fabricated by SPF can be highly oriented, with biaxial orientation present throughout the articles; polymer powders can be processed directly by SPF with compacted powder serving as the blank; and, because several blanks can be heated separately and then combined just before forging, it is possible to fabricate an almost limitless variety of multicomponent structures, many of them unique. The latter feature gives rise to the concept of "coforming," a generalization of "forming" in the same sense that "coextrusion" and "coinjection molding" are generalizations of "extrusion" and "injection molding," respectively.

The various benefits of SPF and Solid-Phase Coforming (COFO) are illustrated for three disparate high-performance thermoplastics: (1) the low-temperature impact strength of polyetherimide (PEI) is increased several-fold because of the orientation imparted by SPF; (2) ultra-high-molecular-weight polyethylene (UHMWPE) powder has been fabricated into thin-wall articles which have enhanced mechanical properties as a result of molecular/crystalline orientation induced by processing; and (3) polyvinylidene fluoride (PVDF) and polymethyl methacrylate (PMMA) have been coformed into a part which has a PMMA core layer encapsulated by PVDF; the PMMA core provides bulk, rigidity, and a raw-material cost advantage while the surface has the chemical resistance of PVDF.

10/10 MULTILAYER CERAMICS (MLC)

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Transistors on logic chips nowadays have switching times in the order of 10^{-9} sec. Within this time span, electric signals travel only a few centimeters. Therefore, in order to utilize the fast chips effectively, it is imperative to keep connections between the chips short, i.e. to integrate also the wiring network.
The MLC technology has enabled IBM to take a great step towards this goal; a MLC substrate, 90 x 90 mm square, consisting of up to 36 layers, carries and connects up to 133 chips for a total of 70 000 logic circuits: one and a half times the number of logic circuits in a medium size computer system a decade ago.

MLC substrates are manufactured according to the following process routing:

1. Dispersing Al_2O_3 powder in an organic binder (a dissolved epoxy resin system) by means of a ball mill.
2. Continuous casting of the slurry so obtained, onto a polyester carrying foil. After drying, separation of the ceramic greensheet from the carrying foil.
3. Blanking of square greensheets (180 mm x 180 mm).
4. Mechanical punching of hole patterns into the blanked greensheets (punched via hole diameter 0,12 mm, up to 40 000 holes).
5. Screen printing of molybdenum paste onto the greensheets in order to generate conductive structures and to fill the via holes.
6. Laminating from 18 to 36 greensheets to form a multilayer structure and cutting to size.
7. Sintering the multilayer (firing temperature 1600°C, linear shrinkage after sintering $17{,}2 \pm 0{,}2$ %).
8. Surface treatment (chemical deposition of Ni and Au films) to render Mo solderable for the connection of contact pins and chips.

10/11

PROCESSING INFLUENCE ON PROPERTIES OF LIQUID CRYSTAL POLYMERS

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During the last years liquid polymers show an increasing interest for electronic applications. The high mechanical strength, the extremely good dimensional stability, the high service temperature and the good dielectrical properties are especially interesting. However, a close attention has to be taken to the processing conditions as these materials are strongly anisotropic.

Different liquid crystal polymer compounds were injection moulded and the influence of different processing characteristics on performance were examined. A test mould was used to determine pressure drops, ejection forces, shrinkage and warpage at various moulding conditions. The anisotropic effects were also analyzed.

The low pressure drops indicate a low stress level. Due to the unique dimensional stability, i.e. shrinkage, warpage and the internal stresses show low values together with a low thermal expansion, the materials will find interesting application possibilities in fiber optical devices.

The mechanical strength is generally claimed to be very good. However, injection moulded multigated cavities create probelms in weldline strength. Results showing the strength versus different moulding conditions will be reported.

The influence of the processing conditions on thermal and dielectrical properties will also be reported.

Futuristic applications will be shown there some advantages can be obtained by using liquid crystal polymer compounds in stead of more traditional engineering plastics.

10/12 PROPERTIES OF LIQUID-CRYSTAL INJECTION-MOULDINGS

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Recently, so-called "self-reinforcing" liquid-crystal polymers (LC's) have been put on the market, which may avoid some disadvantages of fibre filled injection-moulding resins: from this liquid crystalline material parts of high strength and stiffness can be manufactured without having to worry about increased melt-viscosities or mould wear. The striking mechanical properties of these new resins can be explained by the rigid rod behaviour of their molecules. This leads to a uniform orientation of comparatively large-sized molecular groups. These orientations will be frozen when cooling down the melt and remain in the ready-made product. Under these conditions a failure of the part in the direction of the orientations requires a higher amount of covalent bondings to be cracked than one rectangular to the main orientations. For the improvement of hightech mouldings this behaviour of liquid crystal polymers naturally demands trimming the more or less anisotropic orientations according to the expected loads. Up to now there is only little experience about the orientation behaviour of LC-melts in injection moulding, so a straight forward control of orientations by the injection process is not yet possible.

This report examines the shrinkage, the mechanical properties and the properties of welding lines of some liquid crystal polymers. In order to characterize orientations in LC-mouldings, three basic types of flow will be considered: plain divergent, plain convergent and plain parallel flow. These three cases describe flow conditions in each single area of any part. Examinations of different test geometries show nine differently oriented layers in divergent flow channels. A very thin skin on top of the moulding, a second skin layer, and a shear layer with flow wise orientations, and a transitional layer appear twice and symmetrically in a cross section of the moulding. In the core there occur orientations rectangular to the flow. In convergent channels, which show a similiar layer structure, the transitional layers disappear, and in this case the molecules of the core show also flow-wise orientation. In parallel flows, the rheological history of the melt expresses itself most obviously; according e.g. to the gate geometry either flow-wise or rectangular orientations remain in the core zone. Besides, liquid-crystalline polymers alter spontaneously the orientation direction when the cross section of the flow channel changes.

For simplifing the treatment of these liquid crystal polymers some calculation programs for predicting cavity filling and orientation directions are presented. Thus the evaluation of the resulting part behaviour becomes possible regarding the effects of moulding geometry and gate location on weld lines and orientations. The moulding will be modelled by a finite-element shell, which then serves to depict cavity filling by e.g. simulated short shots and velocity vectors. At last orientation directions within the skin and the core layers will be shown.

10/13 EFFECTS OF MOLECULAR WEIGHT ON RHEOLOGY AND MOLECULAR ORIENTATION OF THERMOTROPIC LIQUID CRYSTALLINE COPOLYESTERS

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Rheological properties and molecular orientation behavior were studied for a series of thermotropic liquid crystalline copolyesters of different molecular weights synthesized from poly(ethylene terephthalate) and 60 mol% p-hydroxybenzoic acid. In recent studies, we have shown characteristic features of the rheological properties and flow-induced orientation of the thermotropic copolyester having a certain molecular weight. The major findings are as follows. The rheological features are a remarkable shear-thinning of viscosity and a high compliance at low shear stress as compared with isotropic polymer melts. Molecular orientation in an elongational flow field is dominated by strain because of a very long relaxation time of the molecular orientation, although there exists a size effect on the orientation. The aim of this report is to present the results of studies on the molecular weight dependence of the rheological properties and flow-induced orientation. Weight average molecular weights were determined by ultracentrifugal sedimentation equilibrium. A critical molecular weight, Mc for entanglement coupling was determined from viscosity-molecular weight relations obtained by dynamic and steady shear flow measurements. The compliance at a constant shear stress was, however, almost independent of molecular weight. The viscosity at a low shear stress was found to depend on molecular weight more strongly than 3.4 power in both cases of the dynamic and steady flow viscosities. The higher molecular weight dependence of the viscosity than that for flexible chain polymers might be attributed to a rodlike nature of the polymer chain. This viscosity behavior is consistent with a prediction of the Doi theory for concentrated solutions of rodlike polymers. In addition, molecular weight dependence of molecular orientation behavior in an elongational flow field by spinning was determined.

11/1

FIBRE MANAGEMENT IN COMPOSITE MATERIALS BY MULTI LIVE-FEED INJECTION MOULDING

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Conventional injection moulding supplies the molten material to a cavity through an entrance, which may subsequently be divided into a number of runners, to various gating points within the cavity. The pressure to gating points is, however, supplied by the single feed points. The principal feature of the new moulding process is the splitting of the single feed from the injection moulder into a plurality of feeds in which each is capable of supplying pressure to the cavity independently of the others.

The process provides for substantial improvement in physical properties of components over their conventionally moulded counterparts. This arises because the solidifying melt is caused to undergo shear, and the mould cavity may be considered to be a cell which, by the action of the live feeds, provides for specified shear, pressure and temperature profiles on the solidifying melt. This provides the conditions required for the optimum control over fibre orientation in moulded components without the introduction of preforms.

Technical details of the process and its control will be presented together with the results of its application to the enhancement of internal weld line strength and the tensile modulus of a range of injection moulded fibre reinforced thermoplastics.

This includes results gained from 20 x 20mm cross section bars of glass fibre reinforced polypropylene, where a two live-feed mould packing device was programmed so that the following requirements were met:-

(a) the moulding was efficiently packed

(b) the cycle time was not significantly prolonged by the use of the live-feed device

(c) fibre alignment was enhanced throughout the whole section of the moulding, to give almost total axial fibre alignment throughout the volume of the moulding

(d) the tensile modulus of the bars is significantly increased

(e) fibre degradation - as a result of the use of the live-feed - was to be kept to a minimum.

11/2 MANUFACTURING PROCESSES OF CONTINUOUS FIBER-REINFORCED POLYETHERETHERKETONE

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Reinforcement of plastics by continuous fibers leads to a significant increase in stiffness and strength.

As matrix-material for fiber reinforced composites, thermosetting materials are well established. For thermoplastics other processing techniques are required. For Polyetheretherketone (PEEK), some manufacturing processes are investigated.

At the beginning, CF-PEEK parts were manufactured following the recommendations of the prepreg suppliers. However, improved manufacturing processes were found, depending on the size and shape of the parts.
All manufacturing techniques have to be cost efficient.Also, the techniques should guarantee the full use of fiber efficiency. Examples will show the feasiblitity of different manufacturing processes. The manufacturing capability is demonstrated with the following processing methods:

- heated press
- heated rolls
- autoclave
- DFVLR developed process

Using these methods, various CF-PEEK parts were fabricated e.g. plates, profiles, shells and crash-structures.

11/3

SIMULATION OF COMPRESSION MOLDING WITH MATRIX-FIBRE SEPARATION AND FIBRE ORIENTATION FOR LONG FIBRE-REINFORCED THERMOPLASTICS

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In order to predict the charge pattern, the flow front, the weld line, the orientation of fibres and the separation of matrix-fibre, it is necessary to know the flow state during the molding process. The separation and the orientation are caused by the flow state, and the viscosity of the composites is changed by such factors. In addition, these lead to nonhomogeneities and anisotropies in the molded parts. In case of short fibre-reinforced composites, the change of the viscosity can be disregarded, but it has to be considered for the long fibre-reinforced one. Little has been discussed about simulation under consideration of such an effect as viscosity change.

A theoretical equation for the separation has been derived on the basis of solid-liquid two-phase flow by the authors.

In this paper an equation for the fibre orientation is derived with the introduction of hydrodynamic torque acting on fibres and resistance one resulting from interaction among long fibres. Here the coefficient of rotation resistance is proposed. The viscosity of the composites is assumed to be a function of temperature, velocity gradient, fibre content and fibre orientation angle. Once the distributions of velocity and velocity gradient at a time are obtained by using finite element method, the fibre content and the orientation angle are calculated from the separation and orientation equations respectively on every elements, and the next step's viscosity is expressed in these terms. With the viscosity, the following flow analysis is conducted.

The material used in the experiment is a long glass fibre polypropylene composite sheet. The computational results are compared with the experimental ones for the flow front, the molding load, the separation and the orientation applied to sheetlike parts compression molding. The effect of anisotropy of viscosity on the flow front is also simulated.

11/4 A Study of Fibre Attrition in the Processing of Long Fibre Reinforced Thermoplastics.

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It is generally agreed that fibre lengths are reduced at a number of key stages which take place during the injection moulding process. These are:

A. The screw plasticisation zone
B. The pass through a die
C. The gate region
D. The convergences in the mould itself.

A detailed study of fibre attrition has been carried out in order to enable optimisation of fibre length using long fibre reinforced thermoplastics. It is essential to have an understanding of the fibre attrition in order to realise the benefits from these materials. A stepwise analysis has been carried out taking each inspected fibre breakdown stage in turn. - Clearly it would be impractical to extract material from differing cavaties in the injection moulding machine, so simulated processing has been carried out to prepare data as follows:

1. Long fibre granules were passed through an extruder with a conventional screw and a die with generous dimensions.
2. A plunger type moulding machine was used to provide materials which have only passed a constrained die without a preplasticising step.
3. A conventional moulding machine was used to produce simple test pieces at various conditions.
4. The effect of gate dimensions has also been considered.
5. Comparisons of different matrix polymers have been made. In addition the effect of fibre fraction has been investigated.
6. Moulded components contain complex fibre orientation structures. Along with these effects the fibre lengths can also be broken up by the high shear forces which may occur locally. Some work has also been carried out on this subject.
7. Some measurements have been carried out using long fibre material rework.

This work contributes towards the understanding of fibre attrition in the injection moulding process. The optimation of properties through retention of fibre lengths is also better understood and certain recommendations can be made. In addition to that, the development of a suitable fibre length measurement technique has also been achieved.

11/5 STUDIES OF MICROSTRUCTURE DEVELOPMENT IN PROCESSING OF SHORT-FIBER REINFORCED THERMOPLASTICS

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Microstructure development was studied experimentally, both in simple flows and during injection molding. Distributions of fibers and of the orientations of both the matrix and the fibers were measured and analyzed in light of available theories and to determine the effects of thermal, mechanical and design factors.

11/6 CONTINUOUS PROCESSING OF COMPOSITES

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The extrusion of melt suspensions as a means for fast and inexpensive production of short fiber reinforced polymeric composites is investigated. The analysis is done with an integral constitutive equation for nondilute fiber suspension in Newtonian solvent. The melt suspension flows continuously and solidifies under cooling. The main goal is to control the location of the solidification front in order to catch the fibers at a specified frozen-in orientation. This orientation prevails in the solid state and defines the structure and the mechanical properties of the resulting composite. Theoretical challenges include the solution of the resulting system of nonlinear integrodifferential equations, the computation of the fiber orientation, the determination of the solidification front, and the transition from adherence to the die wall in the liquid state to slip in the solid state. The integrodifferential system is solved by streamline finite elements and Newton iteration. The fiber orientation is calculated by solving the orientation function distribution. The solidification front is determined by tracking the isotherm of the solidification temperature along which the latent heat is released. The wall boundary condition is handled by a sigmoidal relation between stress and velocity. Results appropriate for short glass fibers in epoxy resins will be presented.

11/7 STUDY ON THE MEASUREMENT OF FIBER ORIENTATION DISTRIBUTION IN THE FIBER REINFORCED COMPOSITES

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A simple method for measuring the fiber orientation distribution in fiber composites is proposed in this paper. It is well known that the mechanical properties of fiber reinforced plastics depend on the elastic properties and volume fraction of the constituent materials, and is affected by the fabrication processing. In particular, the fiber orientation and content can be strongly influenced by the material flow in molding. Therefore, a knowledge of the fiber orientation distribution is a requirement for predicting of the mechanical behavior of the fiber composite.

The use of soft X-rays for observing the fiber distribution in glass fiber reinforced plastic(GRP) has been well established. In this paper, the method for measuring the fiber orientation distribution from the radiograph of GRP is disccussed. The proposed procedure is shown as follows;

1) The images of fibers in a soft X-ray photograph are converted into an array of the digitizing values which are called pixels by use of a image analysing system. Each pixel value has the intensity between zero and 255 in proportion to the light and shade of the photograph and is stored in computer memory.

2) In the case that the fiber orientation distribution is measured at any point P, a circle with center at the point P is selected, as shown in Fig.1. This circle is subdivided by drawing parallels to the inclination angles θj and θm, respectively.

3) The orientation index, ξ, is defined by

$$\xi = \frac{S_j}{\mu_j} - \frac{S_m}{\mu_m}$$

,where μj and Sj are the mean and standard deviation of the pixels of each piece with inclination angle of θj, and μm and Sj are those of incliation angle of θm. The orientation index has a tendency to become larger, as the intensity of fiber orientation is large. The distribution of the orientation index is obtained by changing the inclination angle in steps. The fiber orientation distribution at the point P can be estimated by using the orientation angle and the amplitude at the position where the orientation index is the largest.

The proposed technique was applied to the radiographs of glassfiber/epoxy composites with the stacking sequence of $[0_2]$,$[0_3]$,$[0_6]$ and $[0_2/+30_2]$. It was proved that the fiber orientations estimated by using the orientation index agree well with the experimental results. Furthermore, the accuracy of the measurements made by this technique was disscused by appling the random oriented fiber images of known orientation which were generated by Monte Carlo simulation method.

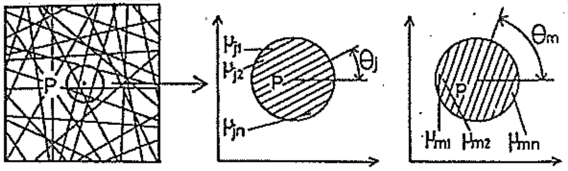

Fig.1 Two kinds of subdivided circles for measurement of fiber orientation distribution

11/8 INVESTIGATION OF THE FLOW BEHAVIOUR OF A GLASS-FIBRE FILLED, UNCROSSLINKED POLYESTER COMPOUND

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Doughy, glass-fibre reinforced polyester compounds (BMC/DMC-compounds) are processed by injection moulding for the manufacturing of heavy-duty prefabricated parts, for example in automobile industry.

For the computer-aided design of injection moulding dies information concerning the rheological properties of these types of compounds is essential. Depending on the type, geometry and filling-grade of the filler material (glass fibres and additional mineral fillers) and the interaction between filler and resin these compounds exhibit an extraordinarily complex rheological behaviour: In addition to their well-known pseudoplastic behaviour considerable effects are expected regarding yield point and wall-slip phenomena.

A comprehensive rheological study of a commercial BMC-compound was carried out in order to determine viscosity and wall-slip velocity in smooth, cylindrical dies under isothermal conditions. An attempt was made to separate the portion of the volumetric flow rate due to flow from the portion due to wall-slip. To begin with, the apparent shear rate (for the total volumetric flow rate $\dot{V}$) as function of the corrected shear stress was determined using the experimental correction procedure as proposed by Bagley. Using three sets of round capillary dies (three die-lengths each) with different diameters, the wall-slip velocity v_g could be determined from the Bagley-corrected apparent flow curves.

The values of $\dot{V}/(\pi \cdot R^3)$ at a constant wall shear stress plotted over 1/R can be approximated by a straight line, the slope of which being the wall-slip velocity v_g and the point of intersection with the $\dot{V}/(\pi \cdot R^3)$ axis being the portion of total volumetric flow rate $\dot{V}$ due to flow with respect to $\pi \cdot R^3$. This correction procedure as proposed by Mooney leads to the material property function "wall-slip velocity as function of shear stress" necessary for the design calculation of cylindrical flow-channel elements. The thus determined wall-slip velocities were used to separate the portion of the total volumetric flow rate due to wall-slip. The portion due to flow was used to determine the corrected flow curve $\dot{\gamma}(\tau)$ using the well-known Weißenberg-Rabinowitsch correction procedure; the flow behaviour of the material was approximated by the Ostwald/de Waele power law.

11/9 MEASUREMENT OF THE DAMPING OF FLEXURAL PROPERTIES OF SHORT FIBRE REINFORCED INJECTION MOULDINGS

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Injection moulded fibre reinforced polypropylene specimens were subjected to transient flexural vibration at room temperature in near vacuum conditions. The effects of fibre volume fraction and orientations with respect to the axis of the specimen on the logarithmic decrement, natural frequency, storage and loss modulus were determined. The dependence of the logarithmic decrement on the frequency was also determined. Static flexural tests were also carried out to establish the mechanical properites of the materials.

The experimental results were compared with those of other researchers and with published theoretical models.

The results show that the Elastic Modulus increases with volume fraction and orientation, whereas the loss modulus increases with volume fraction but decreases with orientation.

The logarithmic decrement was found to decrease with the natural frequency and volume fraction, whereas it reached a maximum value at 45° fibre orientation (to the direction of filling during moulding).

11/10 SHEAR FLOW PROPERTIES OF CARBON-FIBER FILLED POLYETHYLENE MELTS

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There have been reported several papers on the rheological properties of polymer melts filled with fibers according to the increasing demand of fiber reinforced thermoplastics. Both the quantitative and qualitative aspects of the flow properties of fiber filled polymer melts depend strongly on fiber length and its distribution. Shear flow properties of carbon fiber filled polymer melts were measured by means of a cone-plate type rheogoniometer at various temperatures. Two kinds of low-density polyethylene were used as the medium. The carbon-fibers used became short in polymer melts. The content of the fibers ranged from 0 to 20% by volume fraction. The influence of length or aspect ratio,length distribution, loading level of the fibers and temperature on the flow properties is discussed. The effects of compounding and mastication on fiber damage are considered. The shear rate dependence of steady shear stress or viscosity for the systems filled with short fibers was similar to that for the medium but not similar in the case of the systems filled with longer fibers. The length or aspect ratio and loading of the fibers were remarkably influenced on the viscosity at low rates of shear,however, scarcely at high rates of shear. This behavior may be explained in terms of re-formation and breakage of a structure formed by the dispersed fibers or in terms of the changes in fiber orientation with shear rate. Relative viscosity, defined as the ratio of the viscosity of the filled system to that of the medium at same shear stress, increased with increasing aspect ratio and volume fraction of the fiber. The equation of relative viscosity as a function of aspect ratio and volume fraction, which was suggested based on Maron-Pierce's equation, was able to be applied for the fiber-filled systems employed in this study. The normal stress for the fiber filled systems increased monotonously with increasing fiber loading and aspect ratio, and also increased more rapidly than shear stress at low rates of shear. The shear rate dependence of normal stress for both short and long fiber filled systems was not similar to that of the medium. Relative normal stress coefficient defined as same as relative viscosity showed different tendency in comparison with that of relative viscosity for the fiber filled systems. Apparent activation energies of flow as a function of shear rate for fiber filled systems were determined by comparing the temperature-dependent shear viscosity at constant rate of shear. They became smaller than those of the medium all over a wide range of shear rates, and were scarcely influenced by fiber loading. The complex viscosity obtained by dynamic shear flow experiments and steady shear viscosity for the medium coincided well, while those of the fiber filled systems differed at low angular frequency and shear rate. Shear viscosity was generally smaller than complex viscosity at same shear rate and angular frequency. The normal stress coefficient from steady shear flow data and that from dynamic flow data showed fairly good agreement for the medium, however, a slight discrepancy was found between these coefficients for fiber filled systems. Shear and normal stress growth for fiber filled systems were also investigated over a wide range of shear rates.

11/11

THE SURFACE POLYMERIZATION-MODIFIED CaCO AND COMPOSITES

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Composites are provided with heterogeneous or microscopically heterogeneous structure, which stipulates that all components of composites may form a special structure of interface layer through the interaction between their phase surfaces. The structure of interface layer is considered to have important influence on properties of composites. This paper investigated the surface modification of calcium carbonate ($CaCO_3$) powder by polymerization of acrylic acid, vinyl acetate and butyl methacrylate as monomers or comonomers in an aqueous phase with the $CaCO_3$ in order to control the structure of interface layer between $CaCO_3$ powders and polymers.

The surface-modified $CaCO_3$ was used as filler in PVC resin to improve the properties of these material. It was used for straight modeling. The samples made in such a manner had high compressive strength. $CaCO_3$ content was 85% by weight. It was proved from the relationship between the compressive strength of these materials and surface-modified $CaCO_3$ with different acrylic acid-vinyl acetate systems that such factors as modest ductility of polymer sheath, its thickness which achieved an effective critical value (about 100Å), favourable to forming a continuous phase, as well as good adsorption of polymer sheath on $CaCO_3$ surface, had important influence on the properties of these composites. For example, surface-modified $CaCO_3$ with acrylic acid2-vinyl acetate 18 system, being modeled under the conditions of temperature 100 °C and pressure $1300 kg/cm^2$, had compressive strength as high as 1230 kg/cm .

12/1

THE PROCESSING WINDOW FOR BLOCK, GRAFT, AND STAR COPOLYMERS

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Most processing operations for polymers take place between the glass (or melting) temperature and the thermal decomposition temperature. These temperatures define a "processing window." For block copolymer and related copolymers that can undergo microphase separation, the microphase separation temperature (MST) also becomes an important temperature in defining the processing window. A quantitative theory has been developed which can predict the effect of diluent, composition, molecular weight, and molecular architecture on the MST.

It is well known from Flory Huggins' theory that a binary mixture of A and B homopolymers phase separate at a critical value of the interaction parameter χ given by:

$$(\chi N)_c = 4$$

when each of the homopolymers has N/2 monomer units. Leibler in 1980 was the first to point out that a simple 50:50 diblock AB copolymer containing N monomer units has a larger critical χ value:

$$(\chi N)_c = 10.5$$

Since classically χ varies inversely with temperature, this implies that separation is more difficult (requires a lower temperature) in diblock copolymers than in analogous homopolymer systems. Chemically joining two homopolymers of the same size to form a diblock copolymer reduces the critical temperature by a factor of 2.6.

A simple AB graft copolymer having the same composition and molecular weight as a diblock copolymer will always have a lower MST; i.e., graft copolymers have lower MST's than corresponding diblocks. Star copolymers in which each arm of the star is either A or B have MST's which vary little with arm number. In contrast, star copolymers in which each arm is an AB diblock have MST's which increase rapidly with arm number. When an AB diblock is blended with A or B homopolymer, the MST of the diblock will decrease if the length of the homopolymer is short and increase if the length is relatively long.

12/2 ENTANGLEMENT AND FRICTION BETWEEN DISSIMILAR CHAINS IN COMPATIBLE POLYMER BLENDS

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Melt rheological and solid mechanical properties of polymers are largely controlled by entanglement and friction of macromolecular chains. Chemically dissimilar but molecularly compatible polymers may be blended to modify the entanglement and frictional behaviors, and thus improve their rheological and mechanical properties.

In this work, the entanglement and friction between dissimilar chains in compatible polymer blends are analyzed by dynamic oscillation and shear creep measurements. It is found that the specific interchain interactions, which are responsible for molecular compatibility, cause the chain segments to align and stiffen locally, resulting in decreased entanglement and increased friction between dissimilar chains. The probability of entanglement and friction coefficient between dissimilar chains are established, and quantitatively related to Flory-Huggins' χ parameter. The conditions for improved rheological and mechanical properties are thus proposed.

12/3 ON THE INFLUENCE OF INTERFACIAL SLIP ON MELT FLOW PROPERTIES OF POLYMER BLENDS

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Transitions to a steady state structure (and steady state rheological response) in well dispersed discrete two phase polymer blends in simple shear flow (cone & plate geometry, or "closed cone & plate geometry") are studied. In these studies a newly developed laser light scattering eqiupment built on a Rheometrics Mechanical Spectrometer are used to follow structure changes during simple shearing flow. The light scattering measurements may be difficult to interpret and are used in combination with transmission electron microscopy on cooled samples. For selected polymer blends e.g. polystyrene-polymethylmethacrylate blends the influence of dimensionless groups such as viscosity ratio, weber number etc. on phase structure are evaluated. The type of morphology depends on volume fractions, viscosity ratio, normal stress ratio, interface tension and shear stress. Van Oene's criterion (Ref. 1) for transitions from a dispersed type morphology to a stratified morphology is compared with experimental observations on steady state domain structure and domain stability for discrete systems.

One of the interesting observations some times found in studies on capillary flow of two phase blends is the often quite narrow minimum observed in a delineation of zero shear viscosity against volume fraction. Such behavior can also be observed in cone and plate measurements, where a teenfold reduction in viscosity may be obtained upon addition of one polymer to another.

Many different explanations/rationalizations of this behavior has been published. A simplified model expressing the blend viscosity as a function of an interface viscosity, an interface volume and the viscosities and volume fraction of the blend components, respectively, is used to rationalize the influence of interfaces with low frictional resistance - slippage. Experimentally such explanations are confronted against data from experiments where the interphases are changed by selecting a partner which favours a more diffuse interface and/or by addition of increasing amounts of selected diblock copolymers.

Ref. 1: H. Van Oene, J. Colloid Interface Sci., 40, 448, (1972).

12/4

MODIFICATION AND ITS MECHANISM OF PVC/CPE BLENDS WITH COUPLING AGENT

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In this paper, the modification and its mechanism of PVC/CPE blends were investigated. Adding some kind of aromatic diamine into PVC/CPE blends as a coupling agent, the impact strength can increase by 18.3 times in comparison with that of pure PVC, whereas that of the blend without coupling agent can only increase by 10.6 times. And at the same time the other mechanical properties such as the tensile and bending strengthes can be improved as well.

The coupling agent is considered as a kind of nucleophile. It was proved that when the PVC/CPE powders with coupling agent were mixed in banbury at certain temperature, chemical bonds would be formed across the interface of the two phases and inside the disperse phase and matrix, respectively.

The dependence of the concentration of unreacted coupling agent in the blends on reaction time can be determined by UV-spectrometer, which is shown in Fig.1. The relationship between reaction degree and mechanical properties has been discussed.

In PVC/CPE/Coupling agent ternary system, there are six possibilities for forming bonds. By the aid of probability method, the ratios of various chemical bonds can be calculated. The most important chemical bonds in the blends are PVC-Coupling agent-CPE. The coupled molecule is like a block copolymer, which is often referred as COMPATIBILIZER, so it can enhance the interfacial adhesion and result in improved mechanical properties of the blend. The possibility of the block-like molecules formed in the blends is expressed as: $P=2rD(1-r)$, where P is the probability, r is the ratio of chlorine atoms bonding to the PVC or CPE, D is the reaction degree. As may be seen from the Eq., the relationship between P and r is parabolic. So the influence of chlorine content of CPE's or ratio of PVC to CPE on the coupling efficiency can be predicted.

With the aid of solvent etching, a way has been found for studying the microstructure of the blends by scanning electron microscope. The result shows that the blends have a domain structure and the blend with appropriate coupling agent content has a networklike rubber phase.

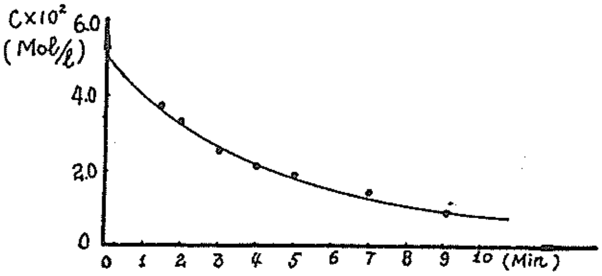

Fig.1. Plot of the concentration of unreacted coupling agent vs reaction time.

12/5 RHEOLOGY AND PHASE SEPARATION IN PS/PVME BLENDS.

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Polystyrene (PS) and poly(vinylmethylether) (PVME) blends were characterized, as a function of temperature and composition, by optical microscopy, light scattering and rheometry. At room temperature, mixtures cast from benzene are miscible and amorphous, whereas, at higher temperatures, phase separation shows up. The process is, however reversible. Oscillatory shear experiments at 50% strain (within the domain of linear viscoelasticity) and in the 10^{-2}-10^{2} s^{-1} frequency range were performed for three compositions (40, 50 and 80% PS) in both miscible and immiscible regions. It was found that the time-dependent temperature superposition principle is obeyed in the miscible region only. On the two-phase region, the changes in loss modulus and storage modulus as a function of frequency suggest a structuration of the medium which is strongly dependent upon the molecular weight of PS ($\bar{M}_w$ = 17.5 and 100 kg/mol and $\bar{M}_w/\bar{M}_w \approx 1$).

12/6 LINEAR LOW DENSITY POLYETHYLENES AND THEIR BLENDS: PART 4 SHEAR FLOW OF LLDPE BLENDS WITH LLDPE AND LDPE

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The steady state and dynamic shear behavior of linear low density polyethylenes (LLDPE) blended with low density polyethylene (LDPE) and with another LLDPE resin were measured in capillary and parallel plate geometries at T = 150, 190 and 230°C. The extrudate swell and the Bagley correction were determined. It was observed that the pressure correction plays a significant role in capillary flow of LLDPE/LDPE blends - an indication of immiscibility. Several others rheological functions also suggest a phase separation for the system. Nevertheless, the blend behaves as a "compatible" mixture of emulsion type. By contrast, blends of two LLDPE resins show expected miscibility. However, even in this case additivity was not always observed.

A new simple method of calculating the relaxation spectrum was developed. The method is analytical and its accuracy depends on adequacy of the semiempirical relation (proposed previously) to describe dynamic viscosity dependence on the test frequency. For all samples the spectrum allowed computation of storage modulus in good agreement with experimental findings.

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12/7 FLOW INDUCED TEXTURES IN MULTIPHASE POLYMERS AND THEIR EFFECT ON PHYSICAL PROPERTIES

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The class of materials known as Thermoplastic Elastomers include a wide range of multiphase polymers having rubber-like behaviour at room temperature but which soften when heated so that they can be formed into shapes using traditional polymer processing technologies. One example of such a material, which has received very widespread attention since its commercial introduction by Shell in 1965 is Kraton 102 (more frequently quoted now as Cariflex 1102). This is a three-block copolymer of polystyrene-polybutadiene-polystyrene, referred to as S-B-S and having 25% wt fraction of polystyrene. The S and B constituents being incompatible, segregate into separate phases with the scale of the phase separation being of the order of tens of nanometres. For this particular material, the dispersed polystyrene phase has a cylindrical morphology. Early work carried out in the Physics Department, University of Bristol showed that a special extrusion procedure could be used to form "single-crystal" samples having uniaxially aligned polystyrene cylinders, arranged transversely in a hexagonal array. The production of such samples enabled a wide range of accurate structure-property correlations to be established including mechanical, optical and swelling properties.

Recently, at Brunel University, we have been examining the effects of more general processing on the microstructure of thermoplastic elastomers. In this case, there is no reason to expect that the microphase morphology after processing will be identical to the equlibrium morphology as observed in idealised specimens such as the "single-crystals" referred to above. Also aside from the possible effects of complex thermal and flow fields on the morphology of block copolymers, many applications for these materials demand significant modifications to their properties, which cannot be achieved by changes to the processing conditions alone. For this reason, the virgin copolymer is frequently blended with other additives e.g. homopolymers to produce a compound having an optimum portfolio of physical properties.

More specifically, we are involved in at least four main areas of activity:-

1) The correlation of the mechanical properties of injection moulded samples of Cariflex 1102 with the orientation distribution of the microphases and their interpretation using composite laminate analysis.

2) Observations of the rheo-optical behaviour of Cariflex 1102 melts as a means of establishing the mechanism of melt flow and its relationship to microstructure changes.

3) The screw extrusion of blends of Cariflex 1102 with homopolymer polystyrene leading to the formation of homopolymer polystyrene fibres in a block copolymer matrix.

4) Preliminary studies of the microstructure of the more recent Kraton G range of thermoplastic elastomers and which contain an ethylene-butylene sequence in place of the polybutadiene. New and unexpected possibilities for structure-property correlations in block copolymers have arisen through this work.

12/8 A STUDY ON POLYMER BLENDING MICRORHEOLOGY: THE PREDICTION OF DOMAIN SIZES

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The paper reports on a study on the phenomenology of the polymer blending process, carried out to gain understanding of the physical mechanisms involved in order to make predictions on the morphology originating from a polymer blending process. In this contribution some phenomena, like droplet break-up, capillary instabilities, coalescence etc. will be inventorised. Some results of model experiments, aimed at extending the knowledge on the specific topics towards polymer blending conditions, will be discussed. Main emphasis will be placed on the, often underestimated, phenomenon of shear induced coalescence.

When two disperse phase elements collide due to a deformation of the matrix, they can form one larger droplet (coalescence) or just bounce and retain their individuality. A first step in assessing the coalescence probability is to combine known relations on the force exerted by the matrix fluid on the pair of colliding droplets, the approach rate of droplets under the action of a known force and the angular velocity of the doublet in a simple shear flow. The thus obtained differential equation describes the approach of droplets in a simple shear flow. Integration of this differential equation yields the closest approach of the droplets. Comparing this value to the critical seperation distance at which van der Waals forces induce coalescence indicate whether coalescence or just collision can be expected.

As the closest approach is governed by both the blending conditions (shear rate, viscosity, droplet size, interfacial tension) and the distance between the trajectories of the colliding droplets, only a limited fraction of the collisions will yield a coalescence. This fraction, the coalescence probability, will be shown to decrease with increasing droplet size, rendering coalescence to be a self extinguishing phenomenon. On the basis of this concept, regions of possible droplet sizes can be assessed as a function of "mixing intensity", the ratio of shear- and interfacial forces. The width and location of these regions appear to depend strongly upon the "mobility" of the polymer/polymer interfaces, i.e. the ability to deform at the same rate as the liquids it is bounding without exerting a tangential stress on them. The higher the mobility of the interfaces, the higher the influence of coalescence is expected to be. Examples of domain size regions will be given for the fully mobile and immobile case.

For a number of polymer/polymer systems, the phenomenon of gravity induced coalescence is used to assess the magnitude of the mobility of molten polymer interfaces. The mobility was observed to be high which lead to the expectation that coalescence increases the avarage domain size considerably upon an increase in disperse phase fraction. These predictions will be compared to scouting blending experiments on a single screw extruder.

12/9

ANALYSIS OF THE EFFICIENCY OF A MIXING DEVICE THROUGH THE DETERMINATION OF A RTD

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Polymer blends are commonly continuously processed on extruders-like machines. In the case of a twin-screw extruder the process parameters are numerous (flow rate, rotation speed, temperature, die design, screw profile). The object of this study is to show how the residence time distribution (RTD) in the machine enables to quantify the intensity of mixing. We studied a polyamid-elastomer blend using a short half-life time radioactive tracer which has been alternatively put in each of the two components.

A characteristic parameter of the mixing efficiency can be deduced from the RTD curves. It allows to determine the influence of the process parameters (flow rate, screw speed) and of the screw geometry. The nature of the different screw elements (mixing disks, reverse flights ...) and their repective positions along the screw have been particularly studied.

12/10 Phase Morphology of a Model Polyblend/Alloy Concomitant to the Melt Flow in a Twin Screw Industrial Mixer

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Within the interlaboratory, endorsed by the Macromolecular Div. IUPAC research program a systematic study of the melt mixing process effects on the phase morphology and melt properties of a model polyblend/alloy is carried out. The polyblend of commercial LDPE and PS at 2:1 ratio and the corresponding polyalloy, containing (additionally) 5 phr of SEB block copolymer (a compatibilizer) is prepared in six types of industrial mixers under well defined process parameters. Since three out of six mixers studied are of the corotating twin screw extruder (TSECOR) type we report here on the preliminary yet quantitative relations between the mixing process, melt rheology and concomitant phase morphology. The latter is characterized by the minor phase (polystyrene) domain size distribution and the domains' spacing as related to the process parameters: energy input, melt temperature and screw geometry. In particular, the correlations are reported for the dispersive and the distributive geometries of the "ZE40"TSECOR; It was found that the change in geometry brings about the polyblend of phase morphology similar to of the polyalloy, (i.e much finer and with lower concentration of the domain's cluster-aggregates). Also the correlations of the polyblend melt properties such as viscoelasticity, specific volume and time dependence of the fluidity (which depends on the coalescence) with the polyblend microstructure are qualitatively different for the two geometries. In the current phase of research the mixing process is being characterized by the residence time distribution (RTD) measurements and the shear stress range.

Preliminary results indicate good corelation of the latter with the domain size predicted from SIMULBLEND (Polymer Eng. Sci. 26,87 (1986) model. RTD is employed in estimating the extend of the domains' coalescence.

Finally, results of the study on TSECOR are to be discussed in terms of the mixing-microstructure trends observed for the other types of mixers.

12/11

A BASIC STUDY ON POLYMER BLENDS CONTAINING A THERMOTROPIC LIQUID CRYSTALLINE COPOLYESTER AND POLYAMIDES

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A series of polymer blends containing a thermotropic liquid crystalline copolyester and polyamides were prepared in a double-screw extruder. The thermotropic liquid crystal used was an aromatic copolyester based on para hydroxy benzoic acid and poly(ethyleneterephthalate). Both Nylon 66(N 66) and Nylon 6(N 6) were used as thermoplastic polymers.

The rheological property of the blends was found to be quite different from that of individual components and the viscosity was markedly reduced even as 5% of liquid crystalline polymer(LCP) was mixed. It could be interpreted in terms of the ordered domains which existed in liquid crystalline melt.

The morphology of the blends has been examined by means of polarized light microscopy(PLM) and scanning electron microscopy(SEM). The morphological textures observed under PLM have shown that N 66 or N 6 existed as matrix and there was a skin region of N 66 observed; the phase separation was clearly appeared as the temperature was reached at melting point of N 66. The results of SEM demonstrated that LCP was a disperse phase with a rod-like shape in the 30 LCP/70 N 66 composition and an interpenetrate two phase texture was formed in the 50 LCP/50 N 66 composition. Upon the DSC and wide angle X-ray scattering measurements it could be concluded that the lattice structure of N 66 was affected by the LCP component since the melting point of the blends was slightly lower than that of pure N 66 and the shape of the diffraction peaks was broadened. The effect of composition on mechanical properties has also been studied.

12/12

POLYETHYLENE TEREPHTHALATE BLENDS - EFFECT OF SELECTIVE CROSSLINKING ON PERMEABILITY & MORPHOLOGY

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Studies on polyethylene terephthalate compositions as blends with ethylene copolymers has been carried out, with reference to their permeability properties and morphology of the phases. While the ethylene copolymers impart a degree of impact toughness, major changes in permeability properties and morphology takes place as the ethylene copolymer is subjected to in situ viscosity/branching enhancement by selective coupling agents e.g. peroxides, epoxides, etc. or high energy electron irradiation. The permeabilities, morphologies of the phases and possible mechanisms will be discussed.

12/13

BULK VERSUS SURFACE COMPATIBILITY OF POLYCARBONATE/POLY(HEXAMETHYLENE SEBACATE) BLENDS AS A FUNCTION OF MOLECULAR WEIGHT

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ABSTRACT

It is well documented that polymer-polymer blend compatibility is influenced by the chemical structure of the polymers, their molecular weight, and the method of blending. Thus, there is a competition between thermodynamic and kinetic factors in determining phase domain relationships. In this work, blends of polycarbonate, PC, and poly(hexamethylene sebacate), HMS, were formed utilizing a wide range of molecular weight of each component.

The compatibility of polycarbonate and poly(hexamethylene sebacate) blends is enhanced by decreasing the molecular weight of either PC or HMS.

Bisphenol-A diphenyl carbonate (dimer) has a slow crystallization rate and can be obtained as a supercooled liquid even at 2.5°/minute cooling rate. On heating to some temperature, it will crystallize because the mobility becomes higher.

Dimer is an excellent monomeric model for PC and is compatible with high molecular weight polycarbonate (HPC)/dimer. The Tg of the blend can be fit reasonably well as a function of composition by the Couchman's equation. The data at small Θ values fit Chow's equation fairly well, suggesting a polymer/diluent system.

There is only one Tg in the high molecular weight poly(hexamethylene sebacate) (HHMS)/dimer mixtures and it is dependent on the composition. None of the equations available can be fit into the experimental data for the Tg vs. composition relationship. The melting point depression analysis of HHMS suggests that HHMS and dimer are not completely compatible in their amorphous region even at low dimer concentration.

In all cases, the surface excess of the low-energy component was found in all the blend systems by contact angle measurements. The extent of surface excess decreased as the low molecular weight polymer pairs were used. This suggests that the blends become more compatible as the molecular weight of the polymer is decreased.

X-ray photoelectron spectroscopy (XPS) results also indicated that the surface segregation of the low energy component occurred in all the blend systems. The high molecular weight polycarbonate (HPC)/dimer blends could not be characterized because the C 1s spectra and the O 1s of the dimer and high molecular weight polycarbonate are very similar to each other by XPS. Surface excess of dimer was found in high molecular weight HHMS/dimer blends even though they are compatible in their amorphous regions.

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12/14 STRUCTURE-PROPERTY RELATIONSHIPS IN POLYAMIDE-ABS BLENDS

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The structures and physical properties of four blends of ABS type materials with nylon 6 have been characterized and the relationship between the structures and the physical properties has been defined. All four blends contained approximately equal amounts of ABS and nylon 6.

The blends were separated into components by selective solvent extraction using the following scheme: The sample was treated with trifluoroethanol. The trifluoroethanol solution was then precipitated into formic acid, and finally the formic acid soluble fraction was precipitated into methanol. The insoluble phase from each step of the fractionation was then extracted with methyl ethyl ketone. All the fractions were analyzed by infra red spectroscopy.

The four blends (A - D) were found to contain different structures. In Blend A the ABS and nylon 6 fractions could be completely separated indicating the absence of a nylon graft. Blend B contained a fraction consisting of nylon grafted onto the insoluble p-SAN grafted rubber phase. In Blend D, nylon was grafted onto both the insoluble, rubber containing phase and the soluble p-SAN phase.

Each of the four blends was further characterized by transmission electron microscopy to determine its morphology. Blend A, with no nylon grafts, had a co-continuous, somewhat laminar structure. The structure of Blend D consisted of an ABS phase dispersed in a nylon continuum. Blends B and C had intermediate structures. In Blend B, a small portion of the rubber particles was, however, well dispersed in the nylon matrix.

All four blends had very similar physical properties despite the variation in structure. These properties included impact strength (both Izod and drop weight), thermal characteristics, and flow properties. Flow and thermal properties were characterized by driven oscillatory rheology in both the melt and the solid state as well as conventional physical testing methods.

These results indicate that in an ABS-nylon blend, physical properties are most strongly controlled by the fundamental nature of the polymers rather than the presence of specific "compatibilizing" agents or the details of the blend structures. These results contrast with those observed in many other blend systems.

12/15

STUDIES ON THE SIMULTANEOUS INTERPENETRATING NETWORKS OF POLYBUTADIENE-BASED POLYURETHANE/POLY (METHYL METHACRYLATE-co-GLYCOL DIMETHACRYLATE)

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Polybutadiene-based polyurethane/poly(methyl methacrylate-co-glycol dimethacrylate) interpenetrating polymer networks(PU (HTPB)/P(MMA-co-EGDMA)-IPN),which has not been reported up to now,was synthesized by simultaneous polymerization.The FTIR and dynamic mechnical spectra show no apparent chemical reactions between the two component polymers.
The composition ratio has an important effect on the morphology and properties of the IPN.The results of transmitting electron microscopy (TEM) indicate that when the amount of P(MMA-co-EGDMA)(component II) is about 20 wt%,the phase sizes are in 100~200 Å,which are near the distance of the cross-linked points of the networks.This the interpenetration of micro phase structure.With the amounts of component II of 40 to 80wt%,the IPN exhibits a kind of cellular structure.The component I forms the" cell walls " and the component II the " contents of the cells ".In the " cell walls " and the" contents of the cells ",there is fine structure belonging a micro phase seperation,the domain sizes of which are in 100~200 Å.The interpenetration appears chiefly at the phase boundaries and is called boundary interpenetration of the cellular structure.With increasing amounts of the component II ,the stree-strain curves of the corresponding IPNs transform from the characteristics of reinforced rubbers to toughened plastics.Both tensile strength and elongation at break of the IPN are higher than those of PU(HTPB) system at about 40 wt% of component II .The breaking energy of the resulting IPN is at a maximum at about 80 wt%.The mechanical properties of the full-IPN are far superior to those of the corresponding linear blend,and also higher than those of the semi-IPN. One of the reasons is the chemical crosslinking of the component polymers,the other is the contribution of the interpenetration and entanglement of the networks.The results of TEM show that in the linear blend the boundaries between the two phases are clearer and the domain sizes are larger in comparision with the full-IPN.The characteristics of morphology of the semi-IPN are between the full-IPN and linear blend.It is the interpenetration of the networks at the boundaries that improves the bonding between the two phases and so raises the mechanical properties remarkably.

P/1

RELATIONSHIP BETWEEN STEADY-STATE AND DYNAMIC RHEOMETRY FOR POLYMER MELTS

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Dynamic measurements have been made on 3 Polyethylene melts, 3 polystyrene "melts" and a Polydimethyl Siloxane polymer; steady-state measurements were also carried out on the same polymer melts in both torsional (between cone and plate) and capillary rheometry. The "complex" dynamic viscosity, η^*, and the dynamic viscosity, η^1, are compared to the steady-state viscosities. In the case of the capillary data, comparison is made with the uncorrected apparent viscosity, η_{app}, the Rabinowitch-corrected viscosity, η_R and the viscosity corrected for entrance and exit pressure drops; η_c. For the polyethylene melts and the pressure drops, η_c. For the polyethylene melts and the PDMS, the following observations were made:

$$\eta^* \sim \eta_R \sim \eta_{ss} \text{ (from cone \& Plate) } > \eta_{app}$$

$$\eta^1 \sim \eta_c$$

for the polystyrene "melts", the results are not related in the same manner; these will be elaborated upon at the presentation.

These findings are examined in view of the well-established Cox-Merz rule, which states that:

$$\eta^* \sim \eta_{app}$$

The results of Yasuda et. al. on Polystyrene solutions (Rheol. Acta., 20, 163 (1981)) of Kulicke and Porter (Rheol. Acta. 19, 601 (1980) on poly-1-olefin melts, and of Onogi et. al. on Polystyrene melts (J. Polym. Sci., Part C, 15, 481 (1966)) are discussed in relation to our data.

P/2 COMPLEX MELT FLUIDITY CONCEPT AS A NEW VISCOELASTIC PARAMETER

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Melt viscosity or mechanical modulus are parameters often used in melt rheological studies. In dynamic experiments the data are expressed in terms of complex viscosity $\mu^*(\omega)$ or complex modulus $G^*(\omega)$. We have attempted to introduce complex fluidity $F^*(\omega)$ as a new concept. This parameter represents the compliance of viscosity. Then the following scheme shows all the rheological parameters definitions and their correlations.

$$\begin{tikzcd}
G^*(\omega)=G'(\omega)+jG''(\omega) \arrow[r, "xj\omega"] \arrow[d, "1/."'] & \mu^*(\omega)=\mu'(\omega)-j\mu''(\omega) \arrow[d, "1/."] \\
J^*(\omega)=J'(\omega)-jJ''(\omega) & F^*(\omega)=F'(\omega)+jF''(\omega) \arrow[l, "xj\omega"']
\end{tikzcd}$$

The most important interest of this concept is to simplify Cole-Cole diagramm and to make easier the determination of fundamental parameters such as newtonian viscosity or relaxation times distribution parameter.

P/3

A PREDICTIVE MODEL FOR THE EFFECT OF MOLECULAR PROPERTIES ON THE STEADY SHEAR VISCOSITY OF POLYSTYRENE

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Over the past few years extensive progress has been made in the mathematical techniques for modeling the flow dynamics in injection molds and in extrusion dies. However, our ability to accurately predict pressure profiles and flow dynamics using these new techniques is often limited to the ability of the viscosity model used in the simulations to accurately predict the viscosity over the shear rate range of interest. In principle one could use phase space models. In practice the complexity and computational time needed for these models make this impractical for most engineering applications where viscosity is only a parameter in the overall model. We have developed and will present a new model which is computationally quite simple and has been demonstrated to fit steady shear viscosity data from limiting shear rate to 50000 1/sec. A very interesting attribute of this model is that it accurately predicts the change in viscosity characteristics as a function of molecular weight from 48000 to 410000, Mw/Mn from 1.05 to 3.5, and temperature from 158 to 250 degrees C. We, also, will show that this simple model predicts the experimental observation of increased activation energy with increased molecular weight distribution as defined by Mw/Mn.

P/4

STUDIES OF THE DEFORMATION BEHAVIOUR OF THICK SECTION POLYPROPYLENE AT HIGH STRAIN RATES IN THE PRODUCTION OF ORIENTED GEOGRIDS

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Polypropylene sheet, extruded to a controlled thickness of 4.5mm and having a controlled morphology, is used in the commercial production of oriented grids for civil engineering applications such as soil stabilisation. Work on the basic deformation behaviour of this material is reported here. Test conditions in the laboratory seek to mimick the production process: this involves initial yield strain rates of the order of 1 /sec, at ambient temperatures of 95 to 110 C, with high velocity air flow over the specimen surface. The draw ratio development is studied, and a model for the neck profile is used together with experimental measurements to obtain strain rate profiles in the neck and to predict deformation power dissipated through the neck. The results are compared with those obtained by a thermal imaging technique.

P/5 A MODIFIED CONE AND PLATE RHEOMETER FOR THE MEASUREMENT OF MATERIAL FUNCTIONS.

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Measurement of first normal stress coefficients of polymer melts is usually difficult when the stresses generated by the fluid are weak. We have found that in these cases an alternative geometry, which is a modification of the conventional cone and plate rheometer, improves significantly the quality of the rheometer output signals for normal stress and torque. It also allows to reach higher shear rates prior to reach the point at which the sample fails in the free surface between the edges of the cone and the plate.

The modification consists in replacing the plate by a cup that minimizes the free surface of the fluid in the rheometer. The height of the lid of the closed cup, where the cone rotates at a steady angular velocity, is equal to the gap between the edge of the cone and the base of the cup which replaces the conventional plate.

A theoretical study of this new geometry is presented. It consists in an approximate analytical solution for a Newtonian fluid and a more general numerical solution for a Non-Newtonian fluid. The mathematical description of the flow in the rheometer allows a proper interpretation of the experimental results. It is shown that the normal forces generated in the new rheometer by the rotation of the cone are equal to those in the normal cone and plate geometry.

The practical advantages to measure normal stresses in different fluids are shown with several examples.

P/6 A NEW SHEAR RHEOMETER FOR MOLTEN PLASTICS

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A new sliding plate rheometer has been developed for the study of non-linear viscoelastic behavior of molten plastics. Sliding plate geometry was selected to make possible studies at much higher shear rates than are possible using rotational rheometers. To eliminate the effect of edge irregularities at high strains, the shear stress is measured locally by means of a novel shear stress transducer. In this way, it is not necessary to infer the shear stress from the total force on one of the plates, rendering the data immune not only to edge effects but also to bearing friction. The maximum strain in one direction is 400, and the maximum strain rate is 500 s^{-1}. The plate gap is adjustable and can be made as small as 0.2 mm. Only a few grams of resin are required to prepare a sample, and loading and cleaning can be done quickly and conveniently.

Of special interest are large, transient deformations involving high shear rates. To make possible a wide range of such flows, a servo-hydraulic linear actuator is used to displace the moving plate, and the strain history is programmed by means of a small computer. Possible shear histories include interrupted shear, large amplitude oscillatory shear, and exponential shear.

Interrupted shear provides useful information concerning entanglement kinetics and the extent of shear modification that is possible for a given resin. Exponential shear is a flow that generates a high degree of molecular orientation and may be useful as an adjunct to extentional flow studies. Large amplitude oscillatory shear is a valuable tool in the evaluation of constitutive equations.

P/7

RHEOLOGICAL PROPERTIES OF FILLED AND BLENDED POLYMERS

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So-called APP-Filler Master Batch(APP-FMB) Technique developed by our cooperative group and widely used in plastics industry of China is proved a prosperous method in the processing of the filled and blended polymers. The basic idea of this technique is the application of the atactic polypropylene and other similar polymeric products to improve the processing behaviour as well as the mechanical properties of the heavy filled and blended polymers.

Systematic research works on the rheological behaviour and the morphology of a series of filled and blended polymers fabricated by APP-FMB Tech. are made, includ different combinations of various APP treated particles(Calcium carbonate, sponites, red mud, wood flour, etc.)and polymers(PP, PVC, rubbers). It is fond that:(1)the particles are well dressed with APP in the filled and blended systems, and it is very effective to improve the processing properties. It is commonly observed that the viscosity is then not sensitive to the filler concentration, comparing with untreated and coupling agent treated systems the effect of APP-Filler Master Batch is dramatic and is of great industrial significance (Fig.1).(2)Our capillary rheometry data fit a modified Casson model pretty well(3)Industrial applications of this technique shows a very good performance in profit, processing and product qualities.

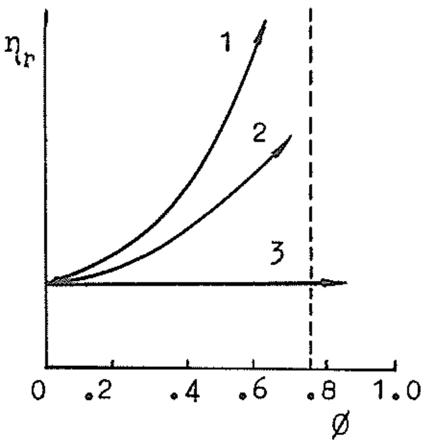

Fig.1 Relative viscosities η_r of filled polymers as functions of volume fraction Ø of fillers 1-untreated samples; 2-coupling agent treated samples; 3-APP-FMB treated samples

P/8 RHEOLOGY OF CONCENTRATED FIBER SUSPENSIONS

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Measurements are reported for the shear flow material functions of semi-concentrated suspensions of rigid fibers in Newtonian and non-Newtonian solvents. There are n fibers each of length L per unit volume. The suspension parameters studied were fiber volume fraction, fiber aspect ratio, and rheological characteristics of the suspending fluid. The studies were done using a parallel plate geometry in steady shear flow, start-up of steady shear flow, and small amplitude, forced oscillation. An experimental function for the effect of the walls on the measured properties has been found.

It is found that the viscous resistance of a randomly oriented fiber suspension is roughly (nL^3) times the resistance observed when the particles lie in the planes of shear. The viscosity shows a transient behavior in start-up of steady shear flow which depends on the total strain and not on shear rate or time separately. The difference of the first and second normal stress coefficients exhibits also a transient behavior in the start-up flow: it is zero for an initial, isotropic fiber orientation distribution, goes through a maximum with increasing strain, and approaches zero at steady state. For Newtonian suspending fluids the suspension viscosity is found to be only a function of the fiber volume fraction and independent of fiber aspect ratio and shear rate, and the suspensions do not show measurable normal stresses at steady state.

A reversibility study was performed in which the direction of the start-up of shear flow was changed in successive experiments. It is found that the transient viscosity is sensitive to the shear direction, and the difference of first and second normal stress coefficients changes signs when the shearing direction is reversed.

P/9 TESTING THE DIE-SWELL BEHAVIOUR OF POLYMERS DURING EXTRUSION

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Extrusion and injection moulding are the most used processes for thermoplastics. The flow behaviour matching the above processes is mainly obtained in controlling the degree of polymerization.

This flow behaviour is influenced and determined by: pressure, temperature, speed, time, and compound recipe.

An important feature of the plastic melting is the visco-elastic behaviour. This phenomenon is made visible by the "die swell": this means that the extruded melt rod expands to a wider diameter than the diameter of the nozzle.
Former measurements of the die swell, also known as "Memory Effect", have proved that this behaviour is due to the structure of the macromolecules. An orientation of the molecules chains takes place when passing a die, followed by the decrease of the entropy. When the mechanical tension disappears, the macromolecules can partly regain their former position. This is why this behaviour is also called "entropy-elasticity" Most of the former articles published on "die swell" base on measurements made with a high pressure capillary viscosimeter. In the present processing method, all polymers are stressed by shearing with screws of different geometries and the stress history has to be considered to determine the visco-elasticity We can go so far and say that the specific flow behaviour of different polymers, can only be tested on a laboratory extruder.
Contrarily to rheometry with high pressure capillary viscosimeters, extrusiometry presents following advantages: homogenization of the examined product, stationary flow state over an optional period of time, simple handling and dosing, greatest possible venting of material, easy simulation of pressure, temperature, speed and delay time under processing conditions.
These favourable requirements allow the exact determination of the die swell under continuous working conditions by use of a laboratory extruder.

This method allows the contactless determination of the diameter with a tolerance of 0.01 mm. It can be used for all moulding and extrusion materials. The results are not influenced by transparency, provided that rods are chosen for the examination.
The method to determine the die swell will be described and some tests examples will be shown. According to Tanner, a mathematical relation exists between the swell values and normal stress.

P/10 PREDICTING SPIRAL FLOW OF THERMOPLASTIC MELTS USING SIMILARITY CRITERIA

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Although melt index values and viscosity data describe the flow behaviour of resins accurately enough, the so-called spiral test, because of the easily interpretable information it provides on the flow properties, is still of importance for the practice, particularly when comparing the flowability of different thermoplastic resins. Basically, the test consists in injecting the melt into a spiral mold and measuring the spiral length under particular operating conditions at a definite spiral geometry.

The different variables, which influence the melt flow in the spiral are, besides the thickness of the mold, the process parameters such as stock temperature, mold surface temperature, injection pressure and shot velocity. In the resin manufacturing industry the effect of these variables on the spiral length is obtained through considerable experimental effort for the different resins concerned.

Although today's knowledge of heat transfer and fluid dynamics of polymer melts permits the analysis of flow in the spiral mold fairly well, what the practicing engineer needs, is an explicit relationship for predicting the spiral length of a given resin at various operating parameters.

Starting from the viscosity data of the polymer, which are measured by the resin manufacturer independent of the spiral test, the paper presents a simple, explicit relationship for calculating the spiral length of thermoplastic resins as a function of the above mentioned variables. This equation is developed by using the dimensionless numbers, Reynolds, Prandtl, Brinkman and Graetz as applied to the non-newtonian fluids.

Values predicted from this equation correlate well with the measured spiral lengths of various resins, obtained under different operating conditions and different geometries of the spiral.

The proposed equation can be used to reduce the experimental effort involved in finding the spiral length of a resin.

P/11 THE SPECKLE PHOTOGRAPHY IN THE RHEOLOGICAL MEASUREMENT OF POLYMER SYSTEMS

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The speckle photography method is used for the measurement of viscosity changes during the curing of polymer compositions. The change in reflective ability of the composite during the hardening, the degree of polymerisation and the properties is examined. On the basis of the obtained specklegrammes a new relation for a time dependence of viscosity is proposed.

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P/12

INFLUENCE OF TITANATE COUPLING ON RHEOLOGICAL PROPERITES OF CaCO FILLER PVC SYSTEM

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Introduction: The partial properties of PVC can be improved by filling with $CaCO_3$ while the raw materials are low price. The addition of $CaCO_3$ results in a loss of strength and the rheological properties will be distinctly decreased. This is because only physical interaction force on the interface between $CaCO_3$ and resin.

Bonding of the filler to the resin by means of the titanate coupling agent helps to prevent the separation leads to a stronger material results. A further action of the surface coating is to prevent agglomeration of $CaCO_3$. The purpose of the present work was to select the convenient coupling agents, its content and coating conditions from the measurement of rheological properties of PVC systems, in order to improve properties of the $CaCO_3$ -PVC system.

Materials and Methods: The titanate coupling agents used in this study were available from Nanking Shu-Guan Chemical Company. The following table lists the titanate to be discussed in the paper with a type and chemical structure:

Code	Chemical Structure
NDZ-102	isopropyl, triisostearoyl, titanate
NDZ-201	isopropyl, tri(dioctylphosphate), titanate
NDZ-311	titanium, di(dibutylpyrophate), oxyacetate
NDZ-401	tereisopropyl, di(dilauroylphosphorous acide) titanate

The surface coating of the filler proceeded as follow: in the high stabilizer, mixer at high velocity stirring, and at 80° C, the coupling agent was dropped on $CaCO_3$. The PVC resins plasticizer and other additions and coated fillers were mixed in GH-10mixer first at 90° C, until a temperature of 115° C was reached. The rheological properties of PVC systems of variable series were measured on the XLY-11 rheometer.

Results and Discussion:

1. Different content of titanate coupling agents

Surface-coated $CaCO_3$ treated by different content of NDZ-201, as a filler of PVC. When the content of NDZ-201 is 2.5%, the melt viscosity is decreased. When the content is more than 2.5%, the viscosity is slightly increased. It is explained that the surface of $CaCO_3$, coated with 2.5% content of coupling agent. Interface is a possible structure of mono-molecular layer, so that the bonding state of the interface is the most best.

2. Different content of filler

From the flow curve of the PVC system, in which $CaCO_3$ coated with 2.5% NDZ-201 respectively contained 5, 10, 20, 30 parts it is obvious that the flow behaviours of those system appears almost the same.

3. Different type of titanate

The surface of $CaCO_3$ particles are coated by coupling agents of four different type, its content is 3% (on $CaCO_3$), and the rheological properties of PVC system contain 15 parts treatmented filler. From the flow curve, the coupling effect may be decided as follows:

NDZ-102>NDZ-201>NDZ-311>NDZ-401.

P/13

A STUDY ON THE CHEMICAL KINETICS OF POLYESTER ALKALINE HYDROLYSIS

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The alkaline reduction of polyester fibers is an important means converting the polyester fibers into silky. In this paper the kinetic equation of polyester alkaline hydrolysis has been established through an analysis of polyphase chemical kinetics of polyester alkaline hydrolysis. It can be written as follows:

$$-dw/dt=k'K^{\neq}C_S S C_{OH}$$

in which:

k': the real constant of action
$K^{\neq}$: the equilibrium constant forming transition complex
C_S: the concentration of the ester bond in the non-covering polyester surface when the adsorption equilibrium is reached
S : the phase contact area
C_{OH}: the alkaline concentration
W : the weight of polyester
t : time

If the variation of the alkaline concentration is smaller, the above formula can be simplified:

$$-dw/dt=kSC$$

in which: $k=k'K^{\neq}C_S$

On the above basis, the reducing formulas, the stripping formulas and the exhausting alkaline formulas of polyester alkaline hydrolysis in various conditions have been derived from the kinetic equation. All these formulas have been verified by experiments. In additon to this, we found that, except alkaline concentration, time and temperature, the crystal size of polyester is the main influence factor on alkaline hydrolysis. The relation between the crystal size and the apparent constant of action can be described by CDT value.

These formulas enable the calculation of stripping and reduction of polyester fibers under laboratory and practical conditions. Its worth lies in the better revealing the nature of polyester hydrolyis, developping Rudakova's formula and Heidemann's formula, modifying the using condition of Heidemann's formula, and understanding operation-specific optimization of the parameters "alkaline concentration", "time", "temperature" and "structure factor".

P/14

HALOGENFREE, FLAME RETARDANT COMPOUNDS FOR SAFETY CABLES

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PVC cable insulation and sheathing produces large quantities of smoke as well as toxic and corrosive gases in the event of a fire, making escape difficult and increasing damage. New halogenfree materials largely overcome these problems, making them particularly suitable for use where there are stringent safety standards designed to protect people and valuable equipment. Halogenfree cables were used initially in the shells of nuclear power reaktors and in the marine sector on board ships and oil rigs where high safety standards had to be met.
With the successful development by SEL of thermoplastic, halogenfree compounds cost of safety cables will decrease and and these cables will replace existing PCV power and communication cables on a much wider scale.
The only practical method of making halogenfree materials flame retardant, is to use $Al(OH)_3$ (Aluminumtrihydrate) filler. Large quantities of filler must be used to achieve adequate flame retardancy eg. 200 parts to 100 parts of polymer in our standard sheathing compound. Only polymers with a low viscosity when melted give good processibility, only soft polymers give good flexiblity. These criteria reduce the choice to a few PE copolymers. Varying requirements can be met by careful selection of the additives.

These halogenfree compounds are processed by extrusion. It is difficult to achieve high line speed, because the melt temperature is limited to 180° where the filler is beginning to remove water. But at these low temperatures the viscosity of the melt is high and it is a problem to avoid heat built up by friction. Only screws with low compression (compression ratio 1,4 : 1), extruders with length to diameter ratio of 20 : 1 or shorter, and optimized channels from barrel to die give high output i. e. about 80 % of PVC output.

The change to halogenfree, flame retardant cables will prove particularly valuable when other areas of industry (building, machine and plant construction) also adopt flame retardant, halogenfree materials. In this sense, development of these new safer materials for cable production is leading the way to higher overall safety standards.

P/15 ANIONIC POLYMERIZATION OF LINEAR, ULTRA-HIGH MOLECULAR WEIGHT POLYAMIDE 6.

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For solution spinning experiments in our laboratory¹⁾ samples were required of linear, ultra-high molecular weight polyamide 6. The well-known technique of anionic polymerization was followed, using acetylcaprolactam as initiator and sodium caprolactam as catalyst. However, only after extensive optimization of the procedure linear polymers with molecular weights above one million were produced.

Caprolactam was used especially produced by DSM for anionic polymerization. It was extensively dried in the reactor vessel at 40°C under vacuum. Sodium caprolactam was formed in situ by adding dry sodium metal. Acetylcaprolactam was added with a microsyringe to adjust concentrations as low as 0.02 mole %.

Optimum molecular weights were obtained under the following conditions:
- a polymerization temperature of 160°C;
- a reaction time not exceeding two days;
- a catalyst/initiator ratio of approximately 1;
- an initiator concentration of 0.015 - 0.025 mole %.

Molecular weights were determined by light scattering of solutions in trifluoroethanol at concentrations of 0.05 - 0.20 mg/ml. Intrinsic viscosities were measured in m-cresol at 25°C using concentrations of 0.25 wt %, or less. Tuzar's relation²⁾

$$[\eta] = 5.26 \times 10^{-4} M_w^{0.745}$$

developed for linear polyamide 6 with molecular weights up to 355,000, proved to be valid for the present fully linear samples having molecular weights up to 1.2×10^6.

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P/16 COMPLETE VISCOELASTIC MODEL FOR NON-ISOTHERMAL EXTRUSION IN A CHANNEL

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Non-isothermal flow of polymeric melts during processing gives rise to a solidified thermal boundary layer at the cold wall. In addressing this rather complicated problem, a simulation of the non-isothermal channel flow of polymeric melt has been performed using the Leonov viscoelastic constitutive equation. In particular, this work is a continuation of our previous investigation, where a non-isothermal flow of viscoelastic fluid has been considered based upon transient one-dimensional conduction. The effects of longitudinal convection and viscous dissipation were later incorporated into the model. In the present work, the model is further advanced by incorporating longitudinal and transverse convection and conduction and viscous dissipation into the energy equation. A relative contribution of each term has been determined. Time and spatial development of velocity, shear rate, shear stress, first and second differences of normal stresses, birefringence and thickness of the thermal boundary layer have been determined.

P/17 A 3-D FINITE ELEMENT MODEL FOR NON-NEWTONIAN FLUID FLOW

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In a continuous attempt to improve the finite element simulation of rheologically complex fluid flow in an industrial context, a new methodology has been developed which combines the use of the augmented Lagrangian method, enriched elements and iterative solvers. In this work, the methodology is applied to the simulation of three-dimensional, unsteady flow of shear-thinning and Bingham fluids in complex geometry situation of practical interest in polymer processing: sudden and tapered contraction, curved channel,... Modelling includes the use of both supercomputer and standard mainframe, which provides an overview of the economical feasibility of three-dimensional numerical simulation with the current computer technology. Results in terms of flowfield and stressfield are compared to experimental data when available.

P/18

NUMERICAL DETERMINATION OF THE SWELLING RATIO FOR VISCOELASTIC INCOMPRESSIBLE LIQUIDS IN AN AXISYMMETRIC GEOMETRY BY USING THE CONCEPT OF STREAM TUBES

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Numerical simulations for the determination of the swelling ratio in extrusion flow problems of Newtonian and non-Newtonian liquids are generally performed in the entire domain of the flow by considering conservation equations. Starting from the incompressibility condition, a novel method for the computation of incompressible flows [Clermont, CRAS Paris, 1983; Clermont, de La Lande, Numeta 85, Engineering Computations(186); André, Clermont, Dieswell of Newtonian Fluids, to appear in JNNFM] enables us to transform the physical flow domain D into a rectangular domain D_1 in which the transformed streamlines are parallel straight lines. From this analysis, the conservation of mass is automatically verified and only(in the isothermal case) the momentum equations, written on the form:

$$\Psi_1 [f, f', f'', f''', \frac{\partial p}{\partial R}] = 0$$

$$\Psi_2 [f, f', f'', f''', \frac{\partial p}{\partial R}, \frac{\partial p}{\partial z}] = 0$$

are to be verified. The unknowns of the problem are the transformation f which maps D_1 into D and the pressure p.

It can be shown that the flow can be computed by investigating separately in D_1, successive bands limited by two transformed streamlines. In particular, the swelling ratio Λ_0/R_0 (Λ_0 maximal jet radius, R_0 tube radius) can be determined by considering only the first band close to the boundary(where the fluid adheres) and the unknown free surface. A minimization technique associated with a singularity analysis at the junction point between the wall and the free surface allows us to compute the swelling ratio Λ_0/ R_0 for an integral constitutive equation. The present method, based upon the concept of stream lines and stream tubes is particularly well-adapted to time-dependent constitutive equations.

From this analysis, the numerical computation leads to considerable reduction of storage and computing time.

P/19 CALCULATING THE MELTING AND PRESSURE PERFORMANCE OF SINGLE SCREW EXTRUDERS BY APPROXIMATION EQUATIONS

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Means of screw design are supposed to give relyable prediction about mixing homogeneity. Therefore it is important to have good knowledge about the melting and pressure performance occuring in the screw channel.

By means of FEM or FDM melting and pressure development can be calculated. Thes expenditure is not realistic in most practical application because of high costs.

A system of approximative equations will be suggested, to calculate the melting performance aiming to obtain knowledge how much melt is abailable in the channel to bring in strain.

Shorter calculation times on smaller computers lead to relyable results by much less expenditure.

This way an optimiation of screw geometry and process data can be obtained with reasonable expenditure.

P/20 OPTIMISATION OF DEVOLATILIZING SINGLE-SCREW PLASTICATING MACHINES

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It is often necessary to get some monomer and moisture out of the semi finished and finished plastics parts before they are produced. One possibility to devolatilize moisture is to predry the nibs in a recirculating air dryer.
This kind of devolatilizing is very expensive and takes much time. Therefore it is better to do this during the plasticating process.

One possibility is the vent extruder with a devolatilizing opening in the barrel. This paper treats with the design of the two stage screw. Some equations for the through-put and the pressure drop for the plasticating and the discharge part of the screw will be shown. The main part is the optimisation of the depth of the discharge screw to realize a high counter pressure. All equations base on the non-newtonian melt flow.

P/21

A NEW METHOD OF PROFILE DIES CALCULATION

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The cross-sectional shapes of profile dies are usually complex. The thickness of the flow channel is non-uniform. Designs of profile dies are founded on a trial basis. That makes it difficult to develop products. In this paper, we have studied the inner structures of hollow profile dies with the unrolling method. According to the structural characteristic of hollow profile dies, we consider that the non-uniformity of flow results mainly in the die's converging zone and land. When the structures of these two zones satisfy with some needed sizes, the flow will become uniform. The analyses are concentrated on these two zones. After the die's converging zone and land have been combined and unrolled for analyses, they must be divided into several channel blocks. Channel blocks can reach uniformity of flow by changing the geometric shapes of the link curves between the die converging zone and land or the transition line, or changing the distribution of entrance gaps in converging zones. Through analyses of flow, we deduce their design formulas.

After channel blocks are combined to form a die, the uniformity of flow will be destroyed even though the flow in channel blocks is uniform. For the sake of overcoming this drawback, the adjacent gaps between the combined channel blocks must be consistent with certain relationships. Hollow profile often have various outer and inner ribs. We study formulas of uniformity of flow of profile with ribs. All of these equations are solved by computer. Through the theoretical analyses and experiments, we draw the following conclusions:

A hollow profile die designed with the balance design theory can reach uniformity of flow. The design method is simple and easy to popularize. The theoretically calculated results and the values measured in the experiments are similar.

P/22 MOLTEN POLYMER FLOW IN A SPIRAL MANDREL DIE

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The flow of polymer melts in spiral mandrel dies is studied using a lumped parameter method. This method enables the calculation of pressure and volumetric flow rates both in spiral and axial direction. The polymer melt is described by a power-law model and calculations are performed under both isothermal and non-isothermal conditions for a variety of geometric, process and material viariables. The effect of chambers above the spirals on flow distribution is studied in detail. Comparisons are made to other methods of calculation available in the literature. Currently efforts are being made to obtain experimental data on flow distribution using a 35 mm single screw extruder with a 10 cm diameter mandrel having four spirals.

P/23 RECENT ADVANCES IN WIRE-COATING SIMULATION

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The wire-coating process is simulated numerically using the Finite Element Method (FEM). Pressure-type dies used in high-speed industrial operations are studied for coating typical polymer resins such as LDPE, HDPE, PS, and PVC. It is found that designs based on the "optimum gum space" theory are free of recirculation and therefore suitable for processing. The simulations show that the analysis for inelastic non-Newtonian fluids under isothermal conditions does not present any major problems and it can be accomplished with relatively coarse grids. For the nonisothermal analysis numerical oscillations in temperature are encountered in high-speed operations due to highly convective heat transfer. These oscillations can only be suppressed by using both "upwinding" and dense grids. The influence of grid density is examined for a range of dimensionless parameters critical in thermal analysis such as the Nahme, Peclet and Graetz numbers. The influence of thermal boundary conditions is also studied between the two cases of isothermal and adiabatic walls. Finally the results are compared with experimental findings for the total pressure vs. wire speed from an industrial operation.

The analysis is extended to the nonisothermal flow of two polymer melts in wire-coating coextrusion. It is shown how a die design which shows recirculation for two Newtonian fluids can be modified to avoid such occurrence, and how the interface location changes along the die to satisfy the velocity and pressure rearrangement of the two fluids. It is found that temperature conditions at the entry greatly influence the final interface location and that a nonisothermal analysis is essential in better understanding the wire-coating coextrusion process.

P/24

SYSTEM ANALYSIS AND MORPHOLOGICAL CLASSIFICATION OF MOULDS FOR INJECTION MOULDING OF POLYMERS

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In our previous publications we have analyzed the flow of materials, energy and information in a number of systems for polymer processing and discussed concepts - hierarchical, functional and structural - involved in injection moulding of polymers in the form of melts (e.g., injection moulding of thermoplastics) or low-viscosity liquids (e.g., RIM of PUR).

In all of these analyses, the mould was viewed as a subsystem. It was established that as an element of the injection moulding system the mould is a true subsystem. This means that it can be analyzed as a true system.

The mould always has the function of making a body of a prescribed macrogeometric shape and surface finish. In reactive injection moulding, the mould is at the same time the reactor, in which polymer material with prescribed physical and chemical properties is made from polymeric substances.

As a system, the mould consists of seven subsystems: runner system cavity, mould cavity, mould alignment system, ejection system, venting system, heat exchange system, and mould base. The flows and concepts mentioned earlier are used in describing the mould defined as a system.

On the basis of morphological classification of systems, moulds for injection moulding are categorized as systems of the following kinds: real, artificial, relatively separated, processing or reaction processing, dynamic, non-linear, continuous, rigid or flexible (with exchangeable mould cavities), stochastic, elaborate, complex.

On the basis of the information input to the mould (consisting of nine sub-inputs) and of the overall structure of the mould, it can be claimed that the mould is the central element of the polymer processing line.

P/25

PRESSURE AND TEMPERATURE DISTRIBUTIONS IN CAVITY DURING INJECTION MOULD FILLING (PART II)

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This study represents the pressure and temperature distributions in the cavity during injection mould filling process continued previous study,reported in the 2nd Anual Meeting of PPS.

In the previous report,we presented irregular phenomena on the temperature distribution,i.e. the temperature decreasing at the near gate,experimentally. It is not clear the mechanism on this phenomena,however, we assumed some considerations on this phenomena,e.g. wall cooling effect,fountain effect and adiavatic expansion. This study carried out to pusue this important phenomena by using three differemt moulding machines for better understanding and prediction,continued.

The used moulding machines were different machine makers in JAPAN,it involved the same machine of previous study used.

The mould and its apparatus were also same,and moulding conditions set up the samely in different moulding machines,respectively. The used materials are polycarbonate and polyacetal.

The results obtained are as follows,tentatively.

(1) The measured temperayure decreasing phenomena are recognized as same in the previous study, but the temperature decreasing values are less than previous results.

(2) It is more clear that the temperature decreasing was affected by the moulding conditions and differed with the moulding machine types under a constant moulding condition.

(3) It seems the effects of moulding machine on the temperature distribution in the cavity varied with temperature uniformity in the clynder head.

(4) The temperature change by the adiabatic expansion theoreticaly is shown as follow,

$$\Delta T_{ad} = \frac{\omega \Delta p}{C_p} \qquad (1)$$

where ω is a constant of Spencer's state equation, Δp pressure drop from injection pressure to the pressure at near the gate, C_p average specific heat at constant pressure.

P/26 FLOW VISUALIZATION OF THE MOTIONS OF ELASTOMERS AND MOLTEN PLASTICS IN BATCH AND CONTINUOUS TWIN SCREW MIXERS

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Experimental apparatus have been built to allow for flow visualization of the motions of elastomers and thermoplastics in batch and modular continuous twin screw mixers. The batch mixer has longitudinal and transverse windows. The continuous mixer has transverse windows. The twin screw machines may be operated counter-currently or co-currently. The modular twin screw machine has screw elements, kneading discs (cams, two tip and three tip). The detailed motions of elastomers and molten plastics in different elements have been observed. The relative blending ability of different rotor and screw designs are described.

P/27 ORIENTATION STUDIES DURING FLOW BY LIGHT SCATTERING MEASUREMENTS

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Experimental evaluation of structural changes in polymer systems are extremely important in processing. This may be achieved by performing light scattering measurements during shear flow.

A light scattering equipment has been built on a Rheometrics Mechanical Spectrometer allowing rapid detection of the angular distribution of scattered light from multicomponent polymer melts during shear flow. A homogeneous flow field is generated in a closed cone and plate geometry.

The device makes it possible to follow changes of orientation taking place in polymer systems undergoing shear flow at a well-defined velocity gradient and elevated temperatures. This technique is suitable for evaluating orientations of short fibers in polymer composites while shear flow is going on at different measuring conditions. In addition it is possible to follow domain stability or course of deformation, orientation, dispersion and possibly homogenizing in many types of polymer melt blends undergoing shear flow.

The experimental evaluations of the structural changes are subjected to (qualitative) interpretation, but some quantitative information is also obtainable e.g. from intensity maxima in systems with a high degree of regularity. The angular position of the maxima is inversely related to the spatial dimensions of the structure.

An example of application of the device for detection of light scattering from a thin polymer composite sample is presented.

P/28

MEASUREMENT OF THREE-DIMENSIONAL FIBER ORIENTATION IN FIBER REINFORCED THERMOPLASTICS

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When short fiber reinforced thermoplastics are injection molded, the flow during mold filling orients the fibers. Fiber orientation has been observed by many workers but there have been relatively few quantitative determinations of orientation, and even fewer determinations of the three-dimensional orientation state. This paper examines the measurement of three-dimensional orientation states by sectioning and polishing the composite and digitizing the nearly elliptical cross-sections of fibers that are obtained. The orientation state is characterized by a second-order tensor. Various sources of error in the measurement are examined. We find that it is critical to correct the data for the fact that fibers normal to the section plane have a higher probability of appearing on the section than fibers parallel to the plane. Measurement errors are found to be much smaller than sampling errors, and we give procedures for placing confidence limits on the measurements. Statistical analysis of measurements on a glass fiber reinforced nylon sample reveal a clustering effect. That is, the orientations of neighboring fibers are highly correlated, over distances of approximately one fiber length. One must allow for the clustering effect when estimating sampling errors. It may also be important to theories of fiber orientation in concentrated suspensions. The orientation states are also found to be nearly planar in the plane of the molding.

P/29 Mathematical Modelling of Fibre Orientation in Polymer Processing

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In processing of fibre filled thermoplastic materials, the flow of the filled melt gives rise to a fibre orientation pattern which is subsequently frozen in the product. The mechanical properties of the product, specifically anisotropy, is strongly dependent on such orientation patterns. The geometry of the orientation pattern depends on the type of flow (in extrusion) and the filling pattern (injection moulding). The degree of orientation depends on the flow parameters in a given direction.

This paper discusses the motion of a fibre suspended in a melt in a steady and transient flow and establishes a mathematical model, predicting the orientation and migration of the fibre. The assumptions made in this analysis are compared with those made in other analyses in the light of consideration of the real problem.

Some experimental results from multiaxial flow (pipe extrusion with rotating mandrel) and transient flow (injection moulding) are presented.

P/30 ON-LINE PARTICULATE ANALYSIS OF POLYMER MELTS AND COMPOUNDS

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A unique optical monitoring system detects, counts, and classifies particles passing through a melt stream, and also allows you to observe them directly on a video monitor - both in real time as the process is running. A relatively new company, Flow Vision Inc. of Clifton, N.J. has introduced the Flow Vision Analyzer, which can give direct information on the quality of dispersion and agglomerate breakdown in a compounding line, as well as other types of q-c information, such as frequency of gels or contaminants in raw materials.

The principle of detection is very simple: two optical probes are inserted opposite each other in a moving melt stream (see diagram); one is a light source, the other a photodetector. The flow rate through the monitoring channel is only about 1 liter or 1 kg per minute; thus, the probes are normally inserted in a side-stream sampling tube, into which a small quantity of melt is diverted from the main extruder.

On a CRT screen, you can obverse a magnified image of 1-10 cc of melt, in which gels an particles are clearly visible, as if a microscope were inserted into the melt stream (see photo). A second CRT can be provided to display countinuously a still image of a quality standard for comparison. In addition, an electronic analyzer, called the Polymer Event Detector, counts the particles in the melt (from 0.1 to 40 mils diam.) and classifies them into size ranges determined by the user. The analyzer can be set to count only particles above a certain "trigger" size. Information provided by the system include total particle counts, particle counts per minute or hour (alarm limits can be set), and size-distribution analysis.

Two versions of the system are available: a 4-ft-tall cabinet containing two CRT's and the Polymer. Event Detector, or a portable model with one CRT and the PED. The analyzer can be located some distance from the detector, und it interfaces with all micro, mini, or mainframe computers, according to the supplier. One analyzer can monitor optical sensors on several lines.

P/31

STATIC MIXING TECHNOLOGY IN THE PRODUCTION OF POLYMERS

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In the production of polymers, new, improved designs of static mixers have only recently been used in full scale plants for production and upgrading of polymers. The ability of the static mixing technology has been demonstrated in polymerization plants on industrial size for difficult mixing duties, reaction, plug flow, heat transfer and stripping.

A static mixer is a specially designed geometric structure placed in a pipe. It has no moving parts. It mixes materials flowing through it solely by redirecting fluid flow to follow the geometry of the channels in the motionless mixing device. The only power required for static mixers is the external pumping power that propels the material through the mixer.

Reaction, heat transfer and mixing requirements in polymerization have traditionally been provided by processing in slow-rotating devices, which are high energy consumers. For many applications, they can be replaced by pumps followed by static mixers used as polymerization reactors, heat exchangers and additive mixers, dispersers or thermal homogenizers.

The new designed static mixer reactor SMR is presented. The mixing elements are composed of hollow crossing tubes carrying a heat transfer fluid, greatly increasing the heat transfer area that contacts the reaction polymer. The SMR reactor allows to controll highly exothermic polymerization reactions with very small transversal temperature gradients. In addition it allows for easy scale-up.

The SMX mixer has many applications in polymerization plants. It is used to mix recovered monomer and solvents into the reacting system. In appropriate design it is able to mix uniformly small amounts of additives to the polymer stream. The viscosity of such additives may be up to 10 million times lower as that of the main stream. Examples of such additives are lubricants, antioxidants, colorants, etc..

Laminar flow heat transfer is inproved by the action of static mixers 4 to 8 times. Shell and tube preheaters in front of devolatilizers with SMXL mixers in the pipes provide short residence time, uniform time-temperature history and prevent undesired reactions or degradation.

An interesting application for dispersive mixing is the dispersion of water to the polymer with SMX mixers prior to a final devolatilization stage. A large internal surface area is produced for mass transfer of monomer and solvent into the steam bubble. The following flashing into vacuum results in decreasing the amount of residual monomer in the final polymer by many times as compared to operation without water dispersion.

Static mixer use is expected to continue to grow in polymer plants due to benefits as unproved quality and lower operating costs, as well as energy savings.

P/32 BLOWN FILM BUBBLE SHAPE - THE INFLUENCE OF THE AIR-RING

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The blown film process has been experimentally investigated and modeled extensively over the last twenty years. However, during this time very littly analysis or data have been reported on the quantitative effect of the air-ring on the bubble shape. During our modeling and simulation of blown film dynamics we found that we had to use bubble pressures almost twice the magnitude of the experimental values reported in the literature to approximate the reported experimental bubble shape. As a result, we devised an experiment which was designed to determine the dynamic pressure acting on the bubble as a function of the air flow rate in the air ring and the bubble shape. These local static pressures, which contribute to the dynamic pressures, will be shown to be of the same order of magnitude as the internal bubble pressure and are a complex function minus 0.5 inches of water, while the internal bubble pressure is about two inches of water. The results of these experiments will be reported and it will be demonstrated that the air-ring-air-flow-dynamics have as much or more influence on the bubble shape as the polymer rheology.

P/33 THE EFFECTS OF PROCESSING VARIABLES ON CARBON FIBRES PROPERTIES IN A CONINUOUS PROCESS

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Introduction: In order to prepare high-performance carbon fibres, a comprehensive study in the evolution of structure and properties in the formation of carbon fibres from PAN precursor fibres by continuous process, is being conducted in our laboratory. This report is devoted to the effects of oxidation parameters on intermediate products (oxidized PAN fibres) and on the properties of the subsequent carbon fibres.

Experimental: A domestic made PAN precursor fibre used in this study was spun, with HNO_3 as solvent, from a copolymer of acrylonitrile with 1.5% itaconic acid, specifications being denier 1.1, filaments 1000, density 1.181 g/cc.

Precursor fibres were drawn by roller systems through 4 2-meter oxidation furnaces, at temperatures 210, 230, 250 and 280° C respectively, and then through a 2-meter carbonization furnace with a temp. profile of 300-1300° C, under pure argon atmosphere. Oxidation time was varied by changing the feeding rate of fibres.

The intermediate products (oxidized fibres) were examined with optical microscope, X-ray diffractometer, density gradient tube and elementary analysis. The tensile strength of the subsequent carbon fibres was also tested on an Instron tensile strength tester by impregnated method.

Results and Discussion: In our experiments the period of stabilization is mostly much shorter than in the conventional stabilization process. The cross-sectional area of all oxidized fibres from 230 to 250° C, examined under optical microscope, revealed the sheath and core structures, though the boundaries between each sheath and core seemed to be too vague to measure. Thus we measured the sheath area of all final oxidized fibres. The results indicate that the stabilization process is limited by the diffusive transport of oxygen.

From the density measurements of oxidized fibres, we have obtained information on the progress of stabilization. As the oxidizing temperature is increased and residence time extended, the density of oxidized fibres is gradually increased to about 1.30 g/cc during the early stage of oxidation (210 to 250° C). As the temperature is further increased and the residence time prolonged, with fibre feeding rates of 10-12 m/hr the increase of density (1.50 g/cc) was larger than with a feeding rate of 16 m/hr (1.42 g/cc). Thus the influence of temperature and residence time on density increasing takes place in the high temperature oxidation range (250 to 280° C). The residence time has much effect on the tensile strength of carbon fibres. The longer the residence time is, the lower is the tensile strength, and vice versa. X-ray diffraction patterns and elementary analysis data show that the morphological structure changed drastically and the polymer chains took up oxygen atoms rapidly, both at temperature above 250° C, a phenomenon suggesting that oxidation and degradation of polymer chains took place vigorously then. These reactions and morphological structure changes can easily create defects and voids reducing the tensile strength of the final carbon fibres. Obviously the high temperature stabilization of PAN fibres very sensitive. To obtain high performance carbon fibres, therefore, the processing variables must be optimized.

P/34 CALENDER LINES FOR THE MANUFACTURE OF PLASTIC FILMS

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The following important processing steps are integrated in a complete line for the calendering of plastic films:

- Storage and conveyance of raw materials
- Dosing and mixing
- Plasticizing
- Calendering
- Part-treatment (take-off, embossing, cooling, etc.)
- Preparation and blending of reclaim material

The equipment, essential for this kind of manufacture, may bear a direct influence on the quality of the finished product, as well as on the efficiency and expenditure of the complete line.

The major criteria is, on the one hand, the selection of the appropriate components and, on the other, the optimal design of the line equipment to the required task. In this respect, the full automation of the line and the develop- ment of devices for the manufacture of special products are becoming more and more imperative, as well as measures to reduce start-up or change-over times (product change).

The construction and dimensioning of the line are dictated by specific customer-own requirements, thus leading to special solutions for each individual case.

P/35 EXPERIMENT RESEARCH FOR CONTROLLING THICKNESS PRECISION OF CALENDERING FILM

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The elastic deformation of rolls in calender working results in error of the calendering film. The rigidity of the rolls is affected by the diameter rate of the length (L/D) of the rolls. The L/D ratio and the method of crown correction of roll are most important factors for the thickness precision of the film. The limits of L/D data in our country and some other countries, such as F.R.G, U.S.A. and Japan, are lying between 2.0 and 3.0 (maximum 3.18) for calender diameters of 0200-0915m/m.

For purpose of increasing the width of the calendering film and keeping low investment, we ordered a type "Γ" four rolls calender with the L/D=4.1 from a machine works. The effective width of the rolls is 2500m/m, and the diameter is 0610m/m. Now it has been operating in a plastic factory. At the beginning of operating we got the film with very big error. The error in the thickness of the film was more than 0.04m/m, the maximum error came to 0.08m/m.

Several means have been designed for correcting the crown of calender rolls. One method of crown compensation that we use is special roll with crown contour by grinding. We have calculated and chosen the different crown correction data of the rolls to do experiments for many times. Finally, we found the appropriate datum for crown correction of rolls and obtained the qualified product. With 0.10-0.15m/m thickness of the calendering film, the error is not more than 0.01m/m, and comes up to the standard of calendering film in our country.

P/36 EXPANDING MATRIX SYSTEMS FOR NEW LAMINATING PROCESSES

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A new process in manufacturing laminates for sandwich constructions is presented. Expanding matrix systems - e.g. EP, PUR, BMI - penetrate reinforcing materials completely without shrinkage during or after cure. This results in demoulding without changes in the shape of the construction. Due to the expansion of the matrix system the construction achieves a pre-tension giving an impact strength over three times higher than conventional laminates.

The method allows sandwich constructions inbetween the matrix system acts as an expanding adhesive, because of penetration of the expanding matrix into the boundary faces of the core material (EPS, PUR foam, rock wool...). In-mould-coating is possible.

The porous structure of the expanded laminate gives improved peel and tear strength. The excellent contact between matrix system and surface of the substrate is given by the pressure of expansion. This allows applications as adhesive on other materials than described above: metals, ceramics, laminates etc.

Various applications in different kinds of industries (automotive, railway, mechanical engineering) are presented.

P/37

LABORATORY UNIT DESMA 966.053 LAB FOR OBTAINING REALISTIC PROCESSING DATA FOR ELASTOMER INJECTION MOULDING PROCESSES

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It is shown that processing data for the injection moulding process can be arrived at with the aid of a standard injection moulding machine equipped with a direct sensing system with pressure and temperature pick-ups and which is also fitted with a set of different nozzles to simulate different shear speed ranges.

The results of this mixture testing method provide processing data which tally closely with those encountered in processing practice and which cannot be obtained with the same quality using conventional laboratory testing methods.

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STRUCTURE/TOUGHNESS VARIATIONS IN POLYPROPYLENE INJECTION MOULDINGS

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Polypropylene has been injection-moulded in carefully controlled conditions, and the morphology of mouldings has been determined using a range of techniques. Instrumented drop-weight and instrumented Izod impact testing has been used to correlate impact strength with structure. It is found that toughness increases as a shear band structure - which is associated with the formation of β-phase spherulites - decreases. This has been demonstrated also for a commercial moulding. The effects of additions of chalk, talc, pigments and a lower molecular weight polypropylene have been ascertained.

P/39 Packing-Cooling Stage in Injection Molding of Thermoplastics

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The mathematical model developed for the packing-cooling stages in injection molding of thermoplastics is actually tested on simplified mould geometries such as plates or disks . The influence of different parameters , namelly packing pressure , mold and melt temperatures , generally assumed to be of importance on the properties of the final moulded articles , has been explored for amorphous and semi-crystalline polymers . The Generalized Power Law model shows good agrement with the measured pressure-time evolution at different locations in the molded parts and predicts with good accurancy the final weight of the moldings as well as the local shrinkage . The model itself is highly sensitive in viscosity-temperature relations , this is confirmed by experience .

P/40 INJECTION MOLDING WITH REDUCED PACKING

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Orientation and frozen-in stress in the mouldings will be caused by shearing of the melt near the walls of the cavity during the filling phase ("filling orientation"). Further orientation will be induced during the packing phase, when the melt is forced into the cavity for compensating thermal shrinkage ("packing orientation"). By the last process the stress in the melt, specially in the gate area, can reach values, which may be detrimental for the quality of the moulding.

Packing orientation can be avoided or reduced by filling the cavity with high pressure and sealing the gate just at the end of the filling phase or shortly after by mechanical devices or with an open gate by lowering the pressure in the cylinder so, that melt will not enter or leave the cavity ("injection moulding with reduced packing").

Mouldings of polypropylene (PP) and polystyrene (PS) with different shapes were made by injection moulding with reduced packing, without packing at all and by conventional injection moulding with constant packing pressure until the cavity will be thermally sealed. The mouldings were evaluated by deviation from the shape of the cavity (shrinkage, warpage), by photoelasticity (only with PS), by morphology (only with PP) and by Youngs modulus of different parts of the mouldings. There are considerable effects, which depend on melt temperature and on the geometry of cavity, gate and runner. Specially in the case of PS, remarkable improvements of quality could be reduced packing.

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EXPERIMENTAL STUDY OF THE FILLING STAGE OF TWO INDUSTRIAL MOLDS: A SKIING SHOE AND A CAR BUMPER, COMPARAISON WITH A CACULATION PROGRAM

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We made an experimental study of the filling stage of two industrial molds: a skiing shoe and a car bumper. These geometries are complex (curvature of the surface and high thickness variation (from 1.5 to 5.0 mm for the bumper and 2.2 to 5.5 mm for the skiing shoe)). In different injection conditions (flow rate and temperature of the melt flow) nine shots, for the bumper and twelve for the skiing shoe permit to follow the evolution of the melt front during the filling. The car bumper is injected by four points. This multi-injection introduce weld lines. The position of the lines depends on the flow rate and the temperature. Pressure measurements in the sprue complete this study for the two geometries. These experimental measurements are compared with theorectical results obtained using a filling computation program written by the "Centre de Mise en Forme des Materiaux". This program has been developped in the following classical way: first, on three elementary geometries (disk, tubular or cone-shaped geometry, two parallel or slightly convergent or divergent plates) theoretical study (the polymer is incompressible) the viscosity depends on the shear rate and on the temperature; momentum and energy equations (solved by a finite difference scheme) are coupled using an iterative process) and the experimental study are done. A complex geometry is described by assembling simple geometry flows. This assembling brings up some difficulties: the boundary conditions between two successive sections, the flow rate distribution at a branching, the description of a three dimensional geometry in a two-dimensional one (lay-flat technique). This model gives attractive results as velocity, temperature and shear rate fields. Some other results given by the calculation are compared with the experimental measurements. Short shots, on the skiing shoe and the car bumper are compared with the calculated flow fronts and the weld lines positions. Experimental and theoretical results depend on the injection conditions.

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EFFECTS OF PROCESSING PARAMETERS ON THE STRENGTH OF WELD LINE IN INJECTION MOLDED FRTP

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The strength of FRTP injection molding parts is reduced by weld line. For an engineering use, such reduction becomes very important problem. However, there are a little systematic investigations of weld line effects on the strength of FRTP injection molding. The aim of this study is to clarify the mechanism of weld line and the effects on strength of molding.

The materials used are six commercial polycarbonate(PC) resins, such as Lexan(EPL), Iupilon(Mitsubishi gas chemical) and PC(Idemitsu Petrochemical), which are 10 to 40wt% glass fiber content. Our previous reports showed that the most effective processing parameter was injection pressure, especially holding pressure, in order to improve the strength of weld line. So in this study, the dumbbell tensile test specimens with weld line are molded at various injection pressure. Two types of mold are used in this investigation. One is a single cavity mold(mold type A) and the other is a multi-cavity mold(mold type B). Cylinder temperature(280°C) and mold temperature(80°C) are constant. The pressure sensor and tempearure sensor are mounted in the cavity near the weld line to measure the melts pressure and tempearture at the weld region. Furthermore, theweld region and fracture surface have been observed microscopically.

The filling pressure affects the strength of weld line. On the other hand, the effects of the holding pressure can be obviously recognized. The effect of fiber content is remarkable. The strength of the samples with weld line decreases slightly, while that of the bulk samples increases conspicuously by increasing of fiber content. Thus the ratio of the tensile strength with weld line to without weld line decreases sharply. The specimens made in mold type B are much stronger and more dependent on the holding pressure than that made of mold type A. It is considered that the difference is due to the melt front behavior after meeting together. The microscopical observation illustrates that in the single cavity mold(type A) glass fibers are oriented prependicular to the flow direction. In multi-cavity mold(type B) "Back Flow" occures, and therefore glass fibers are oriented to the flow direction in weld region.

The strength of the molding with weld line linearly increases with the holding pressure in each filling pressure. This, however, depends on the injection molding machine and the mold composition. From the pressure measured with the pressure sensor and the pressure drop by spiral flow test, the cavity pressure at weld line(Pc) can be calculated. The relationship between the strength and Pc is also linear and not influenced by such factors. So the strength of the sample with weld line can be easily predicted without taking the machine and the mold into consideration.

P/43 EXPERIMENTAL STUDY AND MATHEMATICAL SIMULATION OF THE PROCESSING OF UNSATURATED POLYESTER BY PULTRUSION.

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- The mechanical properties of products obtained by pultrusion are highly dependent of the curing behaviour of unsaturated polyester thermosetting resin. This phenomenon has been monitored by the temperature evolution, in the middle of the die, during the processing. Our results show the effect on these measurements when change in :

. the pulling speed,

. the heater temperatures,

. the resin formulation (catalytic system)

So we perform experimental optimization of the process parameters.

- This procedure appears unobvious and tedious. So, we developp a mathemical simulation approach based on the combination of heat transfer equations with a kinetical modelization of the cure. The calculation used numerical method of finite differences.

- There are a good agreement between experimental results and calculated curves; temperature evolution, and times to reach the peak values, are well predicted, in very different process conditions. We use these valided modelization to estimate temperature and state of cure in each point during the process. These model shows that the reaction begins on the surface and rapidly becomes more intense inside the die.

- Our goal is now to use this mathematical approach for a faster optimization of pultrusion process conditions when several initiators are used.

P144 ROLLING-DRAWING: A PROCESSING TECHNIQUE TO PRODUCE HIGH PERFORMANCE SHEET MATERIALS

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Rolling-Drawing is a novel solid state processing technique for manufacturing oriented polymer sheet products.

This technique entails deformation of polymer billets by rolling and tensile drawing. The method currently employed involves pre-heating the billet and then rolling through a stand of heated "work" rolls. After emerging from the work rolls the polymer strip is tensile drawn and cooled by three stands of "traction" rolls.

Rolling-Drawing is capable of increasing the tensile modulus and strength of polypropylene by more than an order of magnitude with inexpensive equipment and simple controllable techniques.

This paper is intended to give an overview of the i) rolling-drawing process, ii) relevant modeling, and iii) effect of rolling-drawing on the tensile properties of polypropylene. A brief explanation of the rolling-drawing method and associated polymer deformation will be presented. In addition, the relationship between the deformation ratio of the polypropylene and the processing variables will also be shown.

A tensile yield model for polypropylene as a function of deformation ratio, strain rate and temperature is currently being investigated. This work is to be used to develop a tensile drawing model for polypropylene strip. A report on this work as it relates to rolling-drawing will be made.

P/45 QUALITY IMPROVEMENT BY PROGRESS IN PNEUMATIC CONVEYING AND SMALL CHEMICALS WEIGHING

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There is hardly any other sector of industry which is confronted with such a variety of different bulk materials. Beaded carbon black occupies a special place among these bulk materials because it is extremely fragile and, in its destroyed condigion, causes problems such as poor flowing characteristics, proneness to fluidisation, dust contamination, etc. The problem of conveying beaded carbon black is now solved in modern bulk material system construction. Low conveying velocities allow minimum abrasion values to be achieved, sometimes below one per cent per conveying operation. This solution has been made possible by a special conveying system which has proven reliable for many years in other branches of industry and has become know in the field of experts under the name of Pneumosplit. This system is capable of detecting incipient clogging of the pipe and systematically feeds secondary air into this pipe section, thus effectively preventing clogging. This enables the beaded carbon black to be transported through the pipe at a mean velocity of less than 2 m/sec.

A futher bulk material handling problem in the rubber industry is the dosing of small and smallest chemicals. Owing to the multitude of formulae, this is a case of handling various bulk materials with totally differing characteristics. The choice of dosing system depends on the properties of the bulk material and the degree of handling comfort desired. Systems construction nowadays has various systems available, beginning from simple manual weighing, progressing through semi-automatic systems right up to comprehensive, fully-automatic dosing. Besides a great automation effect, environmental control and protection of employees at work are given special significance, for it is quite common for the additives to be of toxic nature.

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INFLUENCE OF PROCESSING VARIABLES ON THE ELECTRICAL CONDUCTIVITY OF POLY (P-PHENYLENE SULFIDE)

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Poly (p-phenylene sulfide), PPS, was the first processible polymer to be made highly conducting. This thermoplastic is an electrical insulator that when chemically doped with the gas $As F_5$ presents a conductivity of aproximately 1 S/cm. This chemical doping is usually a diffusion controlled process. Then the morphology and degree of crystallinity should affect the rate of the absorption and desorption of the dopant and its dispersion into the polymer.

In our work, changes in the morphology and microstructure of PPS were brought about by varying some of the processing parameters. So, PPS samples (films, disks and pellets) were prepared by injection and compression molding and by solvent and melt casting. In the injection molding process (Tm = 280°C), the injection pressure was varied between 75 and 125 Kgf/cm^2 and two mold cooling temperatures were used: 25°C and 90°C; in the compression molding operation a pressure of 70 Kgf/cm^2 at 270°C was used; in the solvent casting technique the solvent used was the n - methyl - 2 - pyrrolidone, at 195°C; and finally, in the melt casting operation two cooling rates and temperatures were employed: 10°C with cold water and 25°C, with air. Thus, it was possible to obtain samples completely amorphous, partially crystalline and crystalline, with different orientations as a result of the high shear rates of the injection molding process and the low shear rates of the compression molding operation. All the samples were then characterized by differential scanning calorimetry (DSC), infrared (IR), small - angle x rays (SAXS), optical microscopy with polarized light, scanning electron microscopy (SEM) and dynamic mechanical analysis (DMA).

The doping experiments were made in a glass reactor, where the conductivity was measured with the standard four point probe technique. The dopants used were SO_3 (gas), $Al Cl_3$ (gas) and the sodium naphthalide anion (in a THF solution).

The doped samples were maintained under argon up to their final characterization due to their air instability.

It was observed that the doping rate was morphology and degree of crystallinity dependent, but it seemed not to be influenced by the amount of orientation of the samples and the crosslinking density. The dopant appeared to be heterogeneously dispersed in the polymer, but this heterogeinity seemed to be lower when the spherulites were small and to be higher in the injection molding samples. Dynamic mechanical tests couldn't be performed on the doped samples because their extreme fragility.

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The Determination of Polymer-Polymer compatibility in Polymer Blends by Ultrasonics

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The ultrasonics has been applied to determine the polymer-polymer compatibility in various Polymer blends. It has been observed that the ultrasonic velocity varies linearly with composition in compatible blends and shows a S type of curvature in incompatible blends. The behaviour of ultrasonic velocity with composition is in between these extremes for semicompatible systems. This overall behaviour is indecated by solid polymer blends and their solutions as well. The absolute viscosity of the solution of polymer blend shows the same behaviour. In some cases of solid blends, the ultrasonic absorption and dielectric constant also vary with composition in the same way. These investigations have been extended to polymer blends of various structurally different polymers of varying molecular weights as well as to the blends of polymers and graftcopolymers. In all cases, the above mentioned behaviour is found in conformity with the determination of compatibility by other methods. In cases of polymeric liquids as well this method applies. The viscosity behaviour of compatible polymeric liquid blends is given by the log additive rule due to Ulracki et al.

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A THEORETICAL APPROACH TO MECHANICAL MODEL OF POLYBLENDS IN PHASE INVERSION AND ITS APPLICATION

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There are a lot of mechanical models which can be used to describe modulus-composition relation of polyblends, but no one of these models can predict such relation in phase inversion precisely. Based on Kerner Model, a theoretical approach was proposed in this paper. For this purpose a contribution factor $f(V_2)$ was introduced and expressed as follows:

$$f(V_2)=[1+\mathrm{th}\alpha(V_2-\beta)]/2 \qquad (1)$$

where V_2 represents volume fraction of component 2; α and β are two fitting parameters.

Thus, the modulus of polyblends can be expressed as:

$$\mathrm{Log}E=(1-f)\mathrm{Log}E^{(L)}+f\mathrm{Log}E^{(U)} \qquad (2)$$

where $E^{(U)}$ and $E^{(L)}$ are upper and lower bounds for modulus predicted by Kerner Model.

Our model as shown by Eq. (2) can describe continuously the modulus-composition relation including the whole range of phase inversion. The phase inversion characteristics of a given polyblend system can be specified uniquely by parameters α and β. The width of phase inversion interval, $\Delta(\alpha,\beta)$, as defined in Eq. (3),

$$\Delta(\alpha,\beta)=\mathrm{th}\alpha(1-\beta)+\mathrm{th}\alpha\beta/\alpha \qquad (3)$$

can serve for determining the phase continuity and phase morphology of a polyblend. One extreme case (i.e. $\lim_{\alpha\to\infty}\Delta=0$) implies the interruption of phase continuity, while the other extreme case (i.e. $\lim_{\alpha\to\infty}\Delta=1$) corresponds to interpenetrating phase morphology.

By using this model the isothermal modulus-composition curves of various polyurethane-polyvinyl blend systems at different temperatures have been plotted. The experiment data fit the theoretical prediction satisfactorily. It has also been found that the plot of α (or Δ) against T gives peaks at Tg of corresponding component respectively, while the value of α (or Δ) remains constant between the two Tg's. Thus, an evidence that phase continuity changes profoundly near the glass transition temperature has been obtained for the first time. An interpretation in terms of segment movement is presented.

Eq. (2) has been further extended to predict the dynamic mechanical property of polyblends. The related mathematical equations have been deduced and checked by experiments.

The present model has also been generalized by concidering the phase volume distribution of two components in polyblends. With the aid of this generalized model the interaction extent between two phases can be evaluated quantitatively. The results of DSC IR measurements are well consistent with the theoretical calculation.

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STUDIES ON POLYBLENDS OF POLYCARBONATE WITH ABS

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Polymer blending is a relative easy method to produce new balance of properties. As to the family of polyblends formed from polycarbonate with ABS, it is often reported that an additive balance of properties is produced.

The present study was undertaken to explore the use of some special types of PC and ABS, and different PC/ABS ratios, with appropriately controlled processing conditions, in producing a synergistic balance of properties.

Two types of PC and ABS were used. One is homemade PC and ABS having selected molecular weights which constitute a PC/ABS polyblend called Type CL, and the another one is PC from General Electric Lexan and ABS from Borg-Warner Cycolac which constitute a PC/ABS polyblend called Type GB.

The experimental polyblends of both types were prepared in PC/ABS ratios from 100/0 to 0/100 under the same processing conditions and tested according to the China standard GB methods. The results of various physico-mechanical properties of both types were collected in this paper.

The most interest results are that Type CL has notched izod impact strength relation as shown in Fig.1, it has an obvious synergistic character; while Type GB has not such character as shown in Fig.2, as comparisons, here also list the data collected from References 1 and 2.

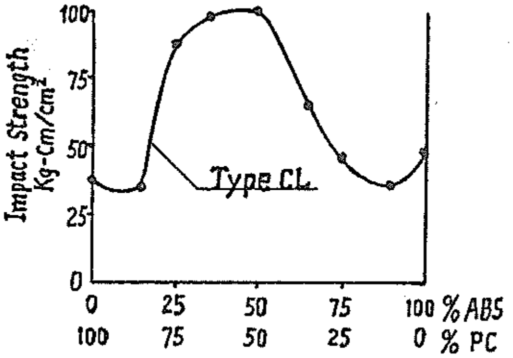

Fig.1 Notched izod impact strength relation of Type CL polyblend

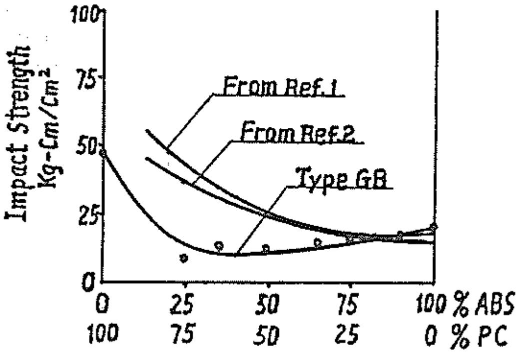

Fig.2 Notched izod impact strength relation of Type GB and other sources

The synergistic character of Type CL polyblend is strongly related to the natures of PC and ABS and the appropriate processing conditions.

Besides, the unnotched izod impact strength and ultimate elongation relations of Type CL are both better than Type GB polyblend, while the other physico-mechanical properties of two types are similar.

Some discussions related to the mechanisms of synergistic character of PC/ABS polyblend were given also in this paper.

References:

1. Hosaka Hanfu, Plastics(Japan), 32 (8), 56 (1981).
2. Chem Systems Inc., Polymer Alloys, (1983).

P/50

THERMAL AND CRYSTALLIZATION BEHAVIOUR OF BLENDS OF POLYPHENYLENE SULPHIDE AND HIGH DENSITY POLYETHYLENE

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The thermal and crystallization behaviour of polyphenylene sulphide (PPS) in its blends with high density polyethylene (HDPE) is reported. Three grades of HDPE ranging in MFI from 0.4 to 52 were used in the investigation. The effect of composition and molecular weight of HDPE on the crystallization process and morphology of PPS in the blends has been investigated by the technique of Differential Scanning Calorimetry (DSC).
In the blends, PPS crystallizes in presence of molten HDPE. It is observed that the morphology of PPS in terms of crystallite size and crystallite size distribution in the blends is significantly affected by blending with HDPE. The temperature onset of melting was found to increase with increasing HDPE content and the melting peak width was found to decrease with increasing HDPE content. This indicates a larger crystallite size and a narrower crystallite size distribution of PPS in blends. The effect is more pronounced in HDPE-rich compositions. The extent of the variation in the temperature onset of melting and peak width were comparable for all the grades of HDPE. The degree of crystallinity of PPS in the blends is reduced significantly (55-70%) in HDPE-rich blends. Therefore, it is concluded that the crystal growth of PPS is affected by the presence of HDPE melt.
The crystallization scans of PPS in the blends, obtained in the cooling mode, did not show any evidence of accelerated nucleation. On the other hand, a marginal reduction in the temperature onset of crystallization was observed. The temperature range of crystallization of PPS in the blends was found to be less for all compositions except for 90/10(PPS/HDPE). In summary it is concluded that blending of HDPE with PPS influences the crystal growth of PPS significantly although the effect on its homogeneous nucleation is not considerable. As a result, the morphology of PPS crystallized in blends is different from that of the homopolymer. The changes in the morphology of PPS are not sensitive to the molecular weight of HDPE probably because of the high temperature of PPS crystallization relative to the melting point of HDPE.

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STUDY OF MORPHOLOGY AND STRUCTURE IN POLYCARBONATE-POLYETHYLENE BLENDS

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In this study, morphology of two phase structure of polycarbonate-polyethylene(PC/PE) blend in injection molding articles was investigated. The morphology of PE domain in PC/PE blend was observed by SEM and phase contrast microscope. Pyrolysis chromatography was employed to measure distribution of PE content in injection article. In the centre of specimen, the PE dispersed phase domains are mostly of spherical shape. From centre to edge, the PE dispersed phase domains are elliptical shape. Major axis of ellipse mainly aligned to the flow direction. The farther away the centre, the greater is the ratio between major and minor axis. The PE dispersed phase domains take place to form rodlike structure until the edge of the specimen. The greater shear stress, the more obvious is this phenomenon. The content of PE in outer is greater than innor and the change of content of PE takes place to form peak-valleylike. It is concluded that PE domains move from centre to outer during injection flow. This result is different from the other publications. This morphology and distribution show that they are strongly dependent on processing conditions (for example shear stress). In order to getting good appearance of artical, it is necessary to selecting low injection speed. In this study, radiant micro fibers were observed by SEM between the two phase boundaries. This fibers probably are PE-PC graft being formed by heat and shear stress during melting blend in extruder. The existance of fiber was postulated to explain this good interface adhesion. It is not to be ignored when one analyzes the toughened mechanism of PC/PE blend.

P/52 MORPHOLOGICAL CHARACTERISTICS OF THERMOTROPIC LIQUID CRYSTALLINE CELLULOSE DERIVATIVES DURING PROCESSING

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The liquid crystalline nature of cellulose derivative including three grades of hydroxypropyl celluloses(HPC E, J, G), ethyl and methyl celluloses(EC and MC), and cellulose acetate butyrate and propionate(CAB and CAP) was investigated. The order of liquid crystallinity was ranked: HPC > EC > MC; neither CAB nor CAP formed liquid crystalline melt. The morphology and orientation of the cellulose derivative ribbons and compression molded films were examined by means of polarized light microscopy(PLM), DSC, scanning electron microscopy(SEM), wide angle X-ray scattering(WAXS), small angle light scattering(SALS), and birefringence measurement. It was shown that HPC exhibited significantly fibrillar structure in character, which formed during shear flow; corresponding to the fibrillar structure observed by SEM, a banded structure could be observed under PLM for the same sample. The results of SALS for the HPC E samples demonstrated that a two lobes Hv pattern could be observed in a range of temperatures from 160°C to 180°C; it becomes four lobes in cross position as the transition temperature is reached at 190° C. All these characteristic structures mentioned could be explained in terms of anisotropic rod-like elements, from which a model correlating them is suggested.

The effect of processing conditions on orientation in both amorphous and crystalline regions for HPC has also studied. It was seen that the orientation of rod-like molecules in amorphous region was markedly affected by processing conditions, however, nearly no influence of processing conditions studied on crystalline orientation was observed.

P/53

INFLUENCE OF MOLECULAR STRUCTURE AND PROCESSING ON THE THERMAL-MECHANICAL PERFORMANCE OF THERMOTROPIC COPOLYESTERS

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Extrusion of main chain thermotropic copolyester results in highly uniaxially oriented structures with tensile moduli typically on the order of 100 GPa and strengths of several GPa. The microstructure of such extrudates has been shown to be hierarchial fibrillar composite covering a size scale from 10's to 1000's of nanometers. Annealing tends to increase the size and perfection of these structural units while simultaneously significantly increasing polymer molecular weight. The monitoring of tensile properties both as a function of temperature and after an imposed thermal history indicates systematic property variation occurring which directly affects end use performance. For example, annealing has been shown to increase tensile strength up to 5X while not significantly affecting modulus levels. Annealing and property measurement at temperature significantly affect the shape of the observed stress strain curves. Models to describe the relationship of the observed mechanical properties to the chemistry and microstructure of typical thermotropic copolyesters will be presented with emphasis on the development of molecular weight and tensile strength during annealing. Where appropriate, data obtained from mesogenic homopolymers and/or blends of main chain mesogenic polymers will be incorporated into the described models.

P/54 PHYSICAL PROPERTIES OF FILMS FROM LDPE/LLDPE AND HDPE/LLDPE BLENDS

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The low density polyethylene (LDPE) respectively high density polyethylene (HDPE) linear density polyethylene (LLDPE) were added. The tubular films of blends were prepared by extruding polymer pellets in different ratios.

The rheological properties, tensile strength at break, elongation at break, tear strength and the thermal properties of the films from binary polyolefin blends have been studied over the entire composition range.

In the presented paper the results of the physical properties of films from blends are disscused.

P/55 BOUNDRY LAYERS OF INJECTION MOLDED POLYPROPYLENE PIECES

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The orientation of boundry layers of thin injection molded Polypropylene plates as a function of the distance from the surface and the runner was studied by birefringence an mechanical measurements on microtome cuts.
By variation of the processing conditions (fill time, melt temperature, mold temperature and pressure holding) and by variation of the molecular weight distribution of the polymer the following results are obtained:
The highly oriented boundry layer is formed during the fill time and only little influenced by pressure hold after filling, as can be shown by measurements on pieces injected without pressure hold after filling. In this latter case the thickness of the boundry layer is determined by the relaxation velocity and not by the cristallisation velocity of the melt because the orientation below the boundry layer is very low. So we can distinguish between orientation caused by filling flow and caused by pressure hold after filling. Own calculations of temperature distribution in the mold on the end of fill time brought better agreement with experiments than calculations after Janeschitz-Kriegl, which assume a parabolic velocity profile in the melt.

Measurements on drawn bars cutted parallel and perpenticular to the flow direction showed that shear zones crazes and cracks start in the region of the highest orientation below the surface in agreement to SAX measurements of Zipper on the same samples.

P/56

INFLUENCE OF INJECTION MOULDING VARIABLES ON KNIT-LINES STRUCTURE OF NYLON-6

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When multigated molds are adopted or pins are present in the mold, separate fronts of molten polymer form. Peculiar morphology and mechanical properties weaker than those of the bulk polymer are obtained in the zones where the fronts meet, these are usually called welds. The decay of mechanical properties in the weld zones is often related to the occurrence of surface defects, called knit-lines. Depending on processing conditions the surface defects can be either grooves or local sample thickening.

An experimental study of knit-lines structure in injection molded nylon 6 is performed in this work. In particular a rectangular cavity, 3mm thickness, was injected through two linear gates occupying entirely opposite sides; the weld formed half a way from the edges. The effect of changes in mold conditioning temperature, injection temperature, filling flow rate, holding time and pressure is analysed by both SEM and optical trasmission microscopy on specimens cut out 1cm far from the edges of the injected samples.

A switch from surface grooves to local sample thickening is observed by effect of an increase of mold conditioning temperature from 30°C to 130°C; the grooves sharpening and depth changed depending upon the other processing variables. The key to the understanding of knit-lines structure seams to be the volume shrinkage of the polymer in the weld zones. In a constant cross section mold much of the shrinkage vents, indeed, in the weld zone as there solidification takes place last and the related shrinkage gives rise to cooling stresses and eventually to surface grooves. The larger is the shrinkage localization at the weld zone, the larger the grooves and viceversa.

Thin specimens containing the weld zone were microtomed and deformed by elongation while under polarised ligth observation; the elongational fracture mode was monitored and the strength of weld zones was compared to the strength outside it.

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THE DEFORMATION OF PEEK - CARBON FIBRE LAMINATES UNDER STRAIN RECOVERABLE CONDITIONS

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The deformation of laminates, fabricated from sheets of PEEK thermoplastic polymer reinforced by continuous uniaxial carbon fibre, has been characterised in the temperature range 380°C to 395°C. Laminates were formed with parallel plies (carbon fibre in all layers parallel), and cross plies (alternate sheets with fibres at 0°C and 90°C). To avoid progressive change in the inter-ply fibre angles, measurements were made in oscillatory shear.

Provided that the normal loading is sufficient to prevent slip, there is a range of shear strain where the deformation is elastically recoverable, and gives identical repeat measurements. The apparent dynamic viscosity and modulus have only a small dependence on the number of layers forming the laminate and approximate to a general composite property. However, these viscous and elastic responses are non-linearly dependent on the shear strain amplitude. Considerable "hindrance" can occur at strains less than 10%, particularly at low angular frequencies of 1 radian/sec or less. This is specifically a function of the carbon-fibre composite system, since PEEK polymers have a linear strain response over a wide range of molecular weights. The frequency dependence of the viscoelasticity, which for a simple unreinforced polymer melt would imply some intermolecular coupling, is shown in this case to represent strong polymer-fibre bonding, and is similar for parallel and cross-ply laminates.

There is a threshold strain above which the viscoelasticity is nominally strain independent, and flow approximates more closely to a viscous fluid. This threshold strain corresponds to an increased fibre-fibre separation of the same order as the PEEK molecular size. As the frequency is increased and the viscoelastic response limited to smaller molecular sizes, the threshold strain decreases.

Easy flow between fibres continues to larger strains beyond the limit of oscillatory technique. The limit of elastic recovery was therefore determined in steady shear.

P/58

CREEP INDUCED BUCKLING OF PLASTIC MATERIALS

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This work consists of experimental and theoretical analysis of creep induced buckling. For polymeric materials demonstrating a substantial creep under regular temperatures and loads, the catastrophic change of shape, i.e. buckling, occurs as a function of applied loads and material properties.

In this study, top displacements of thermoplastic bars were recorded as a function of time under static loading conditions. The recorded times to failure were averaged and correlated with the applied loads. The experiments, conducted for different materials, provided the time-load relationships which are identical in their structure to the relationships for time dependent material strength developed by Zhurkov.

Creep experiments determined a time-displacement dependence close to the relation in the buckling experiments.

Numerical experiments were conducted for eccentric bars of creeping material. Elastic eigenvalue problems were solved for the shapes evolving under applied static loads. The correlation for the time-load data obtained from the numerical simulations coincided with the experimental results.

The developed understanding of buckling phenomenon for polymeric materials establishes a dependence between the time dependent behavior of a plastic structure, i.e. creep, and its load carrying capabilities.

P/59 PROPERTIES OF WOLLASTONITE/MICA FILLED POLYAMIDE 6

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Among the various fillers used in thermoplastics mica and wollastonite are particularly interesting, because they are both natural minerals and both can be ground to a high length/thickness ratio. Moreover, both are minerals whose adhesiveness to polymers can be improved by adhesion promoters.

This study deals with wollastonite and mica used as fillers in polyamide (PA 6). Both fillers have been surface-treated by dry mixing and the compounding of filler and polymer has been performed on a twin-screw mixing extruder. The test specimens have been manufactured by injection moulding and their mechanical properties have been determined by tensile, impact and flexural tests.

Both wollastonite and mica affect the strength properties of polyamide. Mica considerably increases its rigidity but has less effect on the tensile strengt. No marked differences in tensile strengths can be observed between the two fillers. The impact strength tends to decrease slightly with filling but not as much with wollastonite as with mica. Mixtures of wollastonite and mica yield higher impact strength/rigidity combinations than either of these alone. A surface treatment with silane has proved to increase strengths to some extent. Its effect will be most evident after moisture and thermal aging.

P/60 A MINERAL WOOL BASED COMPOSITE

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Mineral wool based composites are common and well-known insulators used in sound and thermal insulating. These applications typically make use of very light structures with low binder contents.

An application of particular technical interst is the filling of thermosets or thermoplastics with mineral wools. Mineral wools essentially consist of fibres with highly variable lengths and thicknesses. The average thickness of the fibres lies in the range of 5...8 µm, depending on the production method. Some production methods may leave part of the material in the form of beads instead of fibres. Such a material is actually a reinforcer consisting of both bead-shaped and fibrous particles. In thermoplasts (PA and PP) a marked increase in stiffness and a slight increase in strengths has been achieved by the use of mineral wools and the effect on impact strengt is very similar as with short glass fibres.

Experiments on composites based on thermosets (phenolformaldehyde resins) have by now produced some relatively light and strong porous structures with markedly high specific strengths.

As far as technical properties and price is concerned, plastic composites based on mineral wools actually turn out potential competitors for various composites based on short glass fibres.

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