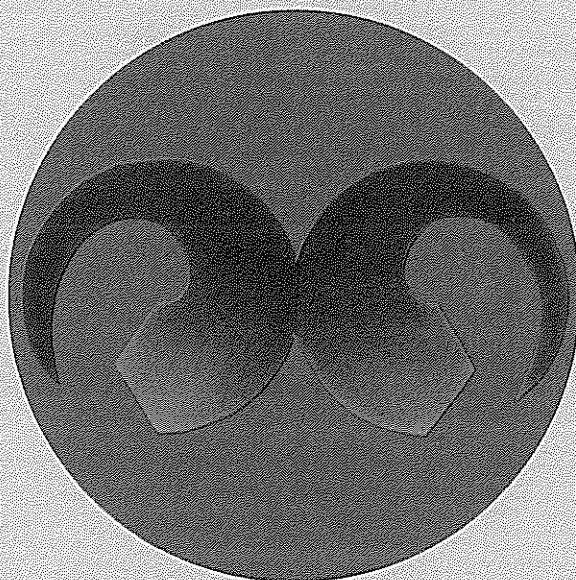SECOND ANNUAL MEETING
MONTREAL, CANADA
BONAVENTURE HILTON
APRIL 1-4, 1986

# PROGRAM AND ABSTRACTS

# POLYMER
# PROCESSING
# SOCIETY
### INTERNATIONAL

COSPONSORED BY THE
## CANADIAN
## RHEOLOGY GROUP

# CONFERENCE COMMITTEE

| | |
|---|---|
| **Chairman** | M.R. Kamal, McGill Univ. |
| **Program** | L.A. Utracki, NRCC/IMRI |
| **Treasurer** | B. Fisa, NRCC/IMRI |
| **Secretary** | P. Carreau, Ecole Polytech. |
| **Publicity** | H. Walser, VW&R |
| **Social Program** | Mrs. C.A. Utracki |

## PLENARY SPEAKER

Prof. R.S. Porter, Univ. of Mass, Amherst, Mass., U.S.A.

## BANQUET SPEAKER

Dr. A.S. Hay, G.E., Schenectady, N.Y., U.S.A.

# SYMPOSIA ORGANIZERS

1. Polymerization Processes: A. Hamielec
2. Reactive Processing: J.T. Lindt and M. Lambla
3. Modeling and Control of Molding Process: M.R. Kamal and L.R. Schmidt
4. Modeling and Control of Extrusion and Other Forming Operations: J. Vlachopoulos
5. Rubber Processing: J.L. White and K. Min
6. New Technologies: A.E. Zachariades
7. Structure Development in Processing: J.L. White and M. Cakmak
8. Fiber Spinning and Drawing Operations: J.E. Spruiell
9. Polymer Processing Rheology: P.J. Carreau
10. "Polyblends-86": L.A. Utracki

# POLYMER PROCESSING SOCIETY EXECUTIVE COMMITTEE

| | |
|---|---|
| **President** | J.L. White |
| **President Elect** | L.A. Utracki |
| **Secretary** | J.L. Throne |
| **Treasurer** | J.F. Stevenson |
| **Member at Large** | L.A. Goettler, J.T. Lindt |

## INTERNATIONAL REPRESENTATIVES

**Europe, Middle East & Africa:** H-G. Fritz, Stuttgart, W. Germany; Z. Tadmor, Haifa, Israel

**East Asia & Australia:** Baojun Qian, Shanghai, People's Rep. of China; J. Shimizu, Tokyo, Japan

**North & South America:** M.R. Kamal, Montreal, Canada; L.F. Ramos de Valle, Saltillo, Mexico

# PROGRAM AT A GLANCE

| DATE | Time | Session 1<br>Salon MT-ROYAL | Session 2<br>Salon HAMPSTEAD | Session 3<br>Salon COTE ST-LUC |
|---|---|---|---|---|
| April 1 | 17h00–20h00<br>19h00–21h00 | REGISTRATION, Foyer (Banquet Level)<br>RECEPTION, Salon WESTMOUNT | | |
| April 2 | 08h00–09h00<br>09h00–10h00 | REGISTRATION, Foyer (Banquet Level)<br>Plenary Lecture: **"Processing for Properties"**, R.S. Porter, (U. Mass), Salon WESTMOUNT | | |
| | 10h30–12h10<br>13h30–15h10 | **"Rubber Processing"** | **"Polymer Processing Rheology"** | **"Fiber Spinning and Drawing Operations"** |
| | 15h30–17h35 | **"Polymerization Processes: Modeling and Control"** | **"Polymer Processing Rheology"** | **"Structure Development in Processing"** |
| | 19h00–22h00 | Beer Session: **"What We Don't Know about Film Blowing"**; Salon Westmount. | | |
| April 3 | 08h30–12h10 | **"Reactive Processing"** | **"Modeling and Control of Extrusion and Related Operations"** | **"Structure Development in Processing"** |
| | 13h30–17h10 | **"Reactive Processing"** | **"Modeling and Control of Extrusion and Related Operations"** | **"Composites"** |
| | 16h00–18h00<br>18h00–19h00<br>19h00–22h00 | POSTER SESSION, Salon WESTMOUNT<br>RECEPTION, Salon LACHINE<br>BANQUET, Salon WESTMOUNT<br>Invited Lecture: **"Commercial Development of NORYL Resins"**, A.S. Hay (GEC, USA) | | |
| April 4 | 08h30–17h35 | **"New Technologies; Processing of High Performance Materials"** | **"Modeling and Control of Molding Processes"** | **"Polyblends – '86"** |

# TECHNICAL PROGRAM

**April 1,**
17h00-20h00 Registration
19h00-21h00 Reception (Wine and Cheese)

**April 2,**
08h00 Registration
09h00 Opening Ceremonies
09h10 Plenary Lecture: R.S. Porter (U. Mass., USA)
**"PROCESSING FOR PROPERTIES".**
10h00 PAUSE

| | **RUBBER PROCESSING,**<br>Session co-chairmen: K. Min and J.F. Stevenson. | **POLYMER PROCESSING RHEOLOGY,**<br>Co-Chairmen: P.J. Carreau, J.-F. Agassant. | **FIBER SPINNING AND DRAWING OPERATIONS,**<br>Session Co-Chairmen: J.E. Spruiell and A. Michel. |
|---|---|---|---|
| 10h30 | 5/1. **"Study on the Methods of Estimating Rubber Processability".**<br>H. Goto, Y. Fujinaga and I. Furuta, (Japan Syn. Rubber Co.) | 9/1. **"On-Line Rheometers and Process Control".**<br>J.M. Dealy (McGill U., Canada). | 8/1. **"Melt Spinnability of High Fluidity Polypropylene: Properties of the Fibres".**<br>A. Michel, C. Prost and G. Nemoz* (CNRS and *Inst. Textile, France). |
| 10h55 | 5/2. **"Questions Concerning Behavior of Carbon Black During Incorporation and Dispersion in Rubber".**<br>N. Nakajima (U. Akron, USA). | 9/2. **"The Influence of Elasticity on the Melt Processing and Properties of Polymers".**<br>J.M. Starita and C.L. Rohn (Rheometrics, USA). | 8/2. **"Steady Spinning of Viscoelastic Liquids".**<br>Z. Chen and A.C. Papanastasiou (U. Mich., USA). |
| 11h20 | 5/3. **"Flow Visualization of Compounding of Elastomers in an Internal Mixer".**<br>K. Min and J.L. White (U. Akron, USA). | 9/3. **"A New Automatic Computerized Extrudate Swell Apparatus".**<br>M.R. Kamal and M.K. Samara (McGill U., Canada). | 8/3. **"Maxwell Viscoelasticity in Dynamic Melt Spinning Model".**<br>S. Kase (Kyoto Inst. Technol., Japan). |
| 11h45 | 5/4. **"Extrusion of Rubber Compounds in Single Screw Extruders".**<br>R. Brzoskowski, K. Kubota, J.L. White, F.C. Weissert, N. Nakajima and K. Min (U. Akron, USA). | 9/4. **"Elastic Fracture of Polymeric Fluids".**<br>R. Chan, R.K. Gupta and T. Sridhar (SUNY, USA). | 8/4. **"Route to Chain-Extended Polymers".**<br>P.J. Lemstra, (Un. Eindhoven). |
| 12h10 | LUNCH | LUNCH | LUNCH |

| RUBBER PROCESSING,<br>Session co-chairmen: K. Min and J.F. Stevenson. | POLYMER PROCESSING RHEOLOGY,<br>Co-Chairmen: P.J. Carreau, J.-F. Agassant. | FIBER SPINNING AND DRAWING OPERATIONS,<br>Session Co-Chairmen: J.E. Spruiell and A. Michel. |
|---|---|---|
| **13h30** 5/5. "Experimental and Theoretical Approach of the Extrusion of Rubber Compounds with a Two-Stage Screw". B. Vergnes, N. Bennani and C. Guichard* (École des Mines and *LRCCP, France). | 9/5. "Rheology and Blown Film Fabrication with LLDPE". A.V. Ramamurthy (U. Carbide, USA). | 8/5. "A Continuous Drawing Process for Preparing a High Performance Polyethylene Fiber". T. Sakai, N. Okui, M. Takahiro and *T. Takahashi (*Showa Denko Co. and Tokyo Inst. Tech., Japan). |
| **13h55** 5/6. "Multidimensional Control of Extudate Dimensions with a Single Roller Die". J.F. Stevenson (GenCorp, USA). | 9/6. "Extensional Flow of Linear Low Density Polyethylenes". B. Schlund and L.A. Utracki (NRCC/IMRI, Canada). | 8/6. "The Characteristic Behavior of the Stretch-Orientation Zone During High-Speed PET Spinning". G. Wu, T. Kuan and B. Qian (China Textile U., China). |
| **14h20** 5/7. "CADGUM — A Rubber Injection Molding Simulation and Mold Design Program". W. Benfer and G. Menges (IKV, West Germany). | 9/7. "Comparison of the Rheology of Polymer Melts in Shear and Biaxial and Uniaxial Extensions". S.A. Khan, R.K. Prud'homme and R.G. Larson (AT&T, USA). | 8/7. "Polybutylene Terephthalate in Extended Crystal Conformation". M.H.G. Deeg (Celanese, USA). |
| **14h45** 5/8. "Recent Studies on Degradation Mechanism of Rubber Vulcanizates by Chemorheology". K. Murakami (Tohoku U., Japan). | 9/8. "Evaluation of the Viscoelastic Temperature and Pressure Shift Factor over the Full Range of Shear Rates". H. Kühnle (IKT, Germany). | 8/8. "On-Line Studies and Computer Simulation of the Melt Spinning of Nylon-66 Filaments". K.F. Zieminski and J.E. Spruiell (U. Tennessee, USA). |
| **15h10** PAUSE | PAUSE | PAUSE |
| POLYMERIZATION PROCESSES: MODELING AND CONTROL,<br>Chairman: A.E. Hamielec. | POLYMER PROCESSING RHEOLOGY<br>Continued. | STRUCTURE DEVELOPMENT IN PROCESSING,<br>Session Co-Chairmen: J.L. White and Z. Tadmor. |
| **15h30** 1/1. "Diffusion in Polymerizing Media". M. Tirrell (U. Minn., USA). | 9/9. "Shear Refining and Entanglement Modification in Commodity Polymers". A. Rudin* and H.P. Schreiber (École Polytechnique and *U. Waterloo, Canada). | 7/1. "Solutions Spinning of UHMWPE". A.J. Pennings, G. ten Brinke, R.J. van der Hooft, A.R. Postema and W. Hoogsteen (U. Groningen, Netherlands). |
| **15h55** 1/2. "Modelling Free Radical Copolymerizations". A.E. Hamielec and J.F. MacGregor (McMaster U., Canada). | 9/10. "Entanglement Density in Polymers". A. Ajji, P.J. Carreau, A. Rudin* and H.P. Schreiber (École Polytechnique and *U. Waterloo, Canada). | 7/2. "The Mechanism and Characteristics of Dry-Jet Wet-Spinning of Acrylic Fibers". B. Qian, D. Pan and Z. Wu (China Textile U.). |
| **16h20** 1/3. "The Computer Modeling of Multi-Component, Semi-Batch Emulsion Copolymerization". S. Omi, K. Kushibiki and M. Iso (Tokyo U. Agric. Technol., Japan). | 9/11. "Rheological Properties of Thermotropic Liquid Crystalline Copolyesters". T. Masuda, M. Takahashi and K. Fujiwara* (Kyoto U. and *Idemitsu Petrochem. Co. Japan). | 7/3. "Flow Visualization, Flow Induced Crystallization and High Speed Spinning of Poly(ethylene terephthalate) Fibers". J.A. Cuculo and D.W. Ihm (N. Carolina U., USA). |
| **16h45** 1/4. "Interactions of Mixing, Diffusion and Reaction in a Fast Step Growth Polymerization". Y.M. Lee and L.J. Lee (Ohio U., USA). | 9/12. "Effect of Plasticizer Type on Viscoelastic Behavior of PVC Plastisol During Gelation and Fusion". N. Nakajima and M.R. Sadeghi (U. Akron, USA). | 7/4. "Orientation and Residual Stress Development in the Melt Spinning of Thick Filaments". H.-J. Kang and J.L. White (U. Akron, USA). |
| **17h10** 1/5. "Reaction Engineering for Step Growth Polymerization". R.L. Laurence (U. Mass., USA). | 9/13. "Ideal Elastic Liquids as Model Fluids in Polymer Processing Flows". D.V. Boger (U. Melbourne, Australia). | 7/5. "Fiber Orientation in Complex Flows". G.G. Lipscomb and M.M. Denn (Lawrence Berkeley Lab, USA). |
| **17h35** 1/6. "Control of Polymerization Reactors". J.F. MacGregor, A. Penlidis and A.E. Hamielec (McMaster U., Canada). | | |

**19h00-22h00** Beer Session:

## "What We Don't Know about Film Blowing";

Salon Westmount.

Chairman: J.M. Dealy.

Panelist: L. Dowd, G.A. Campbell and S.J. Kurtz.

| April 3 | REACTIVE PROCESSING,<br>Co-Chairmen: J.T. Lindt and M. Lambla. | MODELING AND CONTROL OF EXTRUSION AND RELATED OPERATIONS,<br>Co-Chairmen: J. Vlachopoulos and H.-G. Fritz. | STRUCTURE DEVELOPMENT IN PROCESSING<br>Continued. |
|---|---|---|---|
| 08h30 | 2/1. "Fundamental Study of Poly(unsaturated ester) Structure and their Thickening".<br>E. Marechal, M. Brigodiot, A. Fradet (Lab. Synth. Macromol., France). | 4/1. "Design of Various Extrusion Dies with FD and FE Techniques on the Base of a Viscosity Data Bank".<br>H. Kühnle (U. Stuttgart, Germany). | 7/6. "Structure Development in Melt Spinning and Injection Molding Aromatic Polycondensates".<br>S.S. Song, C.M. Hsiung, M. Çakmak and J.L. White (U. Akron, USA). |
| 08h55 | 2/2. "Dynamic Dielectrometry Analysis for Reactive Processing".<br>R. Ramanathan and D.O. Harper (U. Louisville, USA). | 4/2. "Computation of Molten Polymer Flows in Extrusion Dies".<br>J.-F. Agassant and B. Vergnes (ESN des Mines, France). | 7/7. "Investigation of a Mandrel Process to Control the Properties of Poly(p-phenylene terephthalamide) Films".<br>J. Flood and J.F. Fellers (U. Tennessee, USA). |
| 09h20 | 2/3. "Rheokinetics Measurements in a New Rheocalorimeter".<br>J.A. Biesenberger and D. Rosendale (Stevens I.T., USA). | 4/3. "Advances in Computational Methods for Rheologically Complex Flows with Free Surfaces".<br>R. Keunings (U. California, USA). | 7/8. "Stretching Instabilities in Thin Films of Polyethylene Therephthalate".<br>C. G'Sell and A. Marquez-Lucero (E. des Mines, France). |
| 09h45 | 2/4. "Processing Polyurethane-Polyester Interpenetrating Polymer Network (IPN)".<br>T.J. Hsu and L.J. Lee (U. Ohio, USA) | 4/4. "A Double-Node Technique for Finite Element Simulation or Stratified Multiphase Flows".<br>H. Mavridis, A.N. Hrymak and J. Vlachopoulos (McMaster U., Canada). | 7/9. "Scanning Electron Microscopy Studies of Polymer Melt Devolatilization".<br>Y. Talmon, R. Albalak, M. Rumack and Z. Tadmor (Technion, Israel). |
| 10h10 | PAUSE | PAUSE | PAUSE |
| 10h30 | 2/5. "Chemical Modification of Polyvinychloride and Polypropylene in Processing Operations".<br>A. Michel, V. Verney and M. Gonnu (CNRS, France). | 4/5. "Numerical Simulation of Coextrusion".<br>J. Dheur and M.J. Crochet (U. Cath. de Louvain, Belgium). | 7/10. "Structure Formation in Hydroxypropyl Cellulose".<br>T. Kyu and P. Mukherjee (U. Akron, USA). |
| 10h55 | 2/6. "Reactive Olefinic Copolymers: New Developments and Applications".<br>L. Guerdoux, M. Hert and J. Lebez (CdF Chimie, France). | 4/6. "A Finite Element Simulation of Non-Isothermal Polymer Melt Flows".<br>P.A. Tanguy and A. Fortin* (U. Laval and *École Polytechnique, Canada). | 7/11. Structure Development in Polymer Processing".<br>M. Horio (Kyoto U., Japan). |
| 11h20 | 2/7. "Transesterification Reactions in Molten Polymers".<br>M. Lambla, J. Druz and *A. Bouilloux (EAHP and *ATOCHEM, France). | 4/7. "Fluid Flow and Heat Transfer in Wire Coating".<br>E. Mitsoulis (U. Ottawa, Canada). | 7/12. "A Tensor Description to Characterize and Predict Fiber Orientation in Short Fiber Composites".<br>S.G. Advani and C.L. Tucker III (U. Illinois, USA). |
| 11h45 | 2/8. "Computer Controlled Multiple Stream Reinforced RIM".<br>P.D. Coates, A.F. Johnson, P.D. Armitage, J. Hynd and J. Leadbitter (U. Bradford, England). | 4/8. "Real Time Process Control by On-Line Capillary Rheometry".<br>A. Göttfert (Göttfert Werks, Germany). | 7/13. "Mechanism of Cooling Stresses Build-up in Injection Molding of Thermoplastic Polymers".<br>G. Titomanlio*, M.R. Kamal and V. Brucato* (*U. de Palermo, Italy and McGill U., Canada). |
| 12h10 | LUNCH | LUNCH | LUNCH |

4

| April 3 | REACTIVE PROCESSING,<br>Co-Chairmen: J.T. Lindt and M. Lambla. | MODELING AND CONTROL OF EXTRUSION AND<br>RELATED OPERATIONS,<br>Co-Chairmen: J. Vlachopoulos and H.-G. Fritz. | COMPOSITES<br>Session Co-Chairmen: L.A. Goettler and J.L. Throne. |
|---|---|---|---|
| 13h30 | 2/9. "Fountain Flow Visualization Experiments".<br>J.W. Blake, I. Manas-Zloczower and C.W. Macosko (U. Minn., USA). | 4/9. "Modeling of a Production Twin-Screw Extrusion Process (Counter-Rotating, Non-Intermeshing)".<br>H. Tolliver and D.O. Harper* (3M and *U. Louisville, USA). | 11/1. "Present and Future Trends in Polymeric Composites".<br>T. Vu Khanh and L.A. Utracki (NRCC/IMRI, Canada) |
| 13h55 | 2/10. "Fast Molecular Kinetic Study of RIM Reactions by FT-IR: Simultaneous Vinyl Polymerization and Polyurethane Formation".<br>H. Ishida and C. Scott (CWRU, USA). | 4/10. "Analysis of Adiabatic Devolatilization of Moderately Concentrated Polymer Solutions".<br>R. Chella and J.T. Lindt (U. Pittsburgh, USA). | 11/2. "Compounding of Flake-Filled Polypropylene".<br>B. Rémillard, B. Fisa and B. Favis (NRCC/IMRI, Canada) |
| 14h20 | 2/11. "Polymerization of Polyamide-6 in a Twin Screw Extruder: Process Analysis, Aspects of Industrial Use".<br>G. Menges and T. Bartilla (IKV, Germany). | 4/11. "Improvements in Forced — Feeding Single Screw Extrusion".<br>E. Gruenschloss (IKT, Germany). | 11/3. "Orientation-Rheology-Processing Interactions in the Injection Molding of Fiber Reinforced Thermoplastics".<br>M.R. Kamal, T. Mutel and P. Singh (McGill U., Canada) |
| 14h45 | 2/12. "From Caprolactam to Nylon-6: Reactive Processing in a Non-Intermeshing Twin Screw Extruder".<br>J.C. Golba Jr., B.C. Johnson and R.J. Nichols* (GE and *Welding Eng., USA). | 4/12. "Flow and Mixing Phenomena in Co-Rotating Twin-Screw Extruders".<br>P.R. Hornsby (Brunel U., UK) | 11/4. "Continuous Processsing of Composite Materials."<br>A.C. Papanastasiou, A.N. Alexandrou and G. Georgiou (U. Mich., USA) |
| 15h10 | PAUSE | PAUSE | PAUSE |
| 15h30 | 2/13. "Optimization and Automation of a Polymer Compounding Process for the Controlled Peroxide Degradation of PP".<br>H.-G. Fritz (U. Stuttgart, Germany). | 4/13. "Mechanism of Fluoroelastomer Processing aid in Extrusion of LLDPE".<br>S. Nam (3M Co., USA). | 11/5. "A Model for a Three-Layer Flow of Short Fiber-Containing Melts in Expanding Pipe Dies".<br>S.R. Doshi, J.M. Dealy and J.M. Charrier (McGill U., Canada) |
| 15h45 | 2/14. "Reactive Extrusion: Polymerization in Recirculating Flow Fields".<br>D.H. Sebastian and C. Du (Stevens I.T. USA). | 4/14. "Blown Film Modeling — Freeze Line to Frost Line".<br>G.A. Campbell (Clarkson U., USA). | 11/6. "The Fiber Content Distribution of Compression Molded Long Fiber-Reinforced Thermoplastic Products".<br>H. Hojo, E.-G. Kim and K. Tamakawa (Tohoku U., Japan) |
| 16h20 | 2/15. "A Sensitivity Analysis of the Plasticating Extrusion of Reactive Systems".<br>M.E. Ryan and H.C. Hiner (SUNY, USA). | 4/15. "Heat Transfer to Polymer Melt Flow in Profile Extrusion".<br>B. Yang and L.J. Lee (Ohio State U., USA). | 11/7 "The Modeling of Mold Filling in Resin Transfer Molding".<br>R. Gauvin and M. Chibani (École Polytechnique, Canada) |
| 16h45 | 2/16. "Interactions between Reaction Kinetics and Devolatilization in Adiabatic Reactive Processing".<br>J.T. Lindt and R. Chella (Pittsburgh U., USA). | 4/16. "Theoretical Analysis of Tubular Film Extrusion and its Application for HMW-HDPE".<br>T. Kanai (Idemitsu Petrochem., Japan). | 11/8 "Bonding Phenolic Plastic Parts to Fiberglass Reinforced Composite Structures Using an Epoxy Resin with Polyamide Curing Agent as a Primer".<br>H. Novak (McDonnell Douglas, USA) |

**April 3**
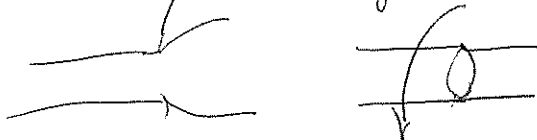16h00-18h00 **POSTER PAPERS:**
Session co-Chairmen: B. Favis and T. Vu Khanh.

P/1."Relation Between Composition, Processing and Mechanical Properties of Rim-Nylon Block Copolymers". J.L.M. van der Loos and A.A. van Geenen (DSM, Netherlands).

P/2. "Elements of Microrheological Modelling". R.J.J. Jongschaap (Twente U., Netherlands).

P/3. "The Flow Behavior of Polyacrylate and Polymethacrylate Solutions". L. Wenduan, X. Changfu, Z. Jiehui, W. He and Xu Xi (U. Sci. & Tech., China).

P/4. "A Critical Evaluation of Integral Constitutive Equations in Simple Flows". R.D. Wesson, A.C. Papanastasiou and J.O. Wilkes (U. Mich., USA).

P/5. "On the Use of End Effects for Polymer Melt Characterization". L. Choplin and P.J. Carreau* (U. Laval and *École Polytechnique, Canada).

P/6. "Molecular Orientation in Combined Extensional and Shear Flows". J.P. Santerre and J.J. Picot (U. New Brunswick, Canada).

P/7. "Determination of Rheological Parameters in Melt Spinning PET Based on Velocity and Temperature Profiles and Freeze Point Tension Data". H.H. George and M.H.G. Deeg* (Westfield Consult. Group and *Celanese, USA).

P/8. "Effects of Rubber Particle Morphology on Yield and Fracture in High Impact Polystyrene". C.B. Bucknall and I.K. Partridge (Cranfield Inst. Technol., UK).

P/9. "X-Ray Study of Polyethylene During Drawing". D.T. Grubb (Cornell U., USA).

P/10. "Space-Time Distribution in Filling a Mold". I. Manas-Zloczower, J.W. Blake and C.W. Macosko (U. Minn., USA).

P/11. "A Study of Poly(vinyl chloride) Blends with Chlorinated Polyethylene and Acrylic Resin". Xu Xi, Z. Liwu and L. Huilin (Chengdu U., China).

P/12. "The Melt Rheology of Chloro-Polyether and Polyepichlorohydrin Blends". Lu Liming, Li Kebin and Li Shijing (East China Inst. Chem. Techn., China).

P/13. "High Performance Products From Gel Like Spherulites of Polyethylene". T. Ohta and F. Okada (Toyobo Co., Japan).

P/14. "Blends of PDMS/Segmented Polyurethanes". J.R. Dylewski and C.L. Beatty (U. Florida, USA).

P/15. "Effect of Stoichiometric Ratio on Epoxy Curing Kinetics via Dynamic Mechanical Spectroscopy". H. Novak*, W.S. Williams and C.L. Beatty (*McDonnell Douglas and U. Florida, USA).

P/16. "Blending of Thermoplastics and Elastomers in an Internal Mixer: Flow Visualization, Influence of Rotor Design and Mixing Conditions on Phase Morphology". K. Min (U. Akron, USA).

P/18. "Theoretical and Experimental Study of the Polymer Plasticization in the Reciprocating Screw of an Injection-Molding Machine". E. Wey, B. Vergnes, J.F. Agassant (École des Mines, France).

P/19. "PET Fiber Obtained from Pseudo-Gel States". M. Ito and K. Tanaka (Science U., Japan).

P/20. "Devolatilization of a Residual Polystyrene/Water Mixture in a Twin Screw Extruder". A.M. Catani and W. Hofer* (NRCC/IMRI, Canada and *Werner Pfleiderer, USA).

P/21. "An Experimental and Numerical Investigation of Peroxide Initiated Degradation of Polypropylene in a Single Screw Extruder". C. Tzoganakis, J. Vlachopoulos and A.E. Hamielec (McMaster U., Canada).

P/22. "Modeling for Computer Integrated Systems in Polymer Processing". G. Salloum, A. Garcia-Rejon (NRCC/IMRI, Canada).

P/23. "The Effect of Processing on the Final Performance and Fine Structure of PET Fiber". H. Xuechao, Z. Yu, D. Zuomin, S. Huili and Q. Baojun (China Textile U., Japan).

P/24. "Lubrication Approximation for the Analysis of Viscoelastic Flow". B. Caswell (Brown U., USA).

P/25. "Compounding Industrial Polymers: Effects of the Mixer Type on Melt Rheology, Dispersion and Texture in Model Polyblend and Polyalloy". A.P. Plochocki, (PPI, U.S.A.), Z. Tadmor, (TECHNION, Israel), and P.S. Hope, (BP Chemicals, Scotland).

P/27. "Optimization of Rubber Extruders". A. Limber (IKV, West Germany).

P/28. "Styrene/Butyl Acrylate Copolymerization with layer morphology: kinetics and viscoelastic properties". L. Rios G., L.A. Lopez-Latorre and A. Garcia-Rejon G. (UNANM–Mexico).

P/29. "The Flow of Upper-Convected Maxwell Fluid in a Porous Tube." M.E. Kim-E, J.S. Brady⁺ and R.A. Brown⁻ (ATT and MIT*, USA)

P30. "Flocculation of Carbon Black in Field Rubber Compounds." M.N. Nguyen and G.G.A. Böhm (Firestone Akron, USA)

**April 3**

18h00-19h00    RECEPTION (Cash Bar)

19h00-22h00    BANQUET, STAGE SHOW, (Folkloric Dance), BUSINESS MEETING,
                      INVITED LECTURE:
                            "Commercial Development of NORYL Resins"
                                                by Dr. Allan S. Hay (GEC, USA).

| April 4 | NEW TECHNOLOGIES: PROCESSING OF HIGH PERFORMANCE MATERIALS, Session co-Chairmen: A.E. Zachariades and T. Kanamoto | MODELING AND CONTROL OF MOLDING PROCESSES, Co-Chairmen: M.R. Kamal and L.R. Schmidt. | "POLYBLENDS-'86 Co-Chairmen: D. Froelich and L.A. Utracki. |
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| 08h30 | 6/1. "Molecular Entanglement — Its Effects on Processing and Properties of Rigid Rod Molecular Composites". D.R. Wiff[1], W-F. Hwang[2] and T.E. Helminiak[3] ([1]GenCorp, [2]Dow Chem. and [3]AFWAL, USA). | 3/1. "Experimental and Theoretical Study of the Injection Molding of Thermoplastic Materials". J.-F. Agassant, H. Alles, S. Philipon and M. Vincent (E.N.S. des Mines, France). | 10/1. "Molecular Control of Interface in Polymer Blends". R. Fayt, R. Jérôme and Ph. Teyssié (U. Liege, Belgium) |
| 08h55 | 6/2. "Flow-Induced Orientation of a Thermotropic Liquid Crystalline Copolyester". K. Fujiwara*, M. Takahashi and T. Masuda (*Idemitsui Petrochem. Co. and Kyoto U., Japan). | 3/2. "Evaluation of the Effects of Various Assumptions in the Mathematical Modeling of Injection Mold Filling". M.R. Kamal, E. Chu and S. Goyal (McGill U., Canada). | 10/2. "Phase Diagrams of Polymer Blends at Various Pressures". S. Rostami (ICI, UK) |
| 09h20 | 6/3. "Process — Property Relationships of a Wholly Aromatic Copolyester Resin". J.J. Duska, F. Scardiglia and N.D. Field (Dartco Man., USA). | 3/3. "Simulation of Balancing Multi-Cavity Molds". H. Ghoneim (Rochester I.T. USA). | 10/3. "Surface Tension of Polymers Liquids". P.R. Couchman and K. VanNess (Rutgers U., USA) |
| 09h45 | 6/4. "Rheological Properties of Thermotropic Liquid Crystalline Aromatic Copolyesters". Z. Zhou, X. Wu and M. Wang (China Textile U., China). | 3/4. "Finite Element Analysis of Injection Mold Filling". H. Mavridis, A.N. Hrymak and J. Vlachopoulos (McMaster U., Canada). | 10/4. "Formation of Dispersed Phase in Incompatible Polymer Blends: Interfacial and Rheological Effects". Souheng Wu (DuPont, USA) |
| 10h10 | PAUSE | PAUSE | PAUSE |
| 10h30 | 6/5. "Structure Formation of Liquid Crystalline Polymers After Cessation of Steady Flow". T. Asada (Kyoto U., Japan). | 3/5. "The Kinematics of Fountain Flow in Injection Molding". D.J. Coyle (GE, USA). | 10/5. "Specific Intermolecular Interactions in Fluorinated Polymer/Additives Systems". N. Del Fanti+, A. D'Alessio*, L. Baini+, P. Vergamini*, M. Pianca+, G. Moggi+, and E. Benedetti* (+Montefluous, C.R.S., Milano and *U. of Pisa, Italy). |
| 10h55 | 6/6. "Processing of Virgin Ultrahigh Molecular Weight Polymers — An Alternative Route to High Performance Materials". P. Smith (DuPont, USA). | 3/6. "Modeling of the Packing Stage Injection Molding of Thermoplastics". R. Deterre, D. Huillier, C. Lenfant and J. Terrisse (E.A.H.P., France). | 10/6. "Phase Transitions During Shear Flow of Two Phase Polymer Blends, I. SAN/PMMA." J. Lyngaae-Jorgensen and K. Sondergaard (Techn. U., Denmark) |
| 11h20 | 6/7. "Fabrication of High Modulus Films by Solid State Rolling". D.M. Bigg, E.G. Smith, M.M. Epstein and R.J. Fiorentino (Battelle Columbus, USA). | 3/7. "Pressure and Temperature Distributions in the Cavity during Injection Mold Filling". Y. Oyanagi and K. Kubota (Kogakuin U., Japan). | 10/7. "Dynamic Mechanical Properties of Polystyrene/Poly(vinymethylether) Blends". D. Froelich and R. Muller (EAHP, France) |
| 11h45 | 6/8. "Equibiaxial, Hydrostatic Deformation of Isotactic Polypropylene, The Solid State: A Rigid-Plastic Model". R.F. Saraf and R.S. Porter (U. Mass., USA). | 3/8. "Adaptive Meshes for the Numerical Simulation of Injection Molding". A. Couniot, M.J. Crochet (U. Cath. de Louvain, Belgium). | 10/8. "Melting and Crystallization Behaviors of a Co-crystallized Blend Based on Propylene Copolymers". Chii-Kai Shih (DuPont, USA) |
| 12h10 | LUNCH | LUNCH | LUNCH |

| April 4 | NEW TECHNOLOGIES: PROCESSING OF HIGH PERFORMANCE MATERIALS, Session co-Chairmen: A.E. Zachariades and T. Kanamoto | MODELING AND CONTROL OF MOLDING PROCESSES, Co-Chairmen: M.R. Kamal and L.R. Schmidt. | "POLYBLENDS-'86" Co-Chairmen: D. Froelich and L.A. Utracki. |
|---|---|---|---|
| 13h30 | 6/9. "Manufacture of High Modulus Polypropylene Sheet by Roll-Drawing". P. Burke, G.C. Weatherly and R.T. Woodhams (U. Toronto, Canada). | 3/9. "Studies in Dynamics and Control of the Thermoplastics Injection Molding". M.R. Kamal, W.I. Patterson and D. Abu Fara (McGill U., Canada). | 10/9. "Interrelationship between the Crystalli: tion Behavior, Injection Molding Conditions a: Morphology of PET/PMMA". V.M. Nadkarni and J.P. Jog (Natl. Chem. Lab., Ind |
| 13h55 | 6/10. "Rolltrusion: Double Orientation Processing and Morphology—Property Relationships for Plastics". M.J. Shankernarayanan and J.H. Magill (U. Pittsburgh, USA). | 3/10. "Birefringence Control in Polycarbonate Injection Molding". S.J. Willey and C.M. Karas (GE, USA). | 10/10. "Some Experiments with Polymer Blend G. Pastuska, W. Lützow and R. Riecke (B.A.M., Germa |
| 14h20 | 6/11. "Preparation of Highly Oriented Polymers by Microwave Heat-Drawing". K. Nakagawa and M. Amano (NTT Ibaraki, Japan). | 3/11. "Numerical Simulation of Compression Molding of Thin Parts in 3-D Space". V.W. Wang and K.K. Wang (Cornell U., USA). | 10/11. "In-Situ Composites: Blends of Isotro and Thermotropic Liquids Crystalline Polymer: G. Kiss (Celanese, USA) |
| 14h45 | 6/12. "Super-Drawing of an Ultrahigh Molecular Weight Polyethylene Single Crystal Morphology Using Solid-State Extrusion". T. Kanamoto, K. Tanaka, M. Takeda and R.S. Porter* (Sci. U., Tokyo, Japan and *U. Mass., USA). | 3/12. "A Boundary Element Simulation of Compression Mold Filling". T.A. Osswald and C.L. Tucker III (U. Illinois, USA). | 10/12. "Structure-Properties Studies of Polym Blends Containing Liquid Crystal Polyesters' M. Pracella, D. Dainelli, M. Paci, G. Galli and E. Chiel (U. de Pisa, Italy) |
| 15h10 | PAUSE | PAUSE | PAUSE |
| 15h30 | 6/13. "Ultradrawn Polyethylene: Determination of Molecular Dynamics". S.K. Roy and R. St. J. Manley (PAPRI and McGill U., Canada) and T. Kyu (Akron U., USA). | 3/13. "Numerical Simulation of Blow Molding Process". A. Cohen (Dow Chem., USA). | 10/13 "Processing of Self-Reinforced Polym Composites". A.I. Isayev and M.J. Modic (U. Akron, USA) |
| 15h55 | 6/14. "New Concepts for Engineering the Mechanical Properties of Polymers". A.E. Zachariades and B. Chung (IBM, USA). | 3/14. "A New Look at Swell and Sag Effects in Parison Formation". W.H. Talbott, D.B. Japikse and W.K. Paul (GE, USA). | 10/14. "Deformation Studies on a Poly(meth methacrylate)/Poly(ethylene oxide) Blend: Molecular Characterization". J.M.R. Lefebvre, R.S. Porter and G.D. Wignall*, (U. Mas and *Oak Ridge National Lab., USA) |
| 16h20 | 6/15. "Mechanical Properties of a Polyurethane Ionomer". W.S. Williams and C.L. Beatty (U. Florida, USA). | 3/15. "Process Optimization in Stretch Blow-Molding". G. Menges and U. Hüsgen (IKV, Germany). | 10/15. "A Study on Poly(vinyl chloride) Blen with Chlorinated Polyethylene and Polyethylene Xu Xi, M. Xiande and C. Kequiang (Polym. Res. Ins CUST, China) |
| 16h45 | 6/16. "The Transport of Water in Poly Aryl Ether Ether Ketone". M.A. Grayson and C.J. Wolf. (McDonnell Douglas, USA). | 3/16. "Use of Rheological Parameters to Indicate the Blow Molding Characteristics of Olefinic Thermoplastic Elastomers". L.A. Goettler and Y. Saito* (Monsanto, USA and *Mitsuibishi-Monsanto, Japan). | 10/16. "Blends of Polycarboante and Poly(he: amethylene sebacate) I. Physical Properties." K.S. Shih and C.L. Beatty (U. Florida, USA) |
| 17h10 | 6/17. "A Novel Stress-Induced Nylon Morphology for Textile Yarns". J.H. Southern, R.W. Miller and W.J. Nunning, (Monsanto, Florida, USA). | 3/17. "General Consequences of Glass-Transition Phenomena in Polymer Fabrication Processes". J. Greener, J.J. Tribone, J.M. O'Reilly (E. Kodak, USA). | 10/17. "Extensive Mixing in Corotating Di: Processors". B. David, Z. Tadmor (Technion, Israel). |

6/14 If you opin die - no die swell very smooth surface

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# PROCESSING FOR PROPERTIES*
by
## PROFESSOR ROGER S. PORTER
Polymer Science & Engineering Department
University of Massachusetts
Amherst, Massachusetts 01003

The traditional modes for polymer processing have involved the heating of polymer pellets to achieve a melt, followed by shaping induced by injection or extrusion, with subsequent cooling to obtain the polymer product. Indeed, this is the very meaning of plastic. These traditional steps for the processing of polymers have been dominated by the viscous (conversion of mechanical energy to heat) component of the pronounced polymer characteristics of viscoelasticity. The contemporary polymer processor can find great advantage in utilizing also the elastic component, i.e., the development of chain orientation and extension, for the achievement of enhanced properties in polymer products. Formerly only in the development of polymeric fibers has this concept been used to generate polymer morphologies that are markedly directionally dependent. Even in the fiber field, dramatic improvements have been made in recent years with the goal of pursuing ultimate polymer properties. By such uniaxial processes, recent studies have approached the goal of making the strongest possible polymers by two diverse ways: (1) by chemically constructing polymers with rigid and linear backbones and (2) by processing conventional flexible chain polymers in ways that result in a transformation of the initial structure and properties to produce maximum anisotropy. The chemical construction of rigid macromolecules has been approached by syntheses of trans-aromatic rings in the polymer backbone. The first generation of these rigid and rodlike polymer molecules were processable only in the solution (lyotropic liquid crystal) state. Examples have been the Monsanto X-500 experimental fiber and the commercial DuPont aromatic polyamide (Aramid) Kevlars (29 and 49). The second generation of rodlike polymers now starting to appear commercially also involve trans-aromatic structures but with connecting groups such as ester and aliphatic spacers of flexible composition to allow processing in the "melt" nematic liquid crystal state. Such compositions are presently available from Tennessee-Eastman, Celanese Corporation and from Darco.

Conventional flexible chain polymers have in recent years been converted to highly oriented and chain-extended conformations with uniaxial properties of markedly increased tensile properties. These polymer processing techniques for ultradraw have been achieved from dilute flowing solutions, or from a gel state, or by extruding a supercooled melt or by solid-state extrusion and by other techniques for drawing below the polymer melting point under controlled conditions. These new experimental and the first commercial drawing processes are being developed by academic and industrial researchers in Europe, North America and in Japan. As properly touted by Allied in the U.S., their uniaxial geldrawn high molecular weight and high density polyethylene offers superior mechanical/weight properties in such diverse applications as rope, sail cloth, and ballistics protection. Moreover, in our laboratories and in others, polyethylenes are being prepared in experimental amounts at yet higher levels of uniaxial properties. Dr. Kanamoto of the Science University of Tokyo and I have shown that single crystal aggregates of ultra-high molecular weight polyethylene and of polypropylene, grown from dilute solutions, exhibit a dramatically high extensibility compared to melt-crystallized forms. Mats of such solution-grown crystals for these two polymers have been drawn to ratios of over 250 for polyethylene and to 66 for polypropylene. Such super-drawn films exhibit extremes of properties including a tensile modulus of up to 220 GPa for polyethylene and at least 33 GPa for polypropylene. These values approach the uncertain theoretical maximum tensile moduli reported for the perfect crystals for each of these two polymers. The first draw step is always solid-state extrusion with the compressive characteristics of this process being of major importance. After this first stage of deformation, alternate methods may be used to achieve the ultradraw.

With such major enhancements of properties for unaxial deformation, challenge arise to achieve planar morphologies of flexible chain polymers. A compressive draw process for uni- and for biaxial orientation is feasible using the techniques of calendaring. Katesuna in Japan, for example, has rolled polyethylene to 40 GPa. Several thermoplastics are being compared in our laboratory on biaxial draw by cross-rolling with properties developed by other biaxial processes such as by tenter framing, forging, and by the Bethlehem Steel mandrel expansion technique. Rodlike polymers may be also biaxially oriented as in the mandrel expansion experiments of James White on Kevlar compositions. The imaginative programs at Wright-Patterson Air Force Base have produced biaxial orientation of rodlike molecules, for principally the compositions of poly(p-phenylenebenzobisthiazole) and related structures, as part of their program on Molecular Composites.

Challenges are evident in the processing of polymers for properties. We thus confront the irony that improved mechanical properties by draw means further resistance to draw deformation. The maximum efficiency and potential for draw of thermoplastics without crystals is in the region closely above, about 25°C, the glass transition temperature. For semicrystalline polymers, the processing temperature range is below the equilibrium melting point. The process thus counts on the ductility of polymer crystals and the survival of chains on draw. For polymers of low polarity, selected deformation conditions appear to accomplish these purposes. For thermoplastics with stronger interchain interactions, innovations are required. For amorphous polymers the concept of Chan Chung is of interest for reversibly (with crystallizable compounds) plasticizing polymer in the processing temperature range. In a patent issued to UMass, ammonia has been shown to reversibly plasticize the amorphous regions of the aliphatic nylons for increasing the ease of drawing. Recently, we have shown that even the crystal lattice of certain nylons may be reversibly disrupted by the intraposition of iodine to aid the draw process.

Further challenges arise in polymer processing in regard to the utilization of the directional properties of both fiber of high modulus polymer. This is facilitated by the development of composites, with major processing goals yet unresolved. This subject includes the new field of polymer prepreg technology. Major advances will likely result for high modulus organic fiber reinforced by thermoplastics. Cautions in prepreg processing include the mismatch of mechanical and thermal properties, the sensitivity of the high modulus polymers for compressive buckling, and the need for design, control and evaluation of the interphase between matrix and fiber.

The potentials for polymer *processing for properties* remain unbounded, with challenges including the develoment of three-dimensional molecular reinforcement comparable to the triaxial weaving of macro-organic fibers. Another opportunity would come through the use of reinforcing fibers with stress-strain characteristics which would allow (1) the prepreg to be draped in appropriate shapes and (2) to provide draw reinforcement in just the high stress regions imposed on the fabricated composite.

Professor Roger, Stephen PORTER was born in Windom, Minn. June 2, 1928. Education: UCLA BS (Phys. Chem.) 1950, U. Washington PhD (Chem.) 1956. Positions: Chevron Res. Co. 1955-66, U. Mass. 1966 — present (professor, department head, spec. res. assist. for president, co-director NSF-Mat. Res. Lab.). Visiting professor and/or lecturer: UCLA, U. So. Miss., Royal Inst. Technol (Stockholm), U. London, Fed. U. Rio de Janeiro, U. Utah, Sci. U. Tokyo. Awards: SPE — Polyolefin Research (1977), ACS — Org. Coat. Plast. (1979), SPE — International Educ. (1980), PIA — Meritorious Service (1980), Okayama U. — Medal (1980), SPE — Intl. Res. Prize in Sci. Eng. (1981), ATAS — Mattler Prize (1983), U. Mass. — Medal (1983), Soc. Rheol. — Bingham Medal (1985). Editor: Polymer Eng. Sci. and Polym. Compos.

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# THE COMMERCIAL DEVELOPMENT OF NORYL® RESINS*
by
## ALLAN S. HAY
General Electric Co.
Corporate Research & Development
P.O. Box 8, Schenectady, N.Y., 12301

High performance polymeric materials with excellent thermal, oxidative and insulation properties were key to the development and growth of the electrical industry. This effort can be traced back to the early part of the century and from this effort over the next several decades at the General Electric Company, new wire enamels, varnishes and paints were developed.

In the fifties polycarbonates were discovered during a search for high temperature wire enamels. Oxidative polymerization was discovered a little later and, although several new families of polymers have been synthesized, commercialization has been limited to one member of one family, the polyphenylene ethers. The discovery and commercial development of the polymer from 2,6-dimethylphenol, PPO® resin, and its blends with polystyrene, NORYL resins, are the principal subjects of this lecture.



2,6-DIMETHYLPHENOL          PPO^R
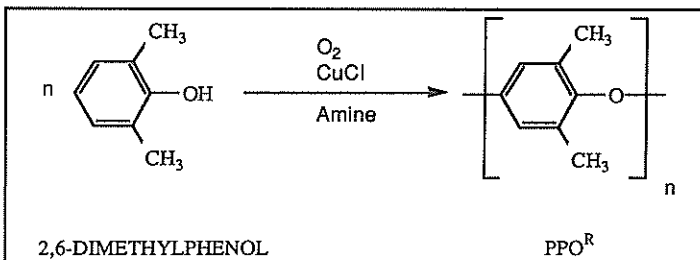
Dr. Allan Stuart HAY was born in Edmonton, Alberta, July 23, 1929. Education: U. Alberta BSc (1950), MSc (1952), U. Illinois PhD (Org. Chem. 1955). Positions: U. Alberta 1950-68, General Electric Co. 1969 — present (Mgr. Chem. Lab. Res. and Dev. Center), U. Mass. 1975 — present (Adj. Prof.). Awards: SPE — Intl. Gold Medal (1975).

# ABSTRACTS

## SYMPOSIUM No. 1:  POLYMERIZATION PROCESSES: MODELING AND CONTROL
### (CHAIRMAN:  A.E. HAMIELEC)

15h30    (1/1)    DIFFUSION IN POLYMERIZING MEDIA, M. Tirrell, Department of Chemical Engineering and Materials Science, University of Minnesota, Minneapolis, MN 55455

Diffusion of monomers and radicals is a strong influence in several phases of polymerization reaction rates.  As theoretical understanding of diffusion processes in polymers has advanced substantially in the last several years, so too, has some of this new understanding been incorporated into new, more physically-based models of polymerization reaction rates.  This course has been pursued about as far as it can be for the moment until our knowledge of the molecular diffusion coefficients increases.  In particular, the dependence of the diffusion coefficients of monomers and radicals on the concentration of polymer in the medium is not definitively known.  Our recent efforts in this vein have been directed toward experimental measurement of diffusion coefficients of small molecules and polymers in concentrated, entangled polymeric media via two new optical techniques: isorefractive dynamic light scattering and holographic relaxation scattering.  Recent results will be discussed.

15h55        (1/2)    MODELLING FREE RADICAL COPOLYMERIZATIONS,  A.E. Hamielec and J.F. MacGregor,  McMaster Institute for Polymer Production Technology, Department of Chemical Engineering, McMaster University, Hamilton, Ontario, Canada, L8S 4L7.

A methodology for the effective modelling of multicomponent free-radical polymerizations for batch, semi-batch and continuous stirred tank reactors is described.  The models account for diffusion-controlled termination and propagation.  Polymer radical reactions which lead to long chain branching and gel formation (reaction with terminal and internal double bonds and transfer to polymer) complicate the analysis considerably.  Approximate methods which are used to account for these branching reactions in molecular weight development are discussed.

16h20    (1/3)    THE COMPUTER MODELING OF MULTI-COMPONENT, SEMI-BATCH EMULSION COPOLYMERIZATION
Shinzo Omi, Koji Kushibiki and Mamoru Iso, Dept. of Chemical Engineering, Tokyo University of Agriculture and Technology, Koganei, Tokyo 184, Japan.

A computer modeling concept developed to deal with multi-component emulsion copolymerization systems was organized as a package of the simulator called NSBEC (n-component, semi-batch emulsion copolymerization system).  NSBEC is capable to carry out any kind  of hypothetical operations involving numbers of monomers with various modes of ingredient feed.  Time dependent variables such as polymer yield, average molecular weight and composition of copolymer can be estimated as well as more microscopic conformations of copolymer such as average sequence lengths of monomers and most probable sequence of copolymer chain.  Demonstrations of the performance of NSBEC and experimental supports of the theory will be presented.  Particular emphasis will be put on the newly acquired data of Acrylonitrile - Vinyliden Chloride system.  Probable control of copolymer composition adopting the semi-batch operation will be clearly understood by this model. The authors expect experimental loads will be reduced a great deal by the cooperation of this simulator.

16h45 (1/4)    INTERACTIONS OF MIXING, DIFFUSION AND REACTION IN A FAST STEP GROWTH POLYMERIZATION, Y.M. Lee and L.J. Lee, Department of Chemical Engineering, The Ohio State University, Columbus, Ohio 43210, USA.

A mathematical model using a slab configuration is used to simulate the interactions of mixing, diffusion and chemical reaction in a fast urethane polymerization. Three dimensionless times are proposed to elucidate these interactions during the reaction. Experimentally, we try to extract the micro-scale information needed for the constitutive equations from several experiments. Kinetic information is determined by conducting premixed reactions in a differential scanning calorimeter (DSC) and a Fourier transform infrared spectrometer (FTIR). The viscosity measurements are carried out in a Haake viscometer and the diffusion effect is estimated by conducting an interfacial polymerization in DSC and FTIR. The results are applied to a RIM type of reactions.

17h10    (1/5)    REACTION ENGINEERING FOR STEP GROWTH POLYMERIZATION - A REVIEW, Robert L. Laurence, Department of Chemical Engineering, University of Massachusetts, Amherst, MA 01003, U.S.A.

The application of reaction engineering tools in polymerizing systems has been greatest in chain growth polymerization processes. That chain growth systems exhibit pathological phenomena at modest conversions, e.g. gel effect, thermal runaway, high viscosity, has prompted considerable research. Step growth polymerization poses its own set of interesting and important problems to the reactor engineer. In this paper is presented a review of these problems and some solutions.

17h35    (1/6)    CONTROL OF POLYMERIZATION REACTORS,    J.F. MacGregor, A.Penlidis, A.E. Hamielec,  McMaster Institute for Polymer Production Technology, Department of Chemical Engineering, McMaster University, Hamilton, Ontario, Canada,  L8S 4L7.

The demand for polymers and polymer latexes having special properties and improved performance has led to a rapid increase in industrial and academic interest in advanced computer modelling and control of polymer reactors. The use of empirical or mechanistic dynamic models for reactor design, for the development of optimal start-up and operating policies, for on-line polymer property estimation, for guiding sensor development and selection, and for the use in designing control algorithms will be discussed and illustrated with applications. The effect of stochastic disturbances such as monomer or water soluble impurities will be further highlighted.

# SYMPOSIUM No. 2:  REACTIVE PROCESSING
## (CHAIRMAN:  J.T. LINDT)

08h30  (2/1)  FUNDAMENTAL STUDY OF POLY(UNSATURED ESTER) STRUCTURE
AND OF THEIR THICKENING
MARECHAL Ernest, BRIGODIOT Maryvonne, FRADET Alain
Laboratoire de Synthèse Macromoléculaire
12, rue Cuvier - 75252 PARIS CEDEX

The structure of unsaturated polyesters is characterized by different techniques : various chromatographies,1H and 13 C NMR, bidimensional NMR. It is shown that the expected monomer units can be deeply altered by isomerisation of both acid and alcohol functions and by addition of hydroxy groups to the double bond which leads to branching. Short and long branches are characterized. The mechanism of the thickening (SMC) is studied and an ionomer - type structure is proposed from X ray diffractometry carried out on models. Several thickeners are used ; most are derived from magnesium.

08h55  (2/2)  DYNAMIC DIELECTROMETRY ANALYSIS FOR REACTIVE PROCESSING, Ravi. Ramanathan and Dean O. Harper, Department of Chemical Engineering, University of Louisville, 2301 South Third Street, Louisville, KY 40292, USA.

Dielectrometry provides a non-intrusive method of following the cure of resins as they develop complex chemical, structural, and thermal histories. The cures of epoxies have been analyzed using dynamic dielectric techniques. Such studies substantiate the correlation of the reaction changes with the AC conductance, capacitance, and dissipation factor. Measurement of these variables may be made either at a single, fixed frequency or at several selected frequencies, in a sweep mode, the results being distinctively different.

Several filled polyester systems were cured in a preheated mold with the reaction followed at a fixed frequency and in the frequency sweep mode. The AC conductance and capacitance were measured and recorded, from which the dissipation factor was calculated. A high speed data acquisition system coupled to a desk-top microcomputer was used. The ability of the measuring ('complete' in one minute) was evaluated, and the relative merits of the fixed frequency and frequency sweep modes were analyzed.

The cure history, gel point, and end of cure are readily seen from the dielectrometric curves. Hence, this method provides an efficient tool for reactive processing, where direct on-line results for the state of cure are required.

09h20  (2/3)  RHEOKINETIC MEASUREMENTS IN A NEW RHEOCALORIMETER, J. Biesenberger and D. Rosendale, Polymer Processing Institute, at Stevens Institute of Technology, Hoboken, NJ 07030

In a previous paper, data were reported which were obtained from the calorimetric portion of our new Rheocalorimeter. A second generation calorimeter section has been designed, constructed, and combined with a rheometer to measure viscosity under steady shear simultaneous with reaction rate. Among the systems used to evaluate the instrument performance were styrene-acrylonitrile co-polymers, epoxies, and linear polyurethanes. The results are reported in this paper.

09h45    (2/4)    PROCESSING OF POLYURETHANE-POLYESTER INTERPENETRATING POLYMER NETWORK (IPN), T.J. Hsu and L.J. Lee, Department of Chemical Engineering, The Ohio State University, Columbus, Ohio 43210, USA.

Kinetics, rheological changes and molding characteristics of an IPN composed of a polyurethane resin and an unsaturated polyester resin are studied. Reaction kinetics is measured using a differential scanning calorimeter (DSC) and a Fourier transform infrared spectrometer (FTIR). Rheological changes during the reaction are measured using a Weissenberg Rheogoniometer and a Haake rheometer. Molding characteristics are determined using the transfer molding technique and an adiabatic reactor. The interaction between the two reactions, and the effect of composition and reaction sequences on mechanical properties of the final product are discussed. Finally, preliminary results and guidelines of processing IPNs in the RIM process are presented.

10h30    (2/5)    ## CHEMICAL MODIFICATION OF POLYVINYLCHLORIDE AND POLYPROPYLENE IN PROCESSING OPERATIONS : STUDY OF REAGENTS DISPERSION

*Alain Michel, Vincent Verney et Michel Gonnu*
Laboratoire des Matériaux Organiques - C.N.R.S.
BP 24 - 69390 Vernaison, France

the grafting onto polyvinylchloride (PVC) is carried out through nucleophilic substitution of chlorine atoms by metal mercaptides and the grafting onto polylpropylene (PP) is carried out in two steps through peroxidation with the help of an air-ozone gas mixture in a fludized bed and polymerization of vinyl monomers.

The dispersion of reagents in the pvc matrix strongly depends on the rheological behaviour and is homogeneous only when the molecular flow (Newtonian behaviour) is reached at temperature higher than 200°C as it is observed by transmission electron microscopy with the help of stainable reagent by $OSO_4$. The molecular flow appears after melting of microcrystallites which are responsible for a temporary network and physical crosslinking. The rheological behaviour of polypropylene copolymers synthesised by vinyl monomers polymerization initiated from polypropylene peroxides is a powerfull tool to study the competitive reactions between grafting initiated from primary alcoxy radicals and secondary reactions as the $\beta$ scission of alcoxy radicals which causes chain scissions, formation of alkyl radicals and in consequence the formation of block copolymers. The previous competitive reactions depend on temperature but also on the concentration and the dispersion of the monomers in the polypropylene particles which may be studied by transmission electron microscopy.

10h55    (2/6)    REACTIVE OLEFINIC COPOLYMERS : NEW DEVELOPMENTS AND APPLICATIONS.

L. Guerdoux, M. Hert, J. Lebez, CdF Chimie, Centre de Recherches Nord, 62670, Mazingarbe, France.

Research work on reactive olefinic copolymers at CdF Chimie has been followed since 1984 by the commercial development of a family of ethylene-maleic acid anhydrid (MAH) and acrylic ester terpolymers. These terpolymers cover a wide range of grades going from semi-crystalline thermoplastics to elastomers, depending on comonomer content. The melt index range is going from 1 to 200. Thus these products have found applications in various fields (coextrusion, lamination, toughening of plastics, hot-melts, powder coating ...).

Outstanding properties are obtained in several applications owing to the chemical reactivity of MAH with polymeric and inorganic substrates in coextrusion and coating, to the reactivity with fillers and polymeric matrixes in blends and composites. Chemical crosslinking, easy to perform with terpolymers, is a way to improve the high temperature mechanical properties (in wire and cable, pipes and hot-melts).

At last, new polymers can be produced on the production lign by chemical modification of MAH.

11h20    (2/7)                        TRANSESTERIFICATION REACTIONS IN MOLTEN POLYMERS, M. Lambla
                                       J. Druz, Ecole d'Application des Hauts Polymères, Institu
                                       Charles Sadron (CRM-EAHP), 4, rue Boussingault, 67000 Strasbour
                                       France, and A. Bouilloux, Atochem, 27470 Serquigny, France.

    The chemical modification of Ethylene-Vinyl-Acetate (EVA) copolymers, using a tran
sesterification reaction has been carried out in the molten state by reactive processing i
a continuous or discontinuous mixing apparatus.  The reaction was performed in the mixin
chamber of an Haake-plastograph or in a twin screw extruder using different catalytic system
and various paraffinic alcohols and diols. The extent of the reaction was followed by I.R
spectroscopy.  First results have shown that it is possible to convert ester groups of an EV
copolymer to alcohol functions to a large extent by transesterification (70 - 80%). Th
expected equilibrium characteristic of a reversible transesterification reaction was confirm
by quantitative analysis of the modified copolymers and the resulting by-products.  Dependen
of the conversion against temperature, reaction time, composition and nature of the reactiv
species or catalyst, has been thoroughly investigated.  The solubility of the paraffini
alcohols in the molten EVA has been verified by diffusion experiments and it was deduced fro
these results that we have an homogeneous system.  A general reaction scheme is the
applicable to this molten reactive mixture and the related kinetics leads to a fair evaluati
of the rate constants of the transesterification equilibrium.

11h45    (2/8)                        COMPUTER CONTROLLED MULTIPLE STREAM REINFORCED
                                       REACTION INJECTION MOULDING, P D Coates, A F Johnson
                                       P D Armitage, J Hynd and J Leadbitter, Polymer
                                       Research Unit, University of Bradford, Bradford,
                                       BD7 1DP, U.K.

    A two reactant computer controlled research RRIM machine, and a four reactant, high
temperature computer controlled RRIM machine have been built and used to explore the RRIM
process and RRIM chemistries.  The outlines of a number of programmes are discussed: these
include a study of the processing and properties of polyurethanes (PUs) containing mixed
reinforcing fillers, exploration of the chemistry and modelling of the reinforced reaction
injection moulding of PUs, acrylics and polyesters, RIM of PU-acrylic inter-penetrating
polymer networks (IPNs), and reaction injection moulding of polyesters and acrylics over
glass mats.

13h30    (2/9)                        FOUNTAIN FLOW VISUALIZATION EXPERIMENTS, J.W. Blake, I. Manas-
                                       Zloczower* and C.W. Macosko, Department of Chemical Engineering and
                                       Materials Science, University of Minnesota, Minneapolis, MN 55455

    Moldability criteria and process optimization for both reactive and thermoplastic injection molding hinge
on the mold filling step.  The fluid mechanics of the filling step is typically described in terms of a
one-dimensional main flow and a complex two-dimensional flow near the advancing front, often termed the
"fountain flow".
    A unique apparatus was constructed permitting direct observation of the fountain flow in a rectangular
cavity.  The motion of a tracer line moving through the fountain flow as well as the pathlines have been
videotaped and photographed.  Both Newtonian and shear thinning liquids have been investigated.  Data show
clearly the main flow, the transition to the front flow, and the deceleration and acceleration zones in the
fountain flow.  In addition, the data permit quantitative comparison to and evaluation of mold filling models.

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13h55    (2/10)                       FAST MOLECULAR KINETIC STUDY OF RIM REACTIONS BY FT-IR:  SIMUL-
                                       TANEOUS VINYL POLYMERIZATION AND POLYURETHANE FORMATION, H. Ishida
                                       and C. Scott, Department of Macromolecular Science, Case Western
                                       Reserve University, Cleveland, Ohio    44106.

    Reaction injection molding (RIM) of simultaneous urethane formation and vinyl polymeri-
zation has been studied using combined capability of computerized micro-RIM machine and Fourie
transform infrared spectroscopy (FT-IR).  Infrared spectra were obtained in every 0.3 second
intervals.  The reaction proceeded essentially in two stages with heavy overlap of two
processes.  Exothermic heat generated by the urethane formation initiates the vinyl polymeriza
tion.  Isothermal kinetics of the complex chemical reactions have been simultaneously and
independently followed.

14h20    (2/11)          POLYMERIZATION OF POLYAMIDE 6 IN A TWIN SCREW EXTRUDER - PROCESS
                         ANALYSIS - ASPECTS OF INDUSTRIAL USE - G. Menges; T. Bartilla,
                         Institut für Kunststoffverarbeitung an der Rheinisch-Westfälisch-
                         Technischen Hochschule Aachen, Pontstraße 49, 5100 Aachen

Polymerization of polyamide 6 in co-rotating twin-screw extruders is a new alternative of
interest in comparison with conventional polyamide processing techniques. The employment of
extruders as "small-reactors" offers the possibility to optimize polyamides according to
special applications in small batches. Polymerisation in an extruder makes it necessary to
apply activated anionic reacting systemes, which are also used in RIM-processing and monomer
casting.

In this special field of application the twin-screw extruder adopts several func-
tions, which have to be take into account by screw konfiguration and processing. The func-
tions include feeding, melting and mixing of the low viscous monomermelt, starting and
leading the reaction, and discharging the polymer melt against the drag of the extrusion
die. Starting the reaction requires the performance of kneading elements, drawing down thin
films next to the barrel surface. The reaction is started by leading the activation energy
into these films. The analysis of the reaction progress over the length of the screws gives
information about the effects of the different function zones and the influence of thermal
mechanism and shear deformation. Beside the extrusion of profiles, there are some other
aspects of technical use, which seem to be rather interesting. The polymerization extruder
can be connected with discontinously working moulding techniques (transfer moulding, com-
pression moulding). This techniques are not only useful for processing polyamide of high
molecular weight but also offer the possibility to make directed use of this property.

14h45    (2/12)          FROM CAPROLACTAM TO NYLON 6:   REACTIVE PROCESSING
                         IN A NON-INTERMESHING TWIN SCREW EXTRUDER,
                         J.C. Golba, Jr., B.C. Johnson, General Electric
                         Company, Polymer Engineering Unit, Chemical Lab-
                         oratories, Schenectady, N.Y. 12345 and R.J.
                         Nichols, Welding Engineers, Inc., 5 Sentry Park-
                         way, East, Suite #101, Blue Bell, Pa. 19422

     An engineering study utilizing a well known reactive system:  Capro-
lactam, Nyrim® catalyst (a magnesium bromide derivative of caprolactam),
and a promoter (such as n-acetyl caprolactam) to study both design and
process variables involved in using non-intermeshing twin screw extruders
as reactors.  The study includes three basic machine configurations; a
non-vented process in which the residual equilibrium caprolactam was not
removed; a vented process in which caprolactam removal was included but
with no provision for catalyst deactivation; and third, a vented process
including injection of a catalyst deactivator.

15h30    (2/13)          OPTIMIZATION AND AUTOMATION OF A POLYMER COMPOUNDING
                         PROCESS FOR THE CONTROLLED PEROXIDE DEGRADATION OF
                         POLYPROPYLENE, H.-G. Fritz, Institut fuer Kunststoff-
                         technologie, Universitaet Stuttgart, Boeblinger
                         Strasse 70, West Germany.

Low-viscosity polypropylene grades suitable for injection-moulding and
fibre-spinning are prepared from an intitially high molecular weight base
material by employing a controlled peroxide degradation process in a twin-
screw extruder system. Measurements of real-time rheological test data
which can be directly correlated to structural parameters ($\bar{M}_w$, MWD) and/or
the MFI-value of the thus generated grade of polypropylene can be obtained
by joining the compounding unit to a dynamic on-line-rheometer system linked
with a computer. Based on this concept, a process control system is present-
ed in which the rheometer/computer link-up system automatically directs the
processing unit to a specified operating point and, at the same time, gua-
rantees a product quality which is to a large extent independent of disturb-
ing influences from outside. Other points of dicussion are choice of the
rheometer system and its arrangement as well as questions concerning the
rheological and structural characterization of the thus produced polymer
grades.                                                                    15

15h45    (2/14)                REACTIVE EXTRUSION: POLYMERIZATION IN RECIRCULATING FLOW
                               FIELDS, D.H. Sebastian and C. Du, Department of Chemistry and
                               Chemical Engineering, Stevens Institute of Technology,
                               Hoboken, NJ 07030

        While many features relating to the flow in single screw extruder channels can be
adequately described by approximating the channel as an infinite slit, proper treatment of
polymer reaction kinetics and subsequent molecular weight development, demand that one follow
particle trajectories.  A simplified model, decoupling viscosity from molecular weight growth
was employed to examine the behavior of random addition polymerization kinetics in the non-
isothermal, three-dimensional, recirculating flow field of an "unwound" extruder channel.
The details of the cross and down channel developments of temperature and concentration pro-
vide valuable insights to the operation of single screw polymerizers.

16h20    (2/15)                A  SENSITIVITY  ANALYSIS  OF  THE  PLASTICATING  EXTRUSION  OF
                               REACTIVE  SYSTEMS,  M.E.  Ryan  and  H.C.  Hiner,  Department  of
                               Chemical  Engineering,  State  University  of  New  York  at  Buffalo,
                               Amherst, New York 14260, USA.

        A mathematical model has been developed for the simulation of the plasticating
extrusion of thermosetting systems.   The model consists of several submodels which
include: (1) flow of polymer solids in the feed hopper, (2) solids conveying in the
extruder, (3) melting of the solid particles in the extruder, and (4) melt flow in both
the screw channel and die.   The models for the melt flow employ a finite difference
technique to solve the basic equations of change.   The non-Newtonian behavior of the
fluid, the effect of temperature and degree of cure on the apparent viscosity, and the
reactivity of the material have been taken into consideration in the analysis.   The
extruder model yields quantitative results for the mass flow rate of the polymer and
pressure, temperature, and concentration or degree of cure profiles along the extruder
screw channel and die.

        The importance and sensitivity of various physical properties, rheological and
kinetic parameters, operating variables, and screw geometry and dimensions with regard to
the plasticating extrusion process were ascertained by perturbing these parameters about
chosen standard values.

16h45    (2/16)                INTERACTIONS BETWEEN REACTION KINETICS AND DEVOLATILIZATION IN
                               ADIABATIC REACTIVE PROCESSING, J.T. Lindt and R. Chella,
                               Department of Material Science and Engineering, University of
                               Pittsburgh, Pittsburgh, PA 15261, U.S.A.

        A mathematical model has been developed to simulate the growth of a population of
bubbles in a reacting polymeric solution under adiabatic conditions, typical of large scale
Reactive Processing operations.   The interaction between neighboring bubbles is represented
using a cell model allowing for radial flow around the bubble as well as through the time
dependent concentration and temperature effects.   The reaction rate is shown to vary con-
tinously from the bubble surface to the cell boundary in a controllable manner as a function
of the physico-chemical parameters of the system and the number of bubbles and their size.
When searching for an optimum reaction path, this analysis provides a tool for a determin-
ation of an optimal strategy to be developed with regard to the choice of the reaction para-
meters, such as catalyst concentration and molecular weight of the prepolymer, and the mass
transfer related factors e.g. the type and initial concentration of the solvent, the level
of vacuum drawn on the system, etc.

        Specific applications of this work to reactive processing include reactive extrusion,
reaction injection molding and processing of cast polymeric foams.  In particular, reactions
susceptible to thermal runaway will be discussed.

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# SYMPOSIUM No. 3: MODELING AND CONTROL OF MOLDING PROCESSES:

## (CHAIRMEN: M.R. KAMAL AND L.R. SCHMIDT)

08h30    (3/1)    EXPERIMENTAL AND THEORETICAL STUDY OF THE INJECTION MOLDING OF THERMOPLASTIC MATERIALS, J.F. Agassant, H. Alles, S. Philipon, M. Vincent, Centre des Mise en Forme des Matériaux, UA CNRS 852, Ecole Nationale Supérieure des Mines de Paris, Sophia Antipolis, 06560 Valbonne, France

Most of the commercially available computation programs for injection molding use restrictive assumptions which lead to simple mechanical and thermal equations. These computations are generally sufficient to predict the flow distribution in the mold but the pressure and temperature distributions are not precise.

Our aim was first to modelize very accurately the filling stage of several molds of elementary geometries. For this purpose, a two-dimensional model has been built which solves at each time step the finite difference forms of the continuity, momentum and energy equations. A refined grid is used near the mold walls to take into account the great temperature gradients. These models have been validated by comparing the pressure field with experimental measurements. The precision of the model is better than 15 % for several mold geometries and several injection conditions.

In a second step, molds of complex geometries have been analysed by assembling elementary geometries. The flow distribution at the branching between several geometries has been studied with special attention. These computations have been compared with short shots and pressure measurements in a four rectangular cavities tool and in a box shaped cavity tool. Experimental and theoretical results are in good agreement. The experimental measurements have been performed by Ato Chimie (B. Gourdon, G. Demay, P. Lerebours), by SMTP (B. Ginglinger) and by "Lycée Technique d'Oyonnax" (C. Faure, Ph. Roybier).

08h55    (3/2)    EVALUATION OF THE EFFECTS OF VARIOUS ASSUMPTIONS IN THE MATHEMATICAL MODELLING OF INJECTION MOLD FILLING, M.R. Kamal, E. Chu and S. Goyal, Department of Chemical Engineering, McGill University, Montreal, Canada H3A 2A7

Recently, a detailed model was proposed for describing the various stages of the thermoplastic injection molding process. The model deals with the flow of a viscoelastic (White-Metzner) polymer melt, with accomodations for fountain flow and crystallization kinetics. Use of the Marker-and-Cell technique, in conjunction with finite difference analysis, yields useful information regarding the melt front region. Some of the recent results obtained with the model will be reported. Moreover, the effects of various assumptions, regarding material properties and system characteristics, on the results obtained with the model will be summarized.

09h20    (3/3)    SIMULATION OF BALANCING MULTI-CAVITY MOLDS

H. Ghoneim

Department of Mechanical Engineering
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Rochester, New York 14623

ABSTRACT

A finite element program is developed for simulating the non-isothermal flow of non-Newtonian liquids in a multi-cavity mold with convergent runners and gates of any arbitrary cross-sectional shape. The program is used to investigate the problem of balancing multi-cavity molds. Results of simulating an actual mold filling show that balancing can be achieved by using a straight runner together with convergent gates having successively increasing angles of convergence. In addition, a strategy for approximating those angles of convergence is suggested.

09h45    (3/4)                FINITE ELEMENT ANALYSIS OF INJECTION MOLD FILLING,
H. Mavridis, A.N. Hrymak and J. Vlachopoulos, Department of
Chemical Engineering, McMaster University, Hamilton,
Ontario, L8S 4L7, Canada.

A general purpose finite element package was used to simulate the flow field in the process of injection mold filling.  Special attention was given to the fountain effect which is described by the deceleration and outward motion of fluid particles as they approach a slower moving interface.  The free surface shape as the fluid fills the cavity was determined for each time step of the mold filling process.

10h30    (3/5)                THE KINEMATICS OF FOUNTAIN FLOW IN INJECTION MOLDING
D.J. Coyle, Polymer Physics and Engineering Branch
General Electric Company, Corporate Rësearch and
Development, P.O. Box 8, Schenectady, New York 12301

Injection molding processes require filling a cold mold with a hot polymer melt.  The flow field far behind the advancing melt front is typically one-dimensional shear flow, while the flow near the front is necessarily two-dimensional as fluid flows outward to the walls, forming a thin skin of rapidly-solidified polymer.  This two-dimensional flow, often called the "fountain effect", is usually neglected in mold-filling analyses.

In this work, Galerkin/finite element analysis is used to predict the isothermal free-surface flow of a generalized Newtonian liquid near the advancing front between parallel plates.  The calculated flow is visualized most clearly by tracking material lines, thus producing numerical tracer experiments.  These results are in agreement with recent experiments by Blake and Macosko, and clarify previous experimental results which did not allow visualization of the entire flow field.  The calculations also allow prediction of shear and extensional deformation histories of fluid elements as they move through the front region, which affects molecular orientation and the skin-core morphology.

10h55    (3/6)                MODELING   OF   THE   PACKING   STAGE   INJECTION   MOLDING   OF
THERMOPLASTICS,   R.   Deterre,   D.   Huilier,   C.   Lenfant   and
J. Terrisse, E.A.H.P., 4 rue Boussingault, 6700 Strasbourg,
France

A model for the packing stage in injection molding is proposed which allows to calculate the evolution of pressure and temperature fields and mass variations in the cavity.  The model can be used for amorphous as well as for cristalline polymers if the kinetics of cristallisation is known for temperatures far from the melting point.

Initial values of pressure and temperature along and perpendicular to the flow direction can be obtained from mold-filling modelisations.  The principle of the model consist of calculating the flow of a compressible non-newtonian fluid in a filled cavity. From pressure and temperature fields that are known at a given time T, the velocity field is calculated, and according to an equation of state the pressure field at time T + DT is determined from the increase of mass in each grid cell.

The model predicts the value of the pressure rise in the cavity as a function of time and position.  For simple geometries, one can calculate the local shrinkage and to a good approximation the final weight or the moldings.

11h20　(3/7)　PRESSURE AND TEMPERATURE DISTRIBUTION IN THE CAVITY DURING INJECTION MOLD FILLING, Y. Oyanagi and K. Kubota, Kogakuin University, Tokyo, Japan.

The cavity pressure (P) and temperature (T) distribution during injection mold filling were measured using a direct P-sensor and infra-red T-device at the wall. The spiral flow mold dimensions were 900 x 20 x 4 mm with gate 5 mm in diameter. The measuring points were located along the flow direction at the gate, at the end of the cavity and at two points in between. Polycarbonate and a polyacetal copolymer were used. We found a remarkable tendency for the T to decrease near the gate. This seems to be due to wall cooling, the fountain effect and adiabatic expansion near the gate.

11h45　(3/8)　ADAPTIVE MESHES FOR THE NUMERICAL SIMULATION OF INJECTION MOLDING, A. Couniot, M.J. Crochet, Unité de Mécanique Appliquée, Université Catholique de Louvain, 2 Place du Levant, B-1348 Louvain-la-Neuve, Belgium.

We present a finite element algorithm for calculating the Hele-Shaw flow of a generalized Newtonian fluid in a mold of arbitrary shape with multiple inserts, gates and vents. An appropriate finite element mesh, covering the whole surface of the mold, is designed a priori. When the liquid front moves through the mold, the elements lying across the interface are automatically adapted to the evolving flow domain. The calculation provides the development of the velocity field and of the fluid front as a function of time, together with the location of the weld-lines. The presentation will include a computer film showing the filling process of several molds.

13h30　(3/9)　STUDIES IN DYNAMICS AND CONTROL OF THE THERMO-PLASTICS INJECTION MOLDING, M.R. Kamal, W.I. Patterson and D. Abu Fara, Department of Chemical Engineering, McGill University, Montreal, Canada H3A 2A7

Recently, emphasis has been placed on the development of computer control schemes to assure improved process economics and product quality and reproducibility in injection molding. A number of commercial control systems are available, but most of these schemes are based on open loop control and rely on cycle-to-cycle modifications instead of in-cycle responses to process changes. In the present work, studies have been carried out to obtain dynamic models, using both deterministic and stochastic experiments, in relation to some of the important process parameters, e.g. hydraulic pressure, nozzle pressure, melt temperature, injection speed, and cavity pressure-time variation. On the basis of these studies, dynamic models have been obtained. Subsequently, these models were employed to compare the performance of alternative controllers. The results of the modelling and control studies will be reported and compared to experimental results.

13h55   (3/10)   BIREFRINGENCE CONTROL IN POLYCARBONATE INJECTION MOLDING, S.J. Willey and C.M. Karas, General Electric Company, Corporate Research and Development Center, Schenectady, New York 12301, USA

The optical anisotropy of transparent injection molded parts reflects frozen orientations produced during the injection molding process. The advent of optically based information storage technologies which utilize polymeric substrates (optical discs) has made minimization of birefringence in injection moldings with radial symmetry a subject of increasing importance. Control of birefringence in injection moldings requires optimization of the molding process to minimize orientation produced both during the filling and holding portions of the molding cycle.

The effects of processing conditions and melt rheology on molded-in birefringence are presented for polycarbonates of bisphenol-A. Elastic stresses generated during filling are shown to dominate the optical properties of the resultant moldings. Optical anisotropy is minimized by reducing the shear stresses associated with the filling process and by controlling the viscosity and elasticity of the melt.

14h20   (3/11)   NUMERICAL SIMULATION OF COMPRESSION MOLDING OF THIN PARTS IN 3-D SPACE V.W. Wang and K.K. Wang, Sibley School of Mechanical and Aerospace Engineering, Cornell University, Ithaca, N.Y. 14853

Modeling the compression molding process has drawn considerable attention in recent years because of the growing interest in sheet molding compounds (SMC), particularly in the automotive industry. However, previous studies have been limited to parts with rather simple planar geometry. This paper presents a hybrid FEM/FDM numerical formulation for simulating the compression-molding process of thin, sheet-like parts in either two-or three-dimensional space. The calculation procedure involves two parts: (1) the initial charge-shape design and (2) the compression-molding-process simulation. The initial charge is determined by opening the mold and reversing the flow from a totally-filled cavity to a partially-filled one. Newtonian flow and isothermal conditions are employed in this approximation. Once the shape of the initial charge and its location are determined, the compression flow due to mold-closing is computed with heat transfer, curing, and non-Newtonian viscosity included. In addition, the simulation continues after the mold is closed in order to determine the heat transfer and degree of cure with respect to time. The formulation can be applied to thin parts in three-dimensional space with variable thickness with the melt-front being advanced (or retracted) automatically in the calculations. This computational tool will enable us not only to simulate the flow in the process, but also to predict (and thereby to "design") the shape as well as the relative location of the initial charge with respect to the mold.

14h45 (3/12) A BOUNDARY ELEMENT SIMULATION OF COMPRESSION MOLD FILLING, Tim A. Osswald and Charles. L. Tucker III, Department of Mechanical and Industrial Engineering, University of Illinois at Urbana-champaign, Urbana, IL 61801

A simulation of compression mold filling can be used to predict the mold filling pattern, the orientation of reinforcing fibers, and the location of knit lines before parts are actually produced. Most of the effort in such a simulation goes into data preparation and mesh redefinition during filling. When using the boundary element technique the input data is reduced to a minimum and the tedious remeshing procedures are completely eliminated. This paper presents the development of the boundary element equations for the compression molding of isothermal Newtonian fluids in thin cavities. The numerical implementation of the boundary element equations are presented along with a simple method of evaluating the domain integral present in the governing equations. The simulation automatically redefines the charge geometry during filling, and runs without any user interaction. The accuracy of the pressure, velocity and velocity gradient fields from the simulation are demonstrated by comparing them to analytical results. The simulation also predicts filling patterns and knit line locations which agree with experimental results. The numerical examples and the experiments show that the boundary element technique is more accurate than the finate element method.

15h30 (3/13) NUMERICAL SIMULATION OF A BLOW MOLDING PROCESS, A. Cohen, The Dow Chemical Company, Materials Engineering Center, 433 Building, Midland, Michigan 48667, USA.

The presentation discusses a method for accurate numerical simulation of a blow molding process and as such is useful in the development of new products made by two-step injection blow molding. The simulation uses commercial finite element software capable of handling the large deformations and interactions with rigid surfaces that happen in blow molding. This method has provided practical guidance for manufacturing plastic containers with optimal material distribution. The incorporated material model for a general purpose polystyrene in a rubbery state enabled efficient selection of the proper temperature profile and predicted evolution of the preform's geometry in the course of blowing. We will show how this approach can be used for the determination of preform dimensions and pre-heating requirements for successful blow molding production. Examples of the simulation for various preform shapes and temperature profiles blown into containers will be reviewed.

15h55 (3/14) A NEW LOOK AT SWELL AND SAG EFFECTS IN PARISON FORMATION. W.H. Talbott, D.B. Japikse*, W.K. Paul**, General Electric Company, Corporate Research and Development, P.O. Box 8, Schenectady, NY 12301

We have been able to show that swell and sag effects may be separated in forming parisons by using an extended variation of the parison-sectioning (or pinch-off mold) technique. The initial results appear to fall within the linear viscoelastic regime of material response. Die geometry effects as they relate to material deformation history are discussed. We suggest the limits of this technique as well as its practical application to very large (e.g., greater than three feet long) parisons.

We present results for several blow-molding grade materials including a polycarbonate resin, a modified polyphenylene oxide resin, and a high-density polyethylene.

*General Electric Company, Noryl Products, Selkirk, N.Y.
**General Electric Company, Plastics Application Center and Laboratory, Louisville, KY.

PROCESS OPTIMIZATION IN STRETCH BLOW-MOLDING, G. Menges and U. Hüsgen, Institut für Kunststoffverarbeitung, Aachen, West Germany

In stretch blow molding, the stretching temperature has the most significant influence on the article performance besides the stretching ratio. Therefore, a sophisticated control system was developed for a laboratory stretch molding plant on which PP-bottles are produced. The processing window for the stretching of the polypropylene homopolymer is within a temperature range between 145°C and 153°C. For that reason, a precisely operating temperature control had to be developed and integrated into the microprocessor, which runs the complete process beginning with moving the preform into the heating chamber and ending with demolding the finished bottle. For the heating, infrared heaters are used, which can heat the preform (6mm wall thickness) in about 60 seconds. During the transient time, shortly before the preform is moved into the mold, its surface temperature is read at four different spots simultaneously using a specially developed device which consists mainly of 4 pyrometers. The temperature signals are fed into the microprocessor which, in case of a deviation from the setpoints, adjusts the power of the IR-heaters. The temperature control is done by a special algorithm, which takes into account that the controlled system is a coupled multivariable system, which can be modelled by a linear system.

Tests have proved that the control system can react fast and precisely to setpoint changes and keeps the preform temperature and its distribution constant throughout the production within a range of approximately 2°C.

16h45    (3/16)

USE OF RHEOLOGICAL PARAMETERS TO INDICATE THE BLOW MOLDING CHARACTERISTICS OF OLEFINIC THERMOPLASTIC ELASTOMERS, Lloyd A. Goettler, Monsanto Chemical Company, Akron, OH 44313, and Yoichiro Saito, Mitsubishi Monsanto Chemical Company, Yokkaichi City, Japan.

The ability to blow mold thermoplastic elastomers (TPE's) allows them to compete in a number of new market segments. One class of these materials comprises a blend of polyolefinic rubber and plastic components.

Selective rheological characterizations of high performance TPE's produced by dynamic vulcanization of the rubber phase (hereafter referred to as Thermoplastic Vulcanizates or TPV's) have been found useful to indicate their processability in extrusion blow molding operations. These tests involve capillary viscometry for analysis of parison formation and extensional properties that relate to its drawing ability. The latter measurements are made on a newly developed extensional rheometer.

Processing windows for stable blowing, including parison gauge and blow ratio as well as thermal conditions, are successfully predicted over the hardness range of SANTOPRENE® thermoplastic rubber, a commercial TPV. Interpreting the rheological data in terms of material structure leads to an understanding of processing behavior and the resulting properties of blow molded parts.

GENERAL CONSEQUENCES OF GLASS-TRANSITION PHENOMENA IN POLYMER FABRICATION PROCESSES, J. Greener, J. J. Tribone, J. M. O'Reilly, Research Laboratories, Eastman Kodak Company, Rochester, New York 14650.

The nonequilibrium nature of polymeric glasses is manifested in a multitude of characteristic phenomena, e.g., physical aging, enthalpy relaxation, pressure-induced densification, and pressure-induced vitrification, which have been studied extensively over the past two decades. Since most polymer fabrication processes involve a vitrification step, some of these phenomena are bound to influence the ultimate properties and dimensions of the formed parts. Glass-transition phenomena are manifested in plastic parts in the form of density fluctuations, dimensional instability, structural inhomogeneity, and crazing. Such effects are particularly relevant in high-precision operations in which the part must be formed and stay within close tolerances. Some of the glass-transition phenomena have been modeled successfully in our laboratory using a phenomenological multiorder parameter model which is an isotropic (nondeviatoric) analog of nonlinear viscoelastic constitutive equations. The model was used to evaluate the response of an amorphous polymer in some simple processing steps and assess the effect of its nonequilibrium characteristics on the ultimate properties of the formed part. The results of this analysis and the implications for high-precision molding processes will be discussed.

# SYMPOSIUM No. 4: MODELING AND CONTROL OF EXTRUSION AND OTHER FORMING OPERATIONS

## (CHAIRMAN: J. VLACHOPOULOS)

8h30   (4/1)       DESIGN OF VARIOUS EXTRUSION DIES WITH FD AND FE
                   TECHNIQUES ON THE BASE OF A VISCOSITY DATA BANK
                   H. Kühnle, Institut fuer Kunststofftechnologie
                   der Universitaet Stuttgart, Boeblinger Str. 70,
                   D-7000 Stuttgart 1, West-Germany.

        First a survey of simple one-dimensional analytical and Finite Diffe-
rence(FD) methods for calculating the standard extrusion dies (Sheet, tube,
and blow moulding parison dies) is given. Then two-dimensional FD and Finite
Element(FE) techniques for designing profile extrusion dies as well as the
more intricate parts of standard dies (e.g. the mandrel holder of a tube die)
are considered.
        Rheological model is the pseudoplastic and temperature-dependent flow
behaviour described by Carreau's formula and temperature shift factors, the
material parameters of which are stored in a comprehensive data bank.
        The principal performance characteristics of the die, including the
pressure distribution, the thermal development, the residence times, and the
critical shear rates (e.g. in case of HDPE processing) can be evaluated.
        From the 2D-calculations, the rise of certain elastic effects, which
become observable by the distortion tendency of the extrudate, can be predic-
ted and minimized by appropriately modifying the design.
        The predictions are compared with experimental results.
        It is tried to assess the scope of the reviewed 1D- and 2D-methods,
resp., in consideration both of the required accuracy and the availability
of suitable computing means in industrial R & D departments.


8h55   (4/2)       COMPUTATION OF MOLTEN POLYMER FLOWS IN EXTRUSION DIES, J.F.
                   Agassant, B. Vergnes, Centre de Mise en Forme des Matériaux,
                   UA CNRS 852, Ecole Nationale Supérieure des Mines de Paris,
                   Sophia Antipolis, 06560 Valbonne, France.

        Some approximations are introduced to compute the flow of a molten polymer in a complex
die geometry : the classical lubrication approximations permit to reduce a three dimensional
flow in a narrow channel to a  one dimensional or a two dimensional one ; in some cases, it
is possible to unroll an annular geometry ; a mean temperature in the flow depth can be
used when the transverse temperature gradient is low.
        The molten polymer is supposed to obey a temperature dependant pseudoplastic power -
law ; this leads to non linear forms of the thermal and momentum equations which have to be
solved simultaneously, using slab methods (one dimensional flow) or finite difference me-
thods (two dimensional flow).
        Several applications are presented : for a coat hanger die, the computation points out
the influence of the die geometry and of the thermal regulation on the output rate  distri-
bution. In the P.V.C. pipe extrusion, the symmetrical overthickness defects can be explained.
For a wire coating die, the polymer distribution around the wire can be predicted ; the ap-
pearance of surface defects and of wire breakage is also studied.

ADVANCES IN COMPUTATIONAL METHODS FOR RHEOLOGICALLY COMPLEX FLOWS WITH FREE SURFACES, Roland Keunings, Center for Advanced Materials, Lawrence Berkeley Laboratory, University of California, Berkeley, CA 94720, U.S.A.

We briefly discuss Galerkin/Finite element methods for solving rheologically complex flows with free surfaces. In particular, we propose a fully implicit algorithm for a class of moving boundary problems involving highly elastic fluids. The methods are applied to the study of the blade coating process and a non-linear analysis of the dynamics of thin viscoelastic films.

9h45    (4/4)        A DOUBLE-NODE TECHNIQUE FOR FINITE ELEMENT SIMULATION OF STRATIFIED MULTIPHASE FLOWS, H. Mavridis, A.N. Hrymak and J. Vlachopoulos, Department of Chemical Engineering, McMaster University, Hamilton, Ontario, Canada L8S 4L7

Interfaces forming between immiscible fluids complicate the analysis of stratified multiphase flow fields not only because the position of the interface is unknown a priori but also due to the discontinuity of the pressure across the interface. A simple technique has been developed that uses double nodes along the interface to handle this discontinuity. Implementation of the method in finite element codes and applications to flat-film coextrusion and immiscible liquid displacement will be discussed. The results agree qualitatively with available experimental observations.

10h30    (4/5)        NUMERICAL SIMULATION OF COEXTRUSION, J. Dheur, M.J. Crochet, Unité de Mécanique Appliquée, Université Catholique de Louvain, 2 Place du Levant, B-1348 Louvain-la-Neuve, Belgium.

We calculate the flow of two non-mixing fluids in the laminar regime, with a special emphasis on problems where the location of the interface is totally unknown a priori. A typical situation is the T-geometry where two different fluids are injected through the branches of the T, and where the origin of the separating streamline is unknown. We consider the flow of generalized Newtonian and viscoelastic fluids as well. The method is based on a full Newton-Raphson iterative scheme where the equations for locating the interface are solved together with the equations of motion. The numerical results are compared with experimental data obtained by K. Walters (University of Wales, Aberystwyth).

10h55    (4/6)        A FINITE ELEMENT SIMULATION OF NON-ISOTHERMAL POLYMER MELT FLOWS, P.A. Tanguy, A. Fortin*, Département de Génie chimique, Université Laval, Québec, Québec, G1K 7P4, *Département de Mathématiques appliquées, Ecole Polytechnique, Montréal, Québec.

A Finite element simulation of a non-isothermal polymer melt flow in a sudden contraction is presented. The model uses an augmented Lagrangian formulation which enables to decouple the computation of the non-linearity introduced by the non-Newtonian behavior from the computation of the velocity and pressure profiles. The powerlaw and the Carreau - A rheological models are used to describe the mechanical behavior of the melt. The temperature equation is solved independently from the momentum equations, and the two problems are subsequently coupled by an iterative process.

Numerical predictions are compared with experimental data when available.

11h20    (4/7)                FLUID FLOW AND HEAT TRANSFER IN WIRE COATING, Evan Mitsoulis,
                                 Department of Chemical Engineering, University of Ottawa,
                                 Ottawa, Ontario, Canada, K1N 9B4.

     Most mathematical models of wire coating are based on the lubrication approximation in
one direction for Newtonian and shear-thinning materials under isothermal conditions.  These
models give unrealistically high predictions for pressure distribution, shear stresses at the
die wall and wire and haul-off tension.  Two-dimensional axisymmetric finite element
calculations permit the analysis of the whole flow domain including the region of impact of
the melt with the wire and the determination of the free coating surface.  The analysis can
be carried out under non-isothermal operating conditions and for different die designs and
wire speeds.

     The finite element analysis shows areas of recirculation if a proper die design is not
implemented.  The inclusion of the energy equation with convection and viscous dissipation
terms shows reasonable temperature rises for typical coating thermoplastic resins, such as
LDPE and plasticized PVC.  Limits of operational parameters can be investigated for smooth
coatings, by examining the maximum shear stresses at the wire and die wall to determine if
they have exceeded critical values associated with melt fracture.  The analysis also provides
a wealth of information about all pertinent quantities of interest in the wire coating
process.

11:45    (4/8)                REAL  TIME  PROCESS  CONTROL  BY  ON-LINE  CAPILLARY  RHEOMETRY
                                 A. Göttfert, Göttfert Werkstoff-Prüfmaschinen GmbH, Siemens-
                                 strasse  2,  P.O.Box  1220,  6967  Buchen,  West  Germany.

There is an increased tendency to improve quality control in raw material manufacturing and
polymer compounding. For that purpose capillary type test instruments (i.e. Melt Indexer;
Capillary Rheometers) are widely used. In general long lag times occur between testing and
actual data feedback into the process. To overcome this problem, on-line capillary rheo-
meters  have  been  designed  to  simulate  these  standard  tests  in  the  process.
To gain best agreement between laboratory test and on-line measurement procedures an on-
line rheometer has to work process independent. Any pressure and temperature deviations in
the process have to be compensated. Test results being presented, show that melt pressures
up to 200 bar and temperature deviations of + 20°C can be compensated. For the rough
environment of the production floor a sturdy and compact rheometer is needed. To support
best sample representation these on-line rheometers show design features to keep connecting
transfer lines as short as possible.

Applications will be presented on:
    a) PETP - manufacturing (2 samples with different MW)
    b) PE, PP and ABS - (comparison between laboratory tests and on-line techniques

Assumed that reasonable agreement between laboratory- and on-line tests can be established,
on-line capillary rheometry is an useful tool for production management to guarantee a
stable and homogenous material quality.

13h30    (4/9)               MODELING OF A PRODUCTION TWIN-SCREW EXTRUSION PROCESS (COUNTER-
ROTATING, NON-INTERMESHING), H. Tolliver, Traffic Control
Materials Division, 3M Co., 553-1-A 3M Center, St. Paul, MN
55119, USA, and Dean O. Harper, Department of Chemical
Engineering, University of Louisville, 2301 South Third Street,
Louisville, KY 40292, USA.

A model for the non-intermeshing, counter-rotating, twin-screw extrusion process
is presented. The model is based on the equations governing isothermal, Newtonian fluid
processing, modified to included non-isothermal, non-Newtonian conditions. The partial
filling phenomenon was developed from the geometry of an annulus, restructured to consider
the presence of the screw flights.

The Welding Engineers extruder, currently used in a PMMA production facility at
Louisville, KY, included vents for the removal of volatiles and ports for introducting
recycled polymer and additives. Its axial length was divided into 'elements', defined as
a length over which the screw geometry remains constant. Four types of elements were
defined: unvented, vented, compounding, and single-screw (the last terminated the extruder
for the purpose of producing rods from a manifold die to be chopped into molding pellets).
Flighted elements which increase the pressure, followed by elements which cause a pressure
drop (for venting purposes) were identified as 'sections', providing larger subdivisions
within the extruder.

13h55    (4/10)              ANALYSIS OF ADIABATIC DEVOLATILIZATION OF MODERATELY CONCENTRATED
POLYMER SOLUTIONS, R. Chella and J. T. Lindt,
Department of Material Science and Engineering,
University of Pittsburgh, Pittsburgh, PA 15261, U.S.A.

A mathematical model was developed to describe the kinetics of foam devolatilization
under adiabatic conditions. Devolatilization in moderately concentrated solutions is greatly
influenced by interactions between heat and mass transfer, and the radial flow induced by the
growth of bubbles. A cell model approach was used to allow for interactions between closely
spaced bubbles. A realistic formulation of the solution thermodynamics, and concentration
and temperature dependence of transport properties for polymer solutions, was incorporated
in the model.

Model predictions of the devolatilization rate (expressed in terms of the change in
solution temperature with time), foam density, etc., were compared with the results of an ex-
perimental batch devolatilization study on polystyrene-ethylbenzene solutions (25-50% by
weight polymer). Careful precautions were taken in the design of the apparatus to ensure
adiabatic operation. Supersaturation was induced by a step reduction in system pressure, and
provisions were made for multi-stage operation. Experiments were carried out under con-
ditions of temperature and pressure typical of industrial extrusion devolatilization
(150-250$^\circ$C and 0.1-1 atm.). Results of the analysis should be useful in determining optimum
operating conditions and in the design of the upstream section of a devolatilizing extruder.

This work also has applications to the injection molding and extrusion of polymeric foams

14h20   (4/11)   IMPROVEMENTS IN FORCED-FEEDING-SINGLE-SCREW-EXTRUSION,
E. Gruenschloss, Institut fuer Kunststofftechnologie,
Universitaet Stuttgart, Boeblingerstrasse 70,
7000 Stuttgart 1,   Federal Republic of Germany.

Due to the different conveying mechanisms, the throughput and pressure in
single-screw-extruders with grooved feed zones is much higher than in those
with smooth feed zones; the maximum pressure is found at the beginning of the
melting zone, and melting and melt zone are as a rule "overridden" by the
feed zone.
Theoretical and experimental results show a significant reduction in pressure
along the feeding, melting and melt zone of screw extruders with grooved feed
sections, when using a screw helix angle in the melting and melt zone in the
range of $25^{\circ}$ ... $45^{\circ}$, instead of the commonly used angle of $17.7^{\circ}$ (The helix
angle in the feed zone has to be unchanged). Accordingly, the necessary
cooling of the feed zone and the wear at screw and barrel is reduced, the
pressure range at the screw tip enlarged (important e.g. for additional sta-
tic mixers), the melting capacity and mass homogenity improved, the starting
torque with completely filled screw reduced, and the running torque only
slightly raised.
For a given volumetric flow rate, which is determined by the feed zone, the
optimal helix angle in the melting and melt zone, which agrees with the angle
at the maximum of the axial pressure gradient, can easily be calculated.

Literature:  E. Gruenschloss, Kunststoffe 75 (1985) 11, p. 850 - 854


14h45   (4/12)   FLOW AND MIXING PHENOMENA IN CO-ROTATING TWIN-SCREW EXTRUDERS
P.R. Hornsby, Department of Materials Technology,
Brunel University, Uxbridge, Middlesex, U.K.

This presentation will consider distributive and dispersive mixing characteristics of a
versatile 40mm co-rotating intermeshing twin-screw extruder, through flow visualisation of
thermoplastics compositions extracted from the screw channels and quantitative determination
of mixing using specially developed microstructural characterisation procedures, incorporating
automatic image analysis.   Mixing effects observed will be discussed in terms of the nature &
magnitude of leakage flows across the intermeshing zone, cross-channel flow within the C-shaped
chambers, together with the influence of screw configuration and processing conditions adopted
during compounding.


15h30   (4/13)   MECHANISM OF FLUOROELASTOMER*PROCESSING AID IN EXTRUSION
OF LLDPE, Sehyun Nam, 3M Company, 3M Center, 201-1W-28,
St. Paul, MN  55144

        Fluoroelastomers are being used as processing aids for extruding thermoplastics.
Mechanism of the function is studied by using Capillary Rheometer and x-ray photo-
electron spectroscopy.  Four different die diameters with a die aspect ratio of 40
were used in extrusion linear low density polyethylene (LLDPE).  Slip velocities at
the same pressure drop increases with the addition of fluoroelastomer from 250 to 1000
PPM.  This helps delay the onset of melt fracture to higher shear rates and produce
smoother extrudates.  Study shows that fluoroelastomer wets the die surface and migrate
to the surface of extrudate.

* Dynamar Brand Polymer Processing Additive PPA-2231, a product of the 3M Company.

15h45  (4/14)  BLOWN FILM MODELING - FREEZE LINE TO FROST LINE, G.A. Campbell, Clarkson University, Potsdam, New York, 13676, USA.

Historically the ability to use modeling techniques to describe the deformation of blown film has been stymied by inability to model the process above the so called freeze line. The actual frost line, the point where the major polymer deformation stops, can be 2 to 3 feet above the freeze line in many real applications. This severely limits the use of modeling in predicting the effects of material molecular properties and process parameter interactions on the ultimate physical properties of the blown film. We have critically investigated the blown film process and evaluated the interaction of the film dynamics with rheological equations of state ranging from Newtonian models to reptation models. All models have one of two limitations which leads to the necessity of stopping the simulation at the freeze line. We will discuss the consequences of these interactions and their effect on the film dynamics and the process boundary conditions. We then will propose an alternative physical model and phenomenological equation of state which is useful to the real process frost line. This model has the potential of being useful in predicting film properties when the rheological parameters have been related to polymer molecular properties. The approach used in this investigation is thought to be applicable to blow molding, vacuum forming and film extrusion where anisotropic stretching dominates the process dynamics.

16h20  (4/15)  HEAT TRANSFER TO POLYMER MELT FLOW IN PROFILE EXTRUSION, Bing Yang and Ly James Lee, Department of Chemical Engineering, The Ohio State University, 140 West 19th Ave., Columbus, OH 43210 USA.

The effect of non-isothermal wall temperature to the flow of polymer melts in simple dies such as a circular capillary and profile dies were studied. At constant flow rates, changes of die pressure drop and extrudate swell at different die wall temperatures were measured. Two extrusion grade polystyrenes, a PMMA and a flexible PVC were used. It is found that wall temperature has a much profound effect on the relative flow rates at different die section, die pressure drop and extrudate swell than the melt temperature. For polystyrenes, when plotted against wall shear stress, the extrudate swell gives rise to correlations which are independent of both melt temperature and wall temperature. A mathematical model based on the heat penetration through the wall was propsed to calculate the difference of die pressure drop between the isothermal and non-isothermal cases, which can be applied to the on-line process control of profile extrusion.

16h45  (4/16)  THEORETICAL ANALYSIS OF TUBULAR FILM EXTRUSION AND ITS APPLICATION FOR HMW-HDPE, Toshitaka Kanai, Idemitsu Petrochemical Co. Ltd., Research Center for Products Development, 1660 Kamiizumi Sodegaura Chiba, 292-01 Japan.

The theoretical analysis of the tubular film extrusion by using a computer simulation presented several interesting results, such as bubble shapes, velocity profiles and maximum stretching stress. From the theoretical analysis, maximum stretching stresses which are closely related to film physical properties were predicted under the various process conditions and various resins.

Those theoretical analysis was applied to HMW-HDPE tubular film process. High strength HDPE film can be produced by keeping the stretching stress high, high out-put rate, high take-up speed and low temperature by reducing the heat generated by viscous dissipation.

# SYMPOSIUM No. 5: RUBBER PROCESSING
## (CHAIRMEN: J.L. WHITE AND K. MIN)

10h30    (5/1)          STUDY ON THE METHODS OF ESTIMATING RUBBER PROCESS-ABILITY, H.Goto, Y.Fujinaga, I.Furuta, Japan Synthetic Rubber Co. Ltd.,100 Kawajiri-cho, Yokkaichi, Mie, Japan.

A new type of viscometer for estimating the rubber processability has been developed. The viscometer has a set of cone-plate type dies. The upper die is flat and fixed to the base, while the lower is conical and controlled to rotate. Its rate of revolution is variable with the maximum rate of 100 rpm. The rotation can be stopped instantaneously so as to obtain stress relaxation data. The viscometer is equipped with two stress sensors. The one is to measure the rotational torque and another is to measure the force perpendicular to the die surface.

The viscometer can execute various ways of measurements such as stress relaxation in shear and in compression, observation of stress-overshoot, steady state shear viscosity with variable shear rate, of which maximum value is 100 sec$^{-1}$ , and stress relaxation following shear viscosity.

The aim of developing present apparatus is to provide the method of estimating the roll processability of raw rubbers and unvulcanized rubber compounds. The measurement of stress relaxation following shear viscosity is thought to be effective for predicting the roll processability of the materials.

10h55    (5/2)          QUESTIONS CONCERNING BEHAVIOR OF CARBON BLACK DURING INCOR-PORATION AND DISPERSION IN RUBBER, N. Nakajima, Polymer Engineering Center, University of Akron, Akron, Ohio, 44325

There have been two different views on the break down of carbon black agglomerates into their constituting elements, i.e. aggregates, in relation to incorporation and dispersion in rubber. One is that rubber penetrates into the inside of the agglomerates, filling cavities but without breaking them down. The complete wetting of carbon black surface is thought to take place at this stage and defined as the end of incorporation. Then, during the dispersion the rubber-wetted agglomerates break down to the rubber-wetted aggregates.

The other view is that the loose carbon black becomes included inside of the rubber during incorporation, which does not make any specific reference to the break down of agglomerates. Accompanying the progress of dispersion, the agglomerates first break into several pieces of the smaller agglomerates and then, they disintegrate into aggregates in one step. Thereupon, the complete wetting of carbon black with rubber takes place.

Both views are based on certain experimental observations. However, they differ distinctly on the timing of wetting carbon black surface with rubber in relation to the progress of break down of agglomerates. In this paper both views have been examined. Some difficulty in accepting the former views is presented.

11h20    (5/3)          FLOW VISUALIZATION OF COMPOUNDING OF ELASTOMERS IN AN INTERNAL MIXER, Kyonsuku Min, James L. White, Polymer Engineering Center, University of Akron, Akron, Ohio, 44325

The addition of carbon black and oil to elastomers in internal mixers has been investigated using a model internal mixer with glass windows normal and parallel to the rotor axis. The influence of rotor design, fill factor and other process variables are examined. This behavior of natural and synthetic rubbers has been examined. The behavior of most synthetic rubbers is dominated by tearing the rubber into crumbs. This leads to stagnant regions and difficulties in developing uniform mixing of carbon black. Natural rubber does not tear during mixing and incorporates carbon black more slowly. Oil added to the internal mixer coats the rotors and induces slippage until the oil is absorbed.

30

11h45   (5/4)   EXTRUSION OF RUBBER COMPOUNDS IN SINGLE SCREW EXTRUDERS,
Ryszard Brzoskowski, Kazuhisa Kubota, James L. White, Frederick C. Weissert, Nobuyuki Nakajima, Kyonsuku Min, Polymer Engineering Center, University of Akron, Akron, Ohio, 44325

The characteristics of screw extrusion of rubber compounds have been investigated using screw pulling experiments with compounds with markers (black and white strips) and determining extrusion rate - pressure rise experiments (screw characteristic curves). These experiments reveal that transverse circulating flows begin near the hopper and appear to continue through the screw. A simple uniform single flighted screw exhibited starved feeding except in regions near the die. The characteristics of flow in a venting screw are also investigated.

13h30   (5/5)   EXPERIMENTAL AND THEORETICAL APPROACH OF THE EXTRUSION OF RUBBER
COMPOUNDS WITH A TWO-STAGE SCREW, B. Vergnes, N. Bennani, Centre de Mise en Forme des Matériaux, UA 852, Ecole des Mines de Paris, 06560 Valbonne, France, and C. Guichard, Laboratoire de Recherche et de Contrôle du Caoutchouc et des Plastiques, 60 rue Auber, 94400 Vitry, France.

The extrusion of EPDM compounds with a two-stage vented screw is studied. Experimentally the pressure and temperature were measured at the end of each stage for different geometries and different processing conditions (screw speed, thermal regulations ..). Extracting the screw from the barrel allowed to observe the partially filling of the different screw sections. The viscosity of the EPDM compounds was measured using capillary and excentred plates rheometers, in the range of 60-100°C and $10^{-1} - 10^3$ $s^{-1}$.

We compute the flow in each stage of the screw, assuming a power-law pseudoplastic behaviour for the rubber compound. The evolution of the pressure and the temperature all along the screw, as well as the filling of the second stage are then obtained. Different screw geometries were experimentally tested : it appears that there is a good accordance between experimental and theoretical results only if we take into account a slip velocity at the barrel wall.

13h55   (5/6)   MULTIDIMENSIONAL CONTROL OF EXTRUDATE DIMENSIONS WITH A SINGLE
ROLLER DIE, James F. Stevenson, Research Division, GenCorp, Inc., 2990 Gilchrist Road, Akron, OH 44305

A single roller die consists of a fixed plate die bounded on one edge by a rotating cylinder; material moves through the die by a combination of drag and pressure flow to balance the input flow rate from an attached extruder. The roller die/extruder combination allows independent control of two extrudate dimensions by manipulating two ratios involving the screw, roller, and line speeds.

Dimensional changes along the extrusion line were predicted by a simple model based on combined pressure and drag flow along the screw and within the roller die for an isothermal Newtonian fluid at steady state. The drawpath analysis using the same fluid model allowed for transients which gave predictions of substantial short-term variations in extrudate areas. An empirical nonlinear model for shape change due to swell (assumed constant) and drawdown allowed for nonproportional changes in thickness and width dimensions. These model equations, together with appropriate empirical constants, gave a simulation of line operation which was in good agreement with data that included transients and steady states for five sets of operating conditions. This experiment, which involved primarily screw and roller speed changes, resulted in opposed dimensional changes: a 10 percent increase in extrudate thickness and a 12 percent decrease in linear weight.

The model was used to conduct a parametric study of line operation for a tread profile in which material swell properties and ratios involving the screw, roller, and line speed were varied systematically. According to this model, a change in extrudate swell can be compensated exactly by altering operating conditions. The model was also used to investigate multivariable process control strategies.

CADGUM – A RUBBER INJECTION MOULDING SIMULATION AND MOULD
DESIGN PROGRAM,
W. Benfer, G. Menges, Institut fuer Kunststoffverarbeitung (IKV),
Pontstraße 49, D-5100 Aachen, West Germany

Processing difficulties in rubber injection moulding can already be discovered in the
planning stage by the use of adequate simulations. The program package CADGUM enables
the user to simulate the flow during the filling phase in the cavity, including a computer-
made filling pattern. Graphic presentations of velocities and pressure distributions can
also be obtained. To check the thermodynamic state of the material during the filling
phase, a computation of the flow-line of any arbitrary particle is implemented. Detailled
computing along such a line, including the influence of crosslinking to the material's
flow, yields the temperature-, velocity- and curing-ratio-profiles. The design of runner
systems for multi-cavity moulds is supported by a computation method, which considers
also dynamic effects and gate entrance pressure drop during the filling of any runner
system. Results are the dimensions of a dynamically balanced runner system, which effects
equal filling conditions in any cavity of the mould.
The description of curing reaction in a cross-section throught the moulding enables
the user to calculate the needed heating time.
Material data can be stored in a material data file, which contents rheological and
thermal properties as well as the composition of the mixture.

RECENT STUDIES ON DEGRADATION MECHANISM OF RUBBER VULCAN-
IZATES BY CHEMORHEOLOGY, Kenkichi Murakami, Chemical
Research Institute of Non-Aqueous Solutions, Tohoku
University, Katahira 2-1-1, Sendai 980, Japan.

The studies presented here should stimulate further research and applications in
areas where the lifetime of rubber vulcanizates may be controlled by means of additives,
chemical modifications, and synthesis. Though for rubber vulcanizates degraded at time
t, $f(t)=n(t)RT(\alpha-\alpha^{-2})$ is said to be applicable, this equation was found to be deviated
from the actual results after a critical degraded time. In the case of the sulfur-
cured ethylene-propylene terpolymer, the relationship between relative stress and time
was found to be expressed by $f(t)/f(0)=A \cdot e^{-k_1 t}+B \cdot e^{-k_2 t}+C \cdot e^{-k_3 t}$. The first two terms in
the right-hand side of this equation are due to typical interchange reaction, and the
third refers to cleavage at the crosslinkage.
A new simple method to determine the chain scission mechainsm of the oxidative
degradation of rubber vulcanizates was proposed. The method involoves the measurements
of oxidative stress decay and the change in sol fraction, which allow us to distinguish
whether scission occurs randomly along the mainchain, nearby crosslinks or at crosslink
sites.

08h30    (6/1)

MOLECULAR ENTANGLEMENT - ITS EFFECTS ON PROCESSING AND PROPERTIES OF RIGID ROD MOLECULAR COMPOSITES, D. R. Wiff*,[1] W-F. Hwang,[2] and T. E. Helminiak,[3] [1]Gen Corp/Research Division, 2990 Gilchrist Road, Akron, Ohio 44305, [2]DOW Chemical/Research Division, Midland, Michigan, [3]Air Force Wright Aeronautical Labs (AFWAL/MLBP), Wright-Patterson AFB, Ohio 45433.

The molecular dispersion of the rigid rod polymer poly(p-phenylene-2, 6-benzbisthiazole) in the host flexible coil polymer poly(hexamethylene adipamide) was studied as a model thermoplastic rigid rod molecular composite. The thermoplastic matrix polymer was the commercially available Nylon 66 (Zytel 42). Holding the molecular weight of the flexible coil polymer matrix constant, the molecular weight of the rigid rod reinforcement ($M_w$) was varied. How this molecular weight affected the flow properties and thus the processing of these rigid rod molecular composites will be discussed with regard to $M_w$ and composition. Mechanical properties of processed materials and ways taken to enhance the entanglement and dispersion will be presented.

08h55    (6/2)

FLOW-INDUCED ORIENTATION OF A THERMOTROPIC LIQUID CRYSTALLINE COPOLYESTER, K. Fujiwara, Idemitsu Petrochemical Co., Ltd., 3-1-1 Marunouchi, Chiyoda, Tokyo 100, Japan, M. Takahashi, and T. Masuda, Department of Polymer Chemistry, Kyoto University, Kyoto 606, Japan.

The processing-structure-property relationships for a thermotropic liquid crystalline copolyester synthesized from poly(ethylene terephthalate) and p-hydroxybenzoic acid were investigated.  Solid filaments prepared by capillary extrusion and spinning of the liquid crystalline polymer melts in the different conditions; varing temperature, shear rate, extension ratio etc.  The structure of filaments in the solid state was analyzed by WAXS, scanning electron microscope(SEM), and polarizing photomicroscope.  The mechanical behavior (tensile modulus, strength and ultimate elongation) was determined by tensile stress-strain measurements.  The experimental results have shown that the most dominant process for orientation of the liquid crystalline copolyester is the elongational flow deformation rather than the shear.

09h20    (6/3)

PROCESS - PROPERTY RELATIONSHIPS OF A WHOLLY AROMATIC COPOLYESTER RESIN, J.J. Duska, F. Scardiglia and N.D. Field, Dartco Manuf. Co., Augusta, GA, USA.

Copolyesters of para-oxybenzoyl and oxybiphenylene terephthaloyl units produces high temperatures, high performance materials which can be described as rigid rod polymers, liquid crystalline in nature, self-reinforcing when cooled from the melt. Parts molded from these materials are composed of highly compacted fibers that have a morphology not unlike that of a composite structure.  Three grades of commercially available resin (unfilled, 50% glass filled and 50% talc filled) will be analyzed for process/property relationships.  The paper will evaluate physical properties of the polymer as a function of mold and barrel temperature settings, injection speed and injection pressure.  A correlation will be presented to describe the interactions of the studied variables.

09h45 (6/4)

RHEOLOGICAL PROPERTIES OF THERMOTROPIC LIQUID CRYSTALLINE AROMATIC COPOLYESTERS, Zhenglong Zhou, Xiuge Wu and Meirong Wang, Dept. of Man-made Fibre Science and Engineering, China Textile University, Shanghai, P.R. of China.

A series of thermotropic liquid crystalline polyesters based on p-hydroxybenzoic acid, naphthalene dicarboxylic acid, hydroquinone diacetate and polyethylene tere-phthalate were prepared via melt polycondensation. The anisotropic melts were studied by means of TOT, DSC, SEM, X-ray diffraction and rheological methods. It was found that the copolyesters in the mesomorphic state exhibit shear-thinning behaviour drastically and the experimental results indicate that the non-Newtonian Index n is in the range of 0.17-0.50, the flow-activation energies $\Delta E_\eta$ are 71.0-43.5 kcal/mol over the shear rate of $10-1000 s^{-1}$ at temperature 225-270°C; and the mesomorphic copolymers are readily crystallized and oriented during processing, resulting in high tenacity, high orientation as-spun fibers.

10h30 (6/5)

STRUCTURE FORMATION OF LIQUID CRYSTALLINE POLYMERS AFTER CESSATION OF STEADY FLOW, T. ASADA, Department of Polymer Chemistry, Kyoto University, Kyoto, 606, JAPAN.

As is commonly known, polymer liquid crystals usually form complex textures, which depend strongly upon their mechanical and thermal histories, the nature of the surface of the wall, and other factors. To investigate the relation between the mechanical history and the structure achieved, re-formation of textures of polymer liquid crystals after cessation of steady flow at various rate have been studied by Rheo-optical techniques. The results mainly obtained for lyotropic polymer liquid crystals( rod-like and semi-rigid polymers) by polariz-ed-light method and spectroscopic method will be introduced. The results will be interpreted by taking into account the effect of disclinations.

10h55 (6/6)

PROCESSING OF VIRGIN ULTRAHIGH MOLECULAR WEIGHT POLYMERS – AN ALTERNATIVE ROUTE TO HIGH PERFORMANCE MATERIALS, Paul Smith, E.I. du Pont de Nemours & Company, In. Central Research & Development Department, Experimental Station, Wilmington, Delaware 19898 USA

High modulus fibers and films currently are produced from medium molecular weight polymers employing a variety of techniques, such as melt-spinning/drawing, solid-state extrusion, etc... Production of high strength polymeric fibers (tenacity 2 GPa) requires high molecular weight polymer. This material can only be drawn to sufficiently high draw ratios after the macromolecules are disentangled. Until now, dissolution followed by crystallization has been the sole explored route for the preparation of high molecular weight polymers with adequate drawability. An obvious drawback of this solution precipitation technique is the relatively large quantity of solvent that needs to be processed (typically) 10 kg solvent/kg polymer).

The present paper describes alternative routes to high performance polymers that do not require the technologically difficult dissolution of high molecular weight material and the expensive solvent recovery. The technique is based on the synthesis of virgin high molecular weight polymer under conditions where the macromolecules are produced directly in a disentangled conformation. Such as-polymerized material can readily be drawn or extruded into high strength filaments or films.

FABRICATION OF HIGH MODULUS FILMS BY SOLID STATE ROLLING, D. M. Bigg, E. G. Smith, M. M. Epstein, and R. J. Fiorentino, Battelle Columbus Division, 505 King Avenue, Columbus, Ohio 43201.

Solid state rolling of semi-crystalline polymers represents a high-speed process for producing oriented, high modulus films, tapes, and sheets. The important process variables include roll temperature, thickness of the initial sheet, roll speed, take-up tension, roll diameter, and initial morphological state of the polymer. Roll temperature controls both the extent of maximum deformation and the rate of rolling. A minimum temperature exists for each polymer below which the orientation process is sharply limited. This condition is similar to the limitation present in the hydrostatic process, in which the alpha crystallization temperature limits the orientation process. Roll speeds as high as 20 m/min have been realized. It is apparent that film thickness and thickness reduction ratio have a strong effect on the ultimate rolling rate. The process, as currently practiced, is adiabatic, and, therefore, heat transfer limited. The take-up tension influences the extent of orientation in the amorphous phase of the polymer. This in turn affects its thermal and chemical stability. The effect of roll diameter is to limit the extent of thickness reduction by causing roll-film slippage when the roll diameter to thickness ratio is below some as yet undetermined value. The initial morphological state of the polymer affects the amount of crystalline deformation possible, the surface texture of the rolled film, and the tear resistance of the oriented film.

EQUIBIAXIAL, HYDROSTATIC DEFORMATION OF ISOTACTIC POLYPROPYLENE, THE SOLID STATE: A RIGID-PLASTIC MODEL, Ravi F. Saraf and Roger S. Porter, Polymer Science and Engineering Department, University of Massachusetts, Amherst, Massachusetts 01003.

Equibiaxial, hydrostatic deformation of isotactic polypropylene (i-PP) of an intermediate $M_w$ of $2.9 \times 10^5$ has been achieved by uniaxial compression. The process consists of two circular cylinders at the draw temperature ($T_{DR}$) which are axially aligned. Independent measurement of load (*i.e.*, stress) and displacement (*i.e.*, strain) is made during the course of the deformation. The data corrected for machine compliance is compared to a theoretically determined stress-strain behavior.

A model assuming a rigid-plastic deformation is proposed to predict the stress-strain behavior of the equibiaxial process, for thickness reduction up to and higher than 700% for various $T_{DR}$ and draw rates. The model quantitatively gives insight into the importance of the Bauschingler effect which is further related to the influence of hydrostatic pressure on the deformation process. A more detailed analysis of the data gives a quantitative estimation of yield behavior in both compression and tension by a single experiment. A systematic variation in $T_{DR}$ (*i.e.*, 30-140°C) and ram speed (0.01, 0.1, and 0.25 in/min.) is studied to understand the plastic deformation behavior of i-PP under hydrostatic pressure.

MANUFACTURE OF HIGH MODULUS POLYPROPYLENE SHEET BY ROLL-DRAWING, P. Burke, G. C. Weatherly, and R. T. Woodhams, University of Toronto, Toronto, Canada M5S 1A4.

Self-reinforced thermoplastic sheet materials produced by tensile drawing, hydrostatic extrusion or rolling possess exceptionally large specific strengths and modulus values which frequently exceed those of the most advanced aramid and carbon fiber composites. In this study the roll-drawing technique has been applied to the manufacture of high modulus unidirectional polypropylene sheet materials from extruded billets. The results confirm that under optimum drawing conditions, draw ratios near 20 can be reached in a single pass to produce clear, transparent sheets with modulus values near 20 GPa and tensile strength values near 0.5 GPa. While the degree of ordering is far from perfect, the mechanical properties of the roll-drawn sheets are comparable to the performance of most advanced composites in the roll direction. For applications that require biaxial strength, it is necessary to laminate the oriented sheets together, as in the case of unidirectional fiber composites. In fact, it is shown that the theory of fiber reinforcement and laminate mechanics adequately describe the behavior of ordered thermoplastic polymer laminates.

**13h55  (6/10)**  ROLLTRUSION:  DOUBLE ORIENTATION PROCESSING AND MORPHOLOGY – PROPERTY RELATIONSHIPS FOR PLASTICS,  M.J. Shankernarayanan and J.H. Magill, School of Engineering, University of Pittsburgh, Pittsburgh, PA  15261, USA.

Commercial polyethylene (HDPE) and polypropylene (PP) have been converted to high strength, high modulus transparent plastics by a rolltrusion operation which is essentially continuous.  Mechanical properties have been enhanced X10 to X20 over the originally manufactured plastics.  Draw ratios of almost x30 for PE and x60 for PP have been obtained. These values should not be regarded as optimum.  We can do better.  Besides, morphological TEM, SEM, optical and orientational characterization studies (X-ray and birefringence) etc. have been made for samples produced under different processing conditions in order to optimize the process which has been applied successfully to several other plastics.

**14h20  (6/11)**  PREPARATION OF HIGHLY ORIENTED POLYMERS BY MICROWAVE HEAT-DRAWING, K. Nakagawa and M. Amano, NTT Ibaraki Electrical Communication Laboratories, Nippon Telegraph and Telephone Corporation, Tokai, Ibaraki, 319-11, Japan.

A microwave heat-drawing technique has been developed as a new process for preparation of highly oriented polymers.  This is based on an idea that the drawing stress is used effectively to orient molecular chains in amorphous and in defect regions within crystals, because these regions are selectively heated more intensely than crystalline regions by means of microwave heating.  This technique is useful for drawing large-section materials such as rods and tubes.

The technique has been successfully applied to polyoxymethylene rods, tube, and tapes.  The attainable tensile modulus and strength were about 60  GPa and 1.7  GPa, respectively.  The drawing conditions for high draw and high modulus has been examined.  The influence of the molecular weight and the precursor size on the drawing behavior and the resultant mechanical properties has been also investigated.  The method has been also used with other crystalline polymers such as poly(ethylene terephthalate), poly(vinyl alcohol) and poly(vinylidene fluoride).

**14h45  (6/12)**  SUPER-DRAWING OF AN ULTRAHIGH MOLECULAR WEIGHT POLYETHYLENE SINGLE CRYSTAL MORPHOLOGY USING SOLID-STATE EXTRUSION PROCESS, Tetsuo Kanamoto, Koji Tanaka, Masatomi Takeda,[1] and Roger S. Porter,[2] [1]Department of Applied Chemistry, Science University of Tokyo, Kagurazaka, Shinjuku-ku, Tokyo 162, Japan, [2]Materials Research Laboratory, Polymer Science and Engineering, University of Massachusetts, Amherst, Massachusetts 01003, USA.

In a previous study of solid-state extrusion of single crystal mats and powder of high density polyethylene, we have shown that the drawability increased greatly for a single crystal morphology over that of a melt-crystallized spherulitic form [*Polym. J.*, 11, 497 (1979)].  The result has been interpreted in terms of the specific morphologies of the samples and particularly the negligible number of chain entanglements and intercrystalline tie molecules in the single crystal morphology.  Thus, it was concluded that interfacial friction-adhesion between crystalline lamellae is the primary mechanism for drawing single crystals.  Based on these results, single crystal mats of ultrahigh molecular weight polyethylene were drawn by several techniques.  The two-stage drawing, *i.e.*, solid-state coextrusion developed by Griswold, Zachariades, and Porter [*Polym. Eng. Sci.*, 18, 861 (1978)] followed by tensile drawing, has given the most efficient draw and the highest draw (DR $\leq$ 350).  The superdrawn films exhibited tensile moduli $\leq$ 220 GPa and strength $\leq$ 5 GPa depending on draw ratio and polymer molecular weight.  Most recently, the solid-state extrusion has been successfully applied for processing the rigid chain polymer, poly(para-hydroxibenzoic acid) (Econol), to prepare continuous rods with the mechanical properties comparable to the commercial products molded by sintering (cooperation with Science University of Tokyo and Kobe Steel Industry).  These facts emphasize the important role of compressive force imposed on crystalline lamellae and aggregates during crystalline state deformation in achieving ultradraw, and suggest applicability of solid-state extrusion for processing rigid chain polymers.

15h30 (6/13)

ULTRADRAWN POLYETHYLENE: DETERMINATION OF MOLECULAR DYNAMICS, Saroj K. Roy, R. St. John Manley, Pulp and Paper Research Institute of Canada, and Department of Chemistry, McGill University, Montreal, Quebec, H3A 2A7, and Thein Kyu, Polymer Engineering Center, The University of Akron, Akron, Ohio 44325, U.S.A.

The $\alpha$, $\beta$ and $\gamma$ relaxations of melt-crystallized and gelation-crystallized ultra-high molecular weight polyethylene ($\overline{M}_w \cong 6 \times 10^6$) UHMWPE, were investigated by dynamic mechanical methods. The melt-crystallized UHMWPE (crystallinity $\simeq$ 55%), showed pronounced $\alpha$, $\beta$ and $\gamma$ relaxation peaks. However the gela-crystallized sample (crystallinity $\simeq$ 90%), exhibits less pronounced $\alpha$ and $\gamma$ peaks and the $\beta$ peak is not discernable. It is concluded that the $\beta$ relaxation must be associated with the molecular motions of the folded chains located at the surface of the lamellae. For the gelation-crystallized samples the $\gamma$ relaxation disappears completely with extensive stretching, indirectly suggesting that this $\gamma$ process may be related to the local motions of chain segments located in the amorphous regions. The $\alpha$-relaxation in the gelation-crystallized UHMWPE is sharper as compared with that in the melt-crystallized sample. The strength of the $\alpha$ relaxation continues to decrease with stretching while shifting to higher temperature, indicating that the contribution of the $\alpha_2$ process becomes dominant over that of the $\alpha_1$ process with increasing drawing. This may be associated with the inability of crystal grain boundary relaxation or crystal orientation relaxations to occur in such highly crystalline (in excess of 96%) and highly oriented ($f_c \simeq$ 1) materials.

15h55 (6/14)

NEW CONCEPTS FOR ENGINEERING THE MECHANICAL PROPERTIES OF POLYMERS, A.E. Zachariades and B. Chung, IBM Almaden Research Center, 560 Harry Road, San Jose, California 95120-6099

Anisotropic polymer morphologies with enhanced tensile properties have been pursued with flexible and semi-rigid polymers using solid state deformation and melt or solution processes. The anisotropic morphologies are uniaxially oriented and therefore their mechanical properties are very directional. In recent studies, we have obtained polyethylene and polypropylene anisotropic morphologies with balanced mechanical properties by inducing flow crystallization in complex flow fields which were generated by superimposing simple flow fields of different symmetries or under oscillatory flow conditions. In this report, we shall discuss the effect of superimposed oand/or oscillatory flow fields on the molecular orientation and the directionality of the mechanical properties of melt extruded and injection molded polymers.

16h20 (6/15)

MECHANICAL PROPERTIES OF A POLYURETHANE IONOMER. W. S. Williams and C. L. Beatty Department of Materials Science and Engineering University of Florida Gainesville, Florida 32611

The properties of a polyurethane ionomer were studied as a function of water content. The polymer studied was manufactured by Wilmington Chemical Corporation and initially contained 30-40% polymer and 60-70% water. Physical property data was obtained via the use of an Instron Tensile Testing machine and a Polymer Laboratories Dynamic Mechanical Thermal Analyzer. The failure stress and strain both decrease with increasing water content. The failure stress changed significantly from 160 psi at 10.2% water to 1811 psi at 0.6% water. The failure strain however only changed by approximately 30% from 10.2 to 0.6% water. The glass transition temperature decreased in a non-linear fashion with increasing water content. Furthermore, we see evidence of a mechanical relaxational process between the soft segment and hard segment presumably due to water plasticized ionic domains. Composites were formed by mixing glass beads (classified by sieving) with different surface modifications into the polyurethane ionomer. Changes in modulus, glass transition temperature, relaxation strength and stress-strain properties of the composites will be discussed.

## THE TRANSPORT OF WATER IN
## POLY ARYL ETHER ETHER KETONE*

Michael A. Grayson and Clarence J. Wolf
McDonnell Douglas Research Laboratories
St. Louis, MO 63166

The solubility and diffusion of water in high-performance resins is of major interest because of the potentially deleterious effects of water on the long-term chemical and mechanical properties of composites made from them. The transport of water in neat poly aryl ether ether ketone (PEEK) coupons (2-6 mm thick) were investigated by gravimetric and mass spectrometric methods to determine the effect of moisture on both the long-term stability of PEEK resins and composites and the effect of moisture during processing. The solubility of water increases from 0.44 wt% at 35°C to 0.55 wt.% at 95°C; the temperature coefficient is 8 kJ/mol (1.9 kcal/mol). The diffusion follows Fick's law (Case I) and the diffusion processes for sorption, desorption, and resorption at 35°C, 65°C, and 95°C are, within experimental error, the same. The activation energy for diffusion is 42.7 kJ/mol (10.2 kcal/mol).

A NOVEL STRESS-INDUCED NYLON MORPHOLOGY FOR TEXTILE YARNS, John H. Southern, Richard W. Miller, and Walter J. Nunning, Monsanto Fibers and Intermediates Company, P.O. Box 12830, Pensacola, Florida 32575

Increased Nylon 66 molecular weight textile fiber produced at spinning speeds in excess of 2000 meters per minute has a novel morphology uniquely suited for friction false twist texturing. Various spin line measurements in conjunction with X-ray defined fiber morphology are consistent with a stress-induced crystallization phenomenon. Significant process/structure/property relationships are defined.

15h30  (7/1)        SOLUTION SPINNING OF ULTRA-HIGH MOLECULAR WEIGHT POLYETHYLENE,
                    A.J. Pennings, G. ten Brinke, R.J. van der Hooft, A.R. Postema and
                    W. Hoogsteen, Department of Polymer Chemistry, University of
                    Groningen, Groningen, The Netherlands.

     In recent years there has been a steadily increasing research activity in the field of
producing super-strong polyethylene fibers by solution spinning of ultra-high molecular weight
polyethylene (UHMPE).  Developments so far have led to processes which are capable of making
fibers with tensile strengths at break of 5 and even 8 GPa and Young's moduli of about 200 GPa
These properties have been attained by optimizing the conditions for spinning semi-dilute so-
lutions of UHMWPE in paraffin oil and by careful extraction of the oil from the gel-filament
with hexane and subsequent hot drawing of the remaining porous  fiber.
     The gel filaments after spinning appear to be composed of large lamellar crystals which
are strung together by thin fibrils.  At higher extrusion rates and wind-up speeds the en-
tanglement network apparently splits up into fibrillar flow units which upon cooling solidify
as shish-kebab structures.  The diameter of the fibrillar units between the platelets in-
creases with spinning temperature and with decreasing stretch rates.  Increasing fibril diame-
ter means also increase in the tensile strength of the macrofiber and the origin of the high
strength has therefore been traced back to the transformation of the entanglement network in
converging flow into fibrillar units with a shish-kebab morphology.  Structural changes as
well as morphological features in relation to the spinning conditions will be discussed.
     Adsorption of molecules on die walls and flow instabilities during spinning affects the
fiber structure and properties.  These phenomena will also be discussed in detail.


15h55  (7/2)        THE MECHANISM AND CHARACTERISTICS OF DRY-JET WET-SPIN-
                    NING OF ACRYLIC FIBERS, Baojun Qian, Ding Pan and
                    Zhenqiu Wu, Man-made Fiber Research Association, China
                    Textile University(Formerly East China Institute of
                    Textile Science and Technology), 1882 Yanan Road, West,
                    Shanghai, P.R.C.

     The jet stretch by the dry-jet and the immersion-jet spinning was first
compared.  In the case of dry-jet spinning, the key to the prevention of void
formation was found to be the reduction of the coagulation rate through the
formation of a thin, dense, hydrophobic cuticle which is relatively less per-
meable to water and more permeable to solvent.  This increase of the ratio
$D_s^*/D_n^*$ was experimentally verified in great detail under a variety of spinning
conditions like jet stretch, dope concentration, bath concentration and bath
temperature.  It will guard against phase separation which will lead to voids
formation.  Unsymmetrical cross-section profile and puncturing of liquids
into the fiber to form voids are all connected with the rate of diffusion.
Finally, the morphological structure of the two types of fibers as studied by
optical methods, electron microscopy and small angle X-ray scattering, all
confirm the correctness of the above view.

16h20   (7/3)   FLOW VISUALIZATION, FLOW INDUCED CRYSTALLIZATION AND HIGH SPEED SPINNING OF POLY(ETHYLENE TEREPHTHALATE) PET FIBERS, John A. Cuculo and Dae Woo Ihm, North Caroline State University, Department of Textile Chemistry, Raleigh, North Carolina 27695-8302.

The objective is to generate in the polymer melt using a converging die geometry an elongational flow regime capable of aligning and orienting molecules into the extended chain conformation and crystallize them in this arrangement before significant chain relaxation occurs. This should result in ultraoriented fibers from ordinary melt spinnable polyester polymers. The combination of flow-induced orientation, elements of the high-speed spinning technique and polymer structure/relaxation parameters may be matched to favor interaction and crystallization of at least a certain proportion of the molecules, in a mode approaching the "continuous crystal" structure. Calculations made from our most recent work indicate that polymer relaxation time is long enough for the fiber to cool below its crystallization temperature and thereby lock in the orientation. This is believed to be the beneficial link between flow-induced ordering and high-speed spinning. Substantial evidence suggests that fibers so formed possess unique properties, for example, tenacities and moduli which approach more closely the theoretical limits. A combined experimental and theoretical approach was used. Flow visualization within and immediately adjacent to the die exit provided experimental data to describe the flow field while computational modeling provided the theoretical basis for comparison. The fiber morphology and physical properties were related to the processing conditions.

16h45   (7/4)   ORIENTATION AND RESIDUAL STRESS DEVELOPMENT IN THE MELT SPINNING OF THICK FILAMENTS, Ho-Jong Kang, James L. White, Polymer Engineering Center, University of Akron, Akron, Ohio, 44325

The development of birefringence in melt spinning of filaments of polystyrene and polycarbonate was investigated. The mean birefringences vary linearly with the spinline stress. Birefringence distributions are determined across the cross-section of filaments. The birefringence is a maximum at the outer radius and decreases to a minimum at the fiber axis. The variation of birefringence has been modelled by simultaneously solving heat and force balances. A tendency to crystallization in the polycarbonate fibers was observed. The development of thermal quench stresses in thick filaments has also been modeled. Stresses in thick filaments can exceed the magnitude of the tensile strength.

17h10   (7/5)   FIBER ORIENTATION IN COMPLEX FLOWS, G.G. Lipscomb and Morton M. Denn, Center for Advanced Materials, Lawrence Berkeley Laboratory, Berkeley, CA 94720 USA.

A continuum theory for fiber suspensions that accounts for the effect of the presence of the fiber on the flow field is applied to flow in contractions and expansions. The presence of the fiber causes a qualitative change in the kinematics. Large recirculating vortices observed in entry flow experiments by Hur, Boger, and Denn are predicted quantitatively.

08h30 (7/6)   STRUCTURE DEVELOPMENT IN MELT SPINNING AND INJECTION MOLDING
AROMATIC POLYCONDENSATES, Sang S. Song, Chang M. Hsiung,
Mukerrem Cakmak, James L. White, Polymer Engineering Center,
University of Akron, Akron, Ohio, 44325

The development of orientation and crystallinity during processing of a range of
aromatic polycondensates have been investigated. These include crystallizable polymers
such as PPS, PPO and PEEK, and those that remain amorphous such as PES and PEI. Anneal-
ing studies indicated that PPS, PPO and PEEK resemble PET in their thermal characteris-
tics.       Fibers spun from all polymers were found to remain amorphous at low to
moderate spinning speeds. Birefringences measured correlated linearly with the spin-
line stresses.

The structure developed in injection molded PPS tensile bars depends on processing
conditions; mold temperature, injection pressure, injection speed. Low mold temperatures
(below 70°C) were found to produce uniformly amorphous structures. However, at mold
temperatures above Tg (85° – 110°C) complex structural gradients across the thickness
direction were observed. In general, skin layers remained amorphous and sparsely scat-
tered spherulites were observed in the core. Depending on other process variables,
injection pressure and speed, an additional intermediate layer of shear crystallized
band was also observed between an amorphous skin and core. These structures are quali-
tatively explained in terms of cooling rates and stress distributions occurring in the
process.

08h55 (7/7)   INVESTIGATION OF A MANDREL PROCESS TO CONTROL THE PROPERTIES
OF POLY (P-PHENYLENE TEREPHTHALAMIDE) FILMS, "John Flood,
John F. Fellers, Materials Science and Engineering, The
University of Tennessee, Knoxville, TN  37996-2207

Kinematic and rheological considerations have been used to design and analyze
the processing steps for obtaining biaxial chain orientation in poly (p-phenylene
terephthalamide) (PPDT) films. A semi-quantitative approach to the mandrel design
allows one to predict the type and degree of molecular orientation obtained. For the
case of PPRD dissolved in $H_2SO_4$, the basic steps are extrusion of the liquid crystalline
solution through an annular die followed by expansion and elongation flow over a
mandrel. The mandrels used include conical, hyperbolic and ogival shapes. Molecular
orientation as well as mechanical properties were found to be dependent on mandrel
shape and presence. Wide angle x-ray diffraction (WAXS) techniques using white-Spruiell
orientation factors, pole figures and WAXS patterns were used to characterize the films.
Mechanical properties as well as the above techniques indicate a high degree of biaxial
orientation can be obtained with a bias in certain film directions depending on the
mandrel used. Tensile strength and Young's modulus values were found to be on the order
of 30,000 psi and one million psi respectively. They also can be equally distributed in
the film plane depending on mandrel shape. White-Spruiell orientation factors were as
high as 0.49 and 0.5 for $f_1^B$ and $f_2^B$ respectively. Scanning electron microscopy was used
to observe the film superstructure as a function of processing conditions. All films
exhibited a skin-core structure. Uniaxially drawn films are fibrillar while the biax-
ial films appear to be more homogeneous.

09h20 (7/8)   STRETCHING  INSTABILITIES  IN  THIN  FILMS  OF  POLYETHYLENE
TEREPHTALATE.  C. G'sell and A. Marquez-Lucero, Ecole des mines
Nancy, France

PET films were stretched under plane strain conditions and the distribution of
local strains was investigated in-situ. It was thus shown that necking develops
perpendicular to the tensile axis at room temperature, conversely at 100°C, the
deformation is highly homogeneous. At slow stretching rates, the effects of stress
triaxiality control the shape of the thickness profile. At fast rates, the effects of
self-heating are predominent, a close simulation of the process is obtained by means of a
finite difference computation method, taking into account the intrinsic constitutive
equation of the material and the mechanical or thermal boundary conditions.

SCANNING ELECTRON MICROSCOPY STUDIES OF POLYMER MELT DEVOLATILIZATION, Y. Talmon, R. Albalak, M. Rumack and Z. Tadmor, Department of Chemical Engineering, Technion-Israel Institute of Technology, Haifa 32000, Israel.

Strands of molten polystyrene were extruded into a vacuum chamber and quickly frozen. The polystyrene contained unreacted styrene of the order of 5000 ppm. Sample taken from the frozen strand surfaces and core were analyzed by scanning electron microscopy. Results reveal a rich variety of morphological features generated by the apparent cavitational or boiling type devolatilization mechanism.

STRUCTURE FORMATION IN HYDROXYPROPYL CELLULOSE, Thein Kyu and Parthe Mukherjee, Polymer Engineering Center, The University of Akron, Akron, Ohio 44325, U.S.A.

Hydroxypropyl cellulose (HPC) exhibits lyotropic liquid crystalline character in the presence of selective solvent. The material also undergoes phase transitions from solid to nematic then to isotropic states during the course of heating. When the HPC material is subjected to squeezing flow in the thermotropic nematic region, layered flow takes place. The rod-like structures align with respect to each other in both tangential and radial directions. Uniaxial shearing is also applied to HPC in lyotropic state which leads to orientation development of rod structures in perpendicular direction to the external stress. The pehnomena of self-polarization and optical diffraction are characterized by various optical methods such as optical microscopy and laser light scattering. The results are analyzed in terms of the paracrystalline theory.

STRUCTURE DEVELOPMENT IN POLYMER PROCESSING, Masao Horio. Institute for Chemical Research, Kyoto University, Gokasho, Uji-City, Kyoto, 611 Japan.

Polymers are processed mainly in the form of solution or melt to be converted into solid materials with desired shapes. In the course of solidification and subsequent processings, the selective planar orientation of polymer crystal can happen. This will be demonstrated with sheets and/or fibers of cellulose, nylon 6, polyethylene, poly(ethylene terephthalate), poly(p-phenylene terephthalamide) and so forth. The mechanism by which the planar orientation takes place can be interpreted for some polymers in terms of the specificities of the crystalline planes concerned. The properties of products relative to the planar orientation will be described.

A TENSOR DESCRIPTION TO CHARACTERIZE AND PREDICT FIBER ORIENTATION IN SHORT FIBER COMPOSITES, Suresh G. Advani and Charles L. Tucker III, Department of Mechanical and Industrial Engineering, University of Illinois at Urbana-champaign, Urbana, IL 61801

The fiber orientation pattern in short fiber composites is the primary feature of the microstructure which controls the physical and mechanical properties of the material. The orientation state of the fibers at any point in the composite plays the role of a structural state variable. Hence, there is a need for concise, quantitative description of the fiber orientation state. Two sets of even-order tensors are defined which describe the distribtuion of orientation of fibers in a short fiber composite. These tensors offer a description which is concise, unambiguous and independent of coordinate system. The description is valid for three dimensions and can be specialized to two dimensions. Several theories of the rheological properties of fiber suspensions and the mechanical properties of short fiber composites are shown to contain forms of these orientation tensors. Equations with orientation tensors as primary variables have been derived up to the fourth order, based on Folgar and Tucker's model for concentrated suspensions, to predict the orientation state from processing conditions. Numerical predictions of orientation states using tensor and distribution function descriptions are compared in various flows. The results show that the orientation tensors can efficiently and accurately describe fiber orientation in flows with intermediate or high interactions among fibers, a situation typical of composite materials.

11h45  (7/13)

MECHANISM OF COOLING STRESSES BUILD-UP IN INJECTION MOLDING OF THERMOPLASTIC POLYMERS G. Titomanlio*, M . R . Kamal**, V. Brucato*

*Istituto di Ingegneria Chimica, Università di Palermo, Palermo, Italy
**Chemical Engineering Department, McGill University, Montreal, Canada

It is well known that cooling stresses distribution is largely influenced by injection molding operating conditions such as holding pressure and time. Very little attention was however devoted to the understanding of features peculiar of the injection moldng operation which contribute to the mechanism of cooling stresses build-up. Indeed experimental data are often discussed on the basis of Aggarwala and Saibel model which was developed for free quenching.

A model for cooling stresses build-up is proposed in this work, identifying the role of both pressure history in the melt during sample cooling and interaction between sample and mold with reference to a simple rectangular cavity.

Numerical calculation of the final cooling stresses distribution as affected by different histories of melt pressure were performed with the aim of evidentiating the effect of different holding pressures and times. The result favorably compare with literature experimental indications.

# SYMPOSIUM No. 8: FIBER SPINNING AND DRAWING OPERATIONS
## (CHAIRMAN: J.E. SPRUIELL)

10h30　(8/1)

MELT SPINNABILITY OF HIGH FLUIDITY POLYPROPYLENE :
PROPERTIES OF THE FIBRES
*Alain Michel,*Catherine Prost*and Guy Nemoz***
 * Laboratoire des Matériaux Orbaniques – C.N.R.S.
BP 24 – 69390 Vernaison, France
** Institut Textile de France Lyon – BP 60 –
69130 Ecully, France

　　　　To study the spinnability of polypropylene with respect to its melt-index, three samples have been prepared by thermal degradation of a commercial polymer peroxidized with the help of an air-ozone gas mixture in a fluidized bed. The molecular weight and melt rheological behaviour (separation of viscous and elastic effects) have been characterized. The fibers have been elaborated at the pilot scale. For each sample　a range　of temperature has been determined for its spinnability. When the molecular weight in weight decreases from 330 000 to 170 000 the temperature of spinnability decreases of about 50°C. The orientation of the polymer chains in the amorphous phase has been characterised from sonic modulus measurements and the orientation function of the polymer chains in the crystalline phase has been determined from wide angle X-rays diffraction diagrams. These orientation functions increase as the melt drawdown and strech ratios raise.
　　　　This tendancy is all the more accurate as the molecular weight is lower. Furthermore modulus and tenacity increase as orientation functions of amorphous and crystalline phases raise.

10h55　(8/2)

Steady Spinning of Viscoelastic Liquids
Zhao Chen and A.C. Papanastasiou, Department of Chemical
Engineering, The University of Michigan, Ann Arbor, Michigan 48109

　　　Isothermal fiber spinning of viscoelastic liquid is analyzed by means of the Curtiss-Bird integral constitutive equation for polymer melt, Galerkin/finite element method and Newton iteration.　The analysis accounts for elongational and shear prehistories, spectrum of relaxation times and specified draw ratio or drawing force (i.e. boundary conditions). The results of the analysis are compared with experimental data from the literature.

11h20　(8/3)

MAXWELL VISCOELASTICITY IN DYNAMIC MELT SPINNING
MODEL, S.KASE, Kyoto Institute of Technology, Sakyoku
Matsugasaki, Kyoto 606, Japan.

　　An upper convected Maxwell constitutive equation was tested in a thin filament theory melt spinning model for steady state and perturbation transient behavior. The viscosity factor in the model was assumed to have a power law dependence on extension rate and an Arrhenius dependence on filament temperature. Effects of air drag, inertia, gravity and surface tension are also included.
Novel findings are:
i) In an instantaneous deformation Maxwell fluids behave as rubber-like elastic
　solids.
ii) Maxwell model predicts an instantaneous die swell which diminishes with
　increasing spinline tension at the spinneret exit to agree with Bogue.
iii) If the flow within the spinneret is fixed unchanged then the upper end
　spinline diameter must vary with tension.
iv) Under iii) the "unattainable draw ratio" predicted by a fixed upper end
　filament diameter disappears and filament tension remains finite as far
　as the take-up speed is finite.
v) Step responses in perturbation transients well demonstrate the spring and
　dashpot nature of the Maxwell model.

ROUTE TO CHAIN-EXTENDED POLYMERS, P.J. Lemstra, (Einsdhoven University of technology, Netherlands)

Amonst the various developments in the area of high-performance fibres, two major routes can be discerned which are completely different in respect to the starting or base materials:  intrinsically rigid versus intrinsically flexible macromolecules.  The prime examples of rigid chain polymers are the aromatic polyamides marketed under the trade names of Kevlar (DuPont) and Twaron (AKZO/ENKA).  The tensile properties of Kevlar-49 are: tenacity appr. 3 GPa and a corresponding modulus of about 130 GPa.  During the past two decades an impressive progress has been made towards the development of high-strength/high-modulus structures based on flexible polymers.   To achieve chain-extension and alignement in this case, solution-spinning/ultra-drawing of high-molecular-weight-polyethylene (PE) proved to be a major break-through.  The basic principles of this process, now often referred to as gelspinning, were established in the late seventies at DSM Central Research.  At present, oriented PE structures possessing moduli of up to 150 GPa and corresponding tenacities of 3-4 GPa can be produced continuously.  Although PE features as the prime candidate in these developments, other flexible polymers have been examined as well and encouraging results have been obtained. The origin and development of various techniques and processes to produce high-strength-high-modulus structures based on flexible polymers will be reviewed and characteristic properties of chain-extended flexible polymers will be presented.

13h30    (8/5)                    A CONTINUOUS DRAWING PRODESS FOR PREPARING A HIGH PERFORMANCE POLYETHYLENE (PE) FIBER, T. Sakai, N. Okui, M. Takahiro, Tokyo Institute of Technology,  O-okayama, Meguro-ku,  Tokyo  and  T.  Takahashi, Showa Denko Co., Chidori-cho, Kawasaki-ku, Kawasaki, Japan.

     Recently many researchers proposed various types of methods for producing a high modulus, high tenacity PE fiber.  Gel spinning method with the ultra high molecular weght PE is considered as the most favarable one  to  manufacture  the high  modulus,  high  tenacity  PE  fiber  practically.  However,  even the Gel spinning method is a time consuming procedure.
     We found that a PE sample with around 140,000 molecular weight also  gave such a high performance fiber as haveing elastic modulus of 130 GPa and tenacity of  3  GPa at room temperature.  The PE sample, MX0438 provided from Showa Denko Co., was formed into an original filament and then  the  original  filament  was drawn  by  the  continuous  draw  process.  The  points  were : 1) sharpness of molecular weight distribution  2) thermal histry  of  original  filament  during preparation   3)  geometry  of original filament 4) drawing conditions.  Details will be presented at the Symposium.

THE CHARACTERISTIC BEHAVIOR OF THE STRETCH-ORIENTATION ZONE DURING HIGH-SPEED PET SPINNING, Gialin Wu, Tiao-sheng Kuan and Baojun Qian, Man-made Fiber Research Association, China Textile University(Formerly East China Institute of Textile Science and Technology), 1882 Yanan Road, West, Shanghai, P.R.C.

A theory is proposed to separate the on-line stress in the stretch-orientation zone during high speed PET spinning into two parts: the thermodynamically equilibrium or quasi-equilibrium stress associated with rubber elasticity and the non-equilibrium driving stress, which leads to coordinated movement of the macromolecular chains. A "viscosity coefficient of coordinated orientation($\eta_{co}$)" is defined. Precise and simultaneous measurements of the on-line tension, birefringence and diameter of filament by one single instrument were conducted at five spinning speeds ranging from 2200 to 4200 m/min. A physical model consisting of a dash pot placed in parallel with a Gaussian network was found to describe well the behavior of the stretch-orientation zone of high speed PET spinning. A stress-optical coefficient $C_{opt}=(7.25/T) \times 10^{-7}$ ($cm^2$/dyne·K°) was found. The equation correlating the stress, temperature, birefringence and velocity gradient is:

$$\sigma(x) = 98.50 \exp[2035/(T+273)] (dv/dx) + 1.34 \times 10^6 \, T \cdot \Delta n \,.$$

POLYBUTYLENE TEREPHTHALATE IN EXTENDED CRYSTAL CONFORMATION, M. H. G. Deeg, Celanese Research Co., 86 Morris Avenue, Summit, New Jersey 07901, U.S.A.

Fiber was spun from 100% polybutylene terephthalate (PBT) and blends of PBT/polyethylene terephthalate (PET). The spun fiber was drawn. As expected, the drawn (oriented) fiber from 100% PBT showed the characteristic plateau in the stress strain curve attributed to the alpha/beta crystal transition. Fiber from blends with up to 25% PET showed no plateau. The drawn fibers were subjected to a hot relax step after which the stress strain curve was that expected for PBT.

To determine if a true conformational difference was present between the drawn and thermally relaxed samples, wide angle x-ray diffraction patterns were determined. These show PBT restrained in a different crystal conformation in the as-drawn state than after relaxation. By adding relatively small amounts of PET to PBT, it is possible to produce a fiber which contains PBT frozen in the extended (beta) crystal conformation.

ON-LINE STUDIES AND COMPUTER SIMULATION OF THE MELT SPINNING OF NYLON-66 FILAMENTS, K. F. Zieminski and J. E. Spruiell, Materials Science and Engineering, The University of Tennessee, Knoxville, Tennessee 37996-2200.

A mathematical model integrating the equations of continuity, motion and energy along with molecular orientation and crystallization processes was developed for the investigation of stress-induced crystallization phenomenon during the high speed melt spinning process. The model consists of a set of ordinary differential equations which describe the diameter, velocity, temperature, birefringence and crystalline index profiles as a function of the processing conditions (extrusion, temperature, mass throughput, take-up speed, cooling conditions, etc.) and the physical properties of the polymer (density, molecular weight, etc.). This model was applied to the monofilament spinning of a 12,000 molecular weight nylon-66. The predicted diameter, birefringence and temperature profiles were compared to experimentally obtained profiles on a running threadline at spinning speeds from 2000 to 7000 m/min.

# SYMPOSIUM No. 9: POLYMER PROCESSING RHEOLOGY
## (CHAIRMAN: P.J. CARREAU)

10h30    (9/1)        ON-LINE RHEOMETERS AND PROCESS CONTROL
                      J. M. Dealy, Department of Chemical Engineering
                      McGill University, 3480 University Street,
                      Montreal, Canada H3A 2A7

A wide range of process viscometers are available commercially, but rather few of these are suitable for use with molten plastics because of the high shear stresses, temperatures and pressures involved and because these melts are usually highly non-Newtonian and viscoelastic. On-line capillary rheometers are fairly widely used to monitor melt quality in the plastics industry, but these instruments have large time constants and measure only apparent viscosity. In order to make use of on-line rheometers for process control, it will be necessary to develop instruments that can measure a wider range of properties and that have shorter time constants. In addition, such process instruments must have modest cost, long-term reliability, and compact size. If such a product were available, it would open many opportunities to make processes more immune to batch-to-batch variations in resin characteristics and to operate processes closer to their optimal conditions. Some recent developments in the field of on-line instrumentation will be presented, and some possible control strategies for using on-line rheometers will be discussed.

                      THE INFLUENCE OF ELASTICITY ON THE MELT PROCESSING AND PROPERTIES
10h55    (9/2)        OF POLYMERS, Joseph M. Starita and Charles L. Rohn, Rheometrics, Inc.
                      One Possumtown Road, Piscataway, New Jersey 08854

For more than three decades, the elasticity of thermoplastics has been known to greatly influence their processing behavior and product performance. Considerable controversy and mis-understanding still exists on the effect of molecular structure, i.e., molecular weight, mole-cular weight distribution, and branching on elasticity of polymer melts. Furthermore, the influence of inorganic fillers and polymeric additives, multiphase blends on their rheology is poorly understood. One major cause for this lack of understanding is because the elasticity of polymer melts have not been properly measured. For example capillary die swell measurements have fallen far short of providing the necessary information to relate the data to structure and processing behavior of polymer melts. This is because the time-dependent effects of elas-ticity are far greater than the time dependent effect of viscosity. Dynamic rheological mea-surement gives more understanding of the elastic behavior of polymer melts. Theoretically, the storage modulus can be related to recoverable shear strain and normal stress difference. Examples of the relationship between storage modulus, and molecular structure will be given. Furthermore, the relationship between storage modulus, orientation and product performance will be reviewed. Also, examples of the effect of polyblends, interpenetrating polymer networks, and fillers on their melt elasticity will be discussed.

11h20    (9/3)        A NEW AUTOMATIC COMPUTERIZED DIE SWELL APPARATUS
                      M.R. Kamal and M.K. Samara, Chemical Engineering
                      Department, McGill University, Montreal, Canada

A computerized automatic die swell apparatus has been designed and constructed. The apparatus supplies both a digital and an analog output of the measurement regarding the diameter of the molten extrudate and its variation with time. Precautions are made to remove the effects of gravitational sag and temperature changes.

The apparatus was used in conjunction with an Instron Capillary Theometer to measure the extrudate swell behavior of five low density polyethylene resins, a short glass fiber filled polypropylene melt, and a thermotropic liquid crystal polymer.

11h45 (9/4)      ELASTIC FRACTURE OF POLYMERIC FLUIDS, R. Chan, R.K. Gupta and T.

Sridhar*, Department of Chemical Engineering, State University of
New York at Buffalo, Buffalo, New York, 14260

The elastic fracture of polystyrene solutions and melts was investigated using a plunger viscometer. The polymeric extrudate emerging from a circular capillary was photographed to determine the onset of fracture. An effort was made to relate this information to the shear stress at the capillary wall, the recoverable shear strain, the entanglement density and the geometrical parameters. It was found that narrow molecular weight polystyrenes dissolved in benzene fractured but the onset of fracture could not be predicted by available criteria. As opposed to this, highly concentrated (polymer volume fraction = 0.57) elastic solutions of a wide molecular weight distribution polymer showed no fracture. Nonetheless, this latter polystyrene fractured as a melt at a value of the wall shear stress less than that achieved in the solution runs. From an examination of the polymer rheology, it is concluded that the recoverable shear strain is the key quantity influencing the onset of elastic fracture. Also, the recoverable shear-shear rate behavior is different for the melt and the solution and it depends on the polymer molecular weight and its distribution as well as on the solvent used. The surprising absence of elastic fracture for highly viscoelastic solutions can be understood assuming existence of a critical value of the recoverable shear strain for fracture.

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                          Monash University, Clayton , Victoria 3168
                          Australia

13h30 (9/5)           RHEOLOGY AND BLOWN FILM FABRICATION WITH LLDPE,

A. V. Ramamurthy, UNIPOL Systems Department,
Union Carbide Corporation, P. O. Box 670,
Bound Brook, NJ 08805

LLDPE resins with narrow MWD are prone to melt fracture, Most commercial blown film fabrication with these resins utilize significantly wider die gaps than those with broad MWD branched LDPE resins for melt fracture-free-operation at acceptable rates. Wide gaps limit the bubble cooling efficiency and reduce the critical properties of the film product.

Results of a comprehensive study of the melt fracture behavior of LLDPE are presented. A criterion and a coherent mechanism for the observed extrudate irregularities with molten polymers in general, and LLDPE in particular, are discussed. Basic methods for the elimination of melt fracture are outlined, and demonstrated for LLDPE. Improvements in critical product properties with LLDPE, when processed through narrow die gaps, are summarized.

13h55 (9/6)      LINEAR    LOW    DENSITY    POLYETHYLENES    AND    THEIR    BLENDS:

PART 1. MOLECULAR CHARACTERIZATION, B. Schlund and L.A.
Utracki, National Research Council Canada, Industrial Materials
Research Institute, 75, de Mortagne Blvd., Boucherville, Quebec, J4B 6Y4

Ten commercial linear low density polyethylenes, LLDPE, were characterized by solution viscosity size exclusion chromatography, SEC, low angle laser light scattering, LALLS, $^{13}C$ nuclear magnetic resonance, $^{13}CNMR$, and atomic absorbance, AA. The resins contained butene, hexene (gas phase polymerization) or octene (solution polymerization) comonomers. The SEC/LALLS data indicated absence of long chain branching. The weight average molecular weights calculated from SEC and intrinsic viscosity agreed quite well. Three types of molecular weigh distribution, MWD, were detected: bimodal very broad MWD for samples polymerized in the gas-phase with vamadium catalyst, narrow MWD for gas-phase products obtained with titanium calatyst and the intermediary for the solution polymer. The comonomer placement was found to be random. Mechanical degradation of LLDPE molecules in solution was observed. The phenomenon was particularly noticeable for the very broad MWD samples.

14h20 (9/7)      COMPARISON OF THE RHEOLOGY OF POLYMER MELTS IN SHEAR, AND BIAXIAL AND UNIAXIAL EXTENSIONS, S. A. Khan, R. K. Prud'homme, R. G. Larson, AT&T Bell Laboratories, Murray Hill, New Jersey 07974.

The experimental properties of different polymer melts -polystyrene, high density polyethylene, and low density polyethylene- are compared for the first time in three different deformations: step shear, step biaxial extension, and steady uniaxial extension. Differences in the properties of the melts are most pronounced in uniaxial extension and least in biaxial extension. In uniaxial extension, the branched material is strongly strain hardening, although its shear and biaxial properties are similar to the other melts. The constitutive model of Larson gives a reasonably good fit to the data in all three deformations for unbranched materials for the same value of the adjustable parameter, but fails to do so in uniaxial extension of the branched melt.

14h45 (9/8)      EVALUATION OF THE VISCOELASTIC TEMPERATURE AND PRESSURE SHIFT FACTOR OVER THE FULL RANGE OF SHEAR RATES, H. Kühnle, Institut fuer Kunststofftechnologie der Universitaet Stuttgart, Boeblinger Str. 70, D-7000 Stuttgart 1, West-Germany.

A method for determining uniquely the best fitting temperature shift parameters of viscosimetric data over the full range of shear rates, based on the Carreau formula, is presented. The method is in accordance with the temperature-time superposition principle of viscoelasticity and works fully numerically, thus providing an objective approximation criterion with optimal compensation of scatter and dispensing with any visual control at all, and includes, if necessary, the Rabinowitsch and Bagley corrections.

Evaluations of this kind have been carried out for a multitude of old and new measurements of current types of plastic resins (PE, PP, PS, PA, PC, PMMA, etc.), for which capillaries as well as rotational systems had been employed. In this way, a comprehensive viscosity data bank is built up containing a 5- or 6- parameter set for each material as a compact information about its flow behaviour, and serving as a valuable means for numerical processing analyses. Incidentally, the usual shift formulas (Arrhenius, Williams-Landel-Ferry, etc.) are compared in respect of their applicability.

The suggested evaluation technique is also suitable for determining the pressure dependence of shear viscosity from capillary measurements, as has been tested by calculating the pressure-shift factor for some materials.

15h30 (9/9)      SHEAR REFINING AND ENTANGLEMENT MODIFICATION IN COMMODITY POLYMERS, Alfred Rudin, Guelph-Waterloo Centre for Graduate Work in Chemistry, University of Waterloo, Waterloo, Ontario, N2L 3G1 and Henry P. Schreiber, Ecole Polytechnique, Department of Chemical Engineering, C.P. 6079, Suc. A, Montreal, Quebec, H3C 3A7.

The viscoelastic properties of some thermoplastic melts can be altered significantly by the effects of prior shear and thermal treatments. Elastic properties such as melt fracture and other processing defects are particularly sensitive to shear history. These phenomena can be rationalized in terms of changes in the state of entanglement of the macromolecules. Shear modification processes and methods for measuring entanglement densities will be reviewed.

## ENTANGLEMENT DENSITIES IN POLYMERS

A.Ajji, P.J.Carreau, A.Rudin* and H.P.Schreiber
Department of Chemical Engineering, Ecole Polytechnique of
Montreal, P.O. Box 6079, Stn. "A", Montreal Que H3C 3A7
* Department of Chemistry University of Waterloo Waterloo
Ontario, N2I 3G1 .

Melt viscosity and swelling ratio of shear and solution modified polymers (LLDPE and PP) were investigated. Important changes in properties were observed. The absence of any change in molecular weight by these modifications, and of thermal or mechanical degradation suggests a morphological change in the polymer structure ,i.e., reduction of entanglement densities $d_e$. A method for evaluating $d_e$ is suggested. The approach is based on the critical molecular weight $M_c$ determined from zero-shear viscosity $\eta_0$ in a given state of entanglement assuming that the relation $\eta_0$ vs $M$ at equilibrium entanglement network is known. Other ways of determining $d_e$ and of evaluating of $\eta_0$ are discussed. The aim of this presentation is to provide a way of evaluating entanglement densities $d_e$ in polymers and stress its importance in polymer processing rationalization.

16h20 (9/11) RHEOLOGICAL PROPERTIES OF THERMOTROPIC LIQUID CRYSTALLINE COPOLYESTERS, T. Masuda, M. Takahashi, Department of Polymer Chemistry, Kyoto University, Kyoto 606 Japan, and K. Fujiwara, Idemitsu Petrochemical Co., Ltd., 3-1-1 Marunouchi, Chiyoda-ku, Tokyo 100 Japan

Viscoelastic and flow properties of thermotropic liquid crystalline copolyesters synthesized from poly(ethylene terephthalate) and p-hydroxybenzoic acid were investigated at high temperatures. The temperature dependence of dynamic viscoelasticity of the samples demonstrates a remarkable change of the modulus at a specific temperature. The behavior looks similar to the rheological transition. No change in the texture of liquid crystalline state was optically observed at the transition temperature. DSC and WAXS measurements, however, clearly show the existence of crystallites in liquid crystalline phase below the transition temperature. Rate of shear dependences of shearing and normal stresses were also measured above the transition temperature, and the elastic properties of the liquid crystalline polymers were compared with those of isotropic polymer melts.

16h45 (9/12) EFFECT OF PLASTICIZER TYPE ON VISCOELASTIC BEHAVIOR OF PVC PLASTISOL DURING GELATION AND FUSION, N. Nakajima and M.R. Sadeghi, Polymer Engineering Center, University of Akron, Akron, Ohio, 44325

A large number of plasticizers are available for the plasticization of PVC. They are used very effectively for controlling gelation and fusion behavior of PVC plastisol. However, their effects are judged primarily on the basis of the end results rather than a quantitative monitoring during the process of gelation and fusion. One of the authors (NN) initiated some time ago a viscoelastic measurement, which follows the course of gelation and fusion.

Representative commercial PVC resins were characterized according to this method. The results were presented as viscoelastic finger-prints, which may be used as a guide for the resin selection to meet requirements of a particular process.

In the present work several different plasticizers have been selected on the basis of different solvent power to PVC. Then, the gelation and fusion behavior are characterized viscoelastically. The different solvent power is clearly manifested as the rate-difference of gelation and fusion. The observed solvent power is not necessarily in agreement with the thermodynamic interaction parameters found in the literature.

17h10  (9/13)   IDEAL ELASTIC LIQUIDS AS MODEL FLUIDS IN POLYMER PROCESSING
FLOWS, David V. Boger, The University of Melbourne, Parkville,
Victoria, 3052, Australia.

The development of non-shear thinning elastic liquids and their impact in bridging the
gap between predictions from continuum theory and practical reality in problems of interest
in polymer processing is described.  It is shown that the highly elastic, constant viscosity
fluids represent a class of fluid behaviour consistent with molecular theory, which can be
described at low shear rates by a constitutive equation developed by Oldroyd in 1950.
Experimental observation with these materials has allowed elastic effects to be observed in
flow fields for the first time in the absence of any effects due to a varying viscosity, and
has also allowed direct comparison to be made with predictions from continuum theory in these
flows.  In squeeze film flows good agreement between observation and prediction is obtained.
In exit flows (extrudate swell) significant elastic effects are observed and predicted but
the agreement between observation and numerical simulation is poor at high levels of
elasticity.  In tubular entry flows (die entry flows) large vortex enhancement due to
elasticity is observed which is not predicted by the appropriate continuum analysis.  It is
not clear why continuum theory is adequate in some flows and inadequate in others.  Neverthe-
less great strides have been made in the solution of flow problems of importance in polymer
processing.  The presentation concludes with a motion picture film illustrating some new
flow phenomenon in tubular entry flows.

08h30 (10/1)    MOLECULAR CONTROL OF INTERFACE IN POLYMER BLENDS; R. Fayt, R. Jérôme and Ph. Teyssié, Laboratory of Macromolecular Chemistry and Organic Catalysis - University of Liège - SART TILMAN 4000 LIEGE.

One of the most efficient ways to control the interface in blends is the use of properly tailored diblock copolymers: they can control the development of different morphologies, reduce domains size, and provide interfacial adhesion. A direct TEM-microscopic observation of the block copolymer will be illustrated for blends of polyolefins with both polystyrene and polyvinylchloride, and its structural and physical implications discussed, as supported by some non-radiative energy transfer measurements. Also, the important and sometimes unexpected influence of the block copolymer on the interface mechanical behaviour will be put in evidence, from direct SEM observations and from bulk mechanical properties of blend materials, including commodity and engineering polymers as well as filled.

08h55 (10/2)    PHASE DIAGRAMS OF POLYMER BLENDS AT VARIOUS PRESSURES

S Rostami, ICI PLC, Petrochemicals & Plastics Division, Research & Technology Department, PO Box 90, Wilton, Middlesbrough, Cleveland TS6 8JE, England

Deterioration in properties of polymer blends is normally attributed to the immiscibility nature of the resins. The role of miscibility and its effect on controlling some of the properties of polymer blends is briefly discussed in this paper.

Phase transition from a homogeneous miscible polymer-polymer system to a two phase structure is discussed by using advanced equation of state theories. Some experimental phase diagrams of polymer blends are presented.

A procedure is described for the simulation of the binodal and spinodal curves of polymer mixtures at various pressures. This covers the range of pressures which are normally observed in a mixer or an injection moulding machine. The results of calculations are compared with experimental results obtained on studying cloud point curves of polymer mixtures under pressures. Both UCST and LCST phase behaviours are presented in this paper.

09h20 (10/3)    SURFACE TENSION OF POLYMER LIQUIDS, P.R. Couchman and K. VanNess, Rutgers University, Piscataway, NJ 08854

Surface tensions and surface entropies for polymer molecules are calculated using a modified cell theory with Lennard-Jones-based interactions. The effect of connectivity on free volume and energy terms is included explicitly. Results are given over a range of temperatures and molecular weights. There are no adjustable surface parameters.

FORMATION OF DISPERSED PHASE IN INCOMPATIBLE POLYMER BLENDS: INTERFACIAL AND RHEOLOGICAL EFFECTS, by Souheng Wu, E. I. du Pont de Nemours & Company, Central Research and Development Department, Experimental Station, Wilmington, Delaware 19898, USA

The formation of dispersed phase in incompatible polymer blends during melt extrusion is studied. Two nylon 66 resins and one poly(ethylene terephthalate) resin are used as the matrix, and fourteen hydrocarbon rubbers of essentially the same chemical composition but different interfacial properties and viscosities are used as the dispersed phase. The dispersed particle size and distribution, interfacial tension in the melt and viscosities are determined. The particle size is found to be directly proportional to the interfacial tension, other factors being equal. A master curve is obtained by plotting the Weber number ($Gd\eta_m/\gamma$) versus the viscosity ratio $\eta_d/\eta_m$, where G is the effective shear rate of the extruder, d the number-average diameter of the dispersed drop, $\eta_d$ the viscosity of the drop and $\eta_m$ the viscosity of the matrix at the effective shear rate G. The master curve is useful for predicting and correlating the interfacial and rheological effects on dispersion.

10h30 (10/5)

SPECIFIC INTERMOLECULAR INTERACTIONS IN FLUORINATED POLYMERS/ADDITIVES SYSTEMS; N. Del Fanti+, A. D'Alessio*, L. Baini+, P. Vergamini*, M. Pianca+, G. Moggi+, E. Benedetti*, + Montefluos,C.R.S., Milano, Italy; * Dipartimento di Chimica e Chimica Industriale, University of Pisa, Italy.

Low molecular weight plasticizers and polymeric additives have been mixed with fluorinated polymers (vinylidene fluoride homopolymer and its copolymers with hexafluoropropene). Intermolecular interactions have been put in evidence by means of FT-IR spectroscopy on the basis of differences between the spectra of the mixtures and those syntesized by addition of the spectra of the pure components. The trends of the width at half-height and the shift of the carbonyl bands of the ester groups of the plasticizers put in evidence competitive intermolecular interactions between the plasticizers among themselves and the plasticizers and the $- CH_2 - CF_2 -$ segments. Increasing the concentration of the copolymer intermolecular interactions between plasticizers and the $- CH_2 - CF_2 -$ monomeric units prevail on those among the same plasticizers.

11h20 (10/7)

DYNAMIC MECHANICAL PROPERTIES OF POLYMER BLEND POLYSTYRENE/
POLY(VINYLMETHYLETHER) BLENDS; D. Froelich and R. Muller,
Institute Charles Adron (CRM-EAHP), 4, rue Boussingault 67000,
Strasbourg, France.

The dynamic mechanical properties of the polystyrene/polyvinylmethylether blend
have been studied in two conditions: at low temperature where the two polymers are
compatible and at temperature higher than the phase separation temperature where there are
two phases.

It has been shown that at low temperature, the time temperature superposition can
be applied and that a blending law giving the zero shear viscosity of the system as a
function of the concentration, can be obtained.

At high temperature, the superposition principle is no longer valid and long
relaxation times characteristics of a two phase system can be observed.

11h45 (10/8)

MELTING AND CRYSTALLIZATION BEHAVIORS OF A CO-CRYSTALLIZED
BLEND BASED ON PROPYLENE COPOLYMERS; Chi-Kai Shih, E.I. du Pont
de Nemours & Co., Polymer Products Department, Experimental
Station, Wilmington, DE 19898, U.S.A.

An unusual compatibility was observed with the melt blends of propylene/$\alpha$-olefin
copolymer with isotactic homopolypropylene. The simple binary blend exhibits a single
glass transition temperature, a single DSC melting and crystallization temperatures over
the entire blending ratios examined. Depending upon the compositions, the
charchteristic temperatures vary between those exhibited by the component polymers.
Vigorous annealings failed to phase separate the components. The melting behaviors of the
annealed polymer sample suggest the crystalline components of the two polymers are co-
crystallized in this unique compatible system.

13h30 (10/9)

INTERRELATIONSHIP BETWEEN THE CRYSTALLIZATION BEHAVIOR,
INJECTION MOLDING CONDITIONS AND MORPHOLOGY OF PET/PMMA ALLOYS;
V.M. Nadkarni and J.P. Jog, National Chemical Laboratory, Pune
411 008, India.

The termal and isothermal crystallization behavior of PET/PMMA alloys was
investigated. The crystallization of PET is accelerated significantly by alloying with
PMMA. As a result, crystalline specimens could be injection molded with the alloy at low
mold temperatures of 19°, 55° and 90°C, whereas a mold temperature of about 120°C is
normally required to develop crystallinity in the virgin PETP grade. The impact strength
of the alloy specimens increased significantly with decreasing mold temperature in spite
of comparable degree of crystallinity. The increase in impact strength is correlated to
the reduction in the crystallite size and broadening of the crystal size distribution with
decreasing mold temperature.

13h55 (10/10)

SOME EXPERIMENTS WITH POLYMER BLENDS; G. Pastuska, W. Lützow,
R. Riecke, Federal Institute for Testing Materials
Sub-Department "Elastomers, Plastics and Coatings"
Berlin-Germany.

Polymer blends are not only mixtures of different polymers with different
quantities. It may happen that chemical reactions occur between the components
under the influence of heat and shearing. This affects different properties in
the technological and physical behaviour of the product as well as in structure
and morphology. By it, difficulties arise in realizing the technical polymer as a
conventional material or as a polymer blend. This is demonstrated at polymer
blends of polyethylene and polyamide. The need of energy for preparation of the
blends is discussed, also the melt flow in dependence on the amount of polyamide
and the changes in spectroscopy, the effect on thermoanalysis and the type of
fracture.

14h20 (10/11)

IN-SITU COMPOSITES: BLENDS OF ISOTROPIC AND THERMOTROPIC LIQUID CRYSTALLINE POLYMERS", G. Kiss, Celanese Corporation, 86 Morris Avenue, Summit, N.J., 07901.

Melt blending of a variety of conventional isotropic polymers (both crystalline and amorphous) has shown that considerable reinforcement is obtained from the inclusion of thermotropic liquid crystalline polymer. When the LCP is a minor component it forms highly elongated domains parallel to the flow direction. The intrinsically high strength and stiffness of the LCP improves the mechanical properties of the resulting blend. This approach is distinguished from the common practice of filling polymers with chopped glass and carbon fibers by the fact that the reinforcing component comes into existence DURING processing (molding or extrusion). Many of the problems associated with fibrous fillers are avoided. Viscosity of the "in-situ composite" is actually lower than that of the pure base polymer. Wear on the compounding and processing equipment is avoided.

14h45 (10/12)

STRUCTURE-PROPERTIES STUDIES OF POLYMER BLENDS CONTAINING LIQUID CRYSTAL POLYESTERS; M. Pracella*, D. Dainelli, M. Paci°, G. Galli+, E. Chiellini+, *Centro Studi Processi Ionici C.N.R.; ° Dipartimento Ingegneria Chimica, + Dipartimento Chimica e Chimica Ind., Università di Pisa, Pisa, Italy

The main goal of the present work is to examine the morphological, thermal and mechanical characteristics of blends of commercial poly(butylene terephthalate), polystyrene, polycarbonate – with liquid crystal polyesters, based on bis(4 – carboxyphenyl)terephthalate and aliphatic glycols of different lenght (HTH). In particular the results obtained for blends of PBT with HTH polyesters, prepared by solution or melt mixing, indicate that the mesophase behaviour, the crystallization kinetics, the melting and glass transitions are strongly influenced by the composition and thermal treatments. The existence of compatibility between the polymers in the amorphous state is discussed on the basis of experimental evidences and of the thermodynamical interaction paramaters calculated with varying the concentration and the molecular characteristics of the mesogenic component. The investigations were carried out by using optical microscopy, X-ray diffraction, differential calorimetry and mechanical-dynamical analysis.

15h30 (10/13)

PROCESSING OF SELF-REINFORCED POLYMER COMPOSITES, A.I. Isayev and M.J. Modic, Polymer Engineering Centre, University of Akron, Akron, Ohio 44325, U.S.A.

Liquid crystal polymers are widely used to manufacture high- strength fibers and are becoming commercial resins for processing of articles having mechanical properties close to those of fiber-reinforced composites. It has been found that the melt processing of blends of liquid crystal and flexible polymers leads to formation in-situ of fiber reinforced composites and that exceptional mechanical properties can be obtained. Rheology, mechanical properties and structure of blends of polycarbonate and wholly aromatic copolyesters have been investigated. Various processing operations have been carried out including blending, extrusion, melt spinning, compression and injection molding. Processing conditions have been identified under which fiber-reinforced polymer composites can be recovered.

DEFORMATION STUDIES ON A POLY(METHYL METHACRYLATE)-POLY(ETHYLENE OXIDE) BLEND: A MOLECULAR CHARACTERIZATION.

Jean-Marc R. Lefebvre, Roger S. Porter, George D.Wignall*
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The deformation behavior of a miscible amorphous/amorphous PMMA/PEO blend has been compared to that of pure PMMA. For this purpose samples were drawn in an Instron capillary rheometer using the solid-state co-extrusion technique. In all cases, the deformation temperature was chosen as Tg + 12 K where Tg refers to the glass transition temperature of each specimen.

To characterize deformation at the molecular level, Small Angle Neutron Scattering (SANS) experiments have been performed on labelled systems made of PEO plus deuterated and protonated PMMA.

Characteristic molecular parameters have been extracted from the coherent scattering cross-sections of the labelled systems, both in the isotropic and drawn anisotropic states.

In the isotropic state such parameters as the radius of gyration, Rg, and molecular weight, Mw, of the PMMA chain give clear indication of the state of miscibility in the blend. It is shown that anisotropic radii of gyration parallel ($Rg_P$) and transverse ($Rg_T$) to the draw direction provide information on the draw efficiency in fairly good agreement with shrinkage tests results.

By considering the scattering behavior over the entire scattering vector range, we are able to evaluate the degree of anisotropy retained at shorter distances within the polymer coil in pure PMMA as compared to the PMMA/PEO blend.

A STUDY ON POLY(VINYL CHLORIDE) BLEND WITH CHLORINATED POLYETHYLENE AND POLYETHYLENE,

Xu Xi, Meng Xiande and Chen Keqiang, Polymer Research Institute, Chengdu University of Science and Technology, Chengdu, Sichuan, The People's Republic of China.

By means of a twin-roll masticator and Brabender rheometer, the effect of chlorinated polyethylene(CPE) and polyethylene(PE) on the impact resistance and processing property of poly(vinyl chloride) (PVC) was studied. The experimental results show that CPE is an efficient modifier, but is not ideal as far as the toughness at low temperature is concerned. Addition of 1-5 parts PE to PVC/CPE (100:12) mixture makes the impact strength increased by more than 30 kg.cm/cm$^2$ at 20°C and more than 7 kg.cm/cm$^2$ at 0°C. The effect of PE increases with the decrease of its degree of crystallinity. Addition of PE makes the melt viscosity of PVC/CPE blend lower, the flow behavior better and the article surface more smooth. By dynamic viscoelastometer, differential scanning calorimetry, small angle X-ray scaterring, scanning electron microscopy and transmission electron miscroscopy, the compatibility of PVC/CPE/PE system and its morphology were examined. We found that, at room temperature, CPE can make PVC/PE compatible and increase the toughness of the blend but has no effect on toughness at about its $T_g$. Besides, addition of PE increases the volume fraction CPE in PVC/CPE mixture and creates a structure resembling a cross-liked system. This is why the PVC/CPE/PE blend has higher impact strength than that of PVC or even that of PVC/CPE blend.

16h45 (10/16)
BLENDS OF POLYCARBONATE AND POLY(HEXAMETHYLENE SEBACATE) I. PHYSICAL PROPERTIES.
K. S. Shih* and C. L. Beatty
Department of Materials Science and Engineering
University of Florida
Gainesville, Florida  32611

The compatibility of polymer blends of high molecular weight polycarbonate, PC, and high molecular weight poly(hexamethylene sebacate), HMS, have been characterized.  Samples were prepared by solution blending the samples in methylene chloride followed by doctor blade casting.  Optical spectroscopy, tensile stress-strain, differential scanning calorimetry and dielectric relaxation spectroscopy were employed to determine the physical and mechanical properties of the blends. These high molecular weight blends exhibit a limited solubility of HMS in PC as evidenced by a decrease in the glass transition temperature of PC.  In fact, HMS solubility increases PC mobility sufficiently to allow partial crystallization of PC.  Over most of the composition range, HMS phase separates and crystallizes.

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17h10 (10/17)
EXTENSIVE MIXING IN COROTATING DISK PROCESSORS, B. David, Z. Tadmor, Department of Chemical Engineering, Technion-Israel Institute of Technology, Haifa 32000, Israel

Extensive or laminar mixing studies were carried out in a parallel chamber corotating disk processor.  Velocity profiles, flow patterns and interfacial area distribution functions were studied experimentally and theoretically.  Results indicate the role of reorientation of the direction of shear with respect to the interfacial area, in the circulating pools.  The efficiency of recycle over the channel block, and of mixing pins inducing radial flow was also studied experimentally.

# SYMPOSIUM No. 11: COMPOSITES
## (CHAIRMAN: L.A. GOETTLER)

13h30 (11/1)

PRESENT AND FUTURE TRENDS IN POLYMERIC COMPOSITES, T. Vu Khanh and L.A. Utracki, NRCC/IMRI, 75 Boul. De Mortagne, Boucherville, Québec, Canada J4B 6Y4.

The volume of plastics production has exceeded that of raw steel. The growth rate of the plastics industry is about 6.3% per annum, significantly higher than of other industries. From that perspective, consumption of polymeric composites by different markets was analyzed. Although severely depressed by reluctance, by the fear of the unknown of designing engineers, the percentage of resins which goes into production of composites is constantly increasing. The biggest markets such as transportation and construction exhibit the highest growth rates for new applications of composite materials. It has been projected that by 1990 about one-third of polymer production will be used in composites.

13h55 (11/2)

COMPOUNDING OF FLAKE-FILLED POLYPROPYLENE
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Council Canada, Industrial Materials Research Institute,
75 De Mortagne, Boucherville, Qué. Canada J4B 6Y4

Extruder compounding of flake reinforced polypropylene usually gives compounds with relatively high void content. This adversely affects physical properties (strength, electrical conductivity, permeability) as well as surface texture of extruded products. In this work various means for producing void free compounds of polypropylene reinforced with mica, glass flake and nickel coated mica were investigated. In single screw extrusion, the entrapped air can be easily removed by operating the extruder in the starve feeding mode. With the twin-screw extrusion degassing can be achieved only by vacuum venting. The effect of void content on properties will be also discussed.

14h20 (11/3)

ORIENTATION-RHEOLOGY-PROCESSING INTERACTIONS IN THE INJECTION MOLDING OF FIBER REINFORCED THERMOPLAST-ICS, M.R. Kamal, T. Mutel and P. Singh, Department of Chemical Engineering, McGill University, Montreal, Canada H3A 2A7

During the processing of fiber reinforced thermoplastics, fiber distributions and orientations change under the influence of the prevailing shear and elongational flow fields. As a result, in injection molding for example, the redistribution and reorientation of fiber is not uniform throughout the mold cavity. This leads to anisotropies in the mechanical propperties and their distributions in the molding. The presenttion will combine results obtained regarding the characteristics of injection molded parts with data obtained on the microstructure of these parts and the rheological properties, under shear and elongation, of the corresponding fiber reinforced melts. Emphasis will be placed on orientation and its development during simple rheological experiments and under injection molding conditions. The various techniques employed to generate the data will be described.

14h45 (11/4)

## CONTINUOUS PROCESSING OF COMPOSITE MATERIALS

A.C. Ppanastasiou, A.N. Alexandrou, and G. Georgiou
Department of Chemical Engineering, The University of Michigan
Ann Arbor, Michigan 48109

Continuous processes of composite materials are attractive due to the low cost, the short processing time, and the controlability of the fiber orientation. This paper addresses the computer-aided analysis of extrusion of fiber suspensions. The analysis predicts the flow field and the resulting fiber orientation. The driving pressure, the extrudate swelling, and the frozen-in orientation are presented in relation to the fiber concentration and the cooling rate.

15h30 (11/5)

## A MODEL FOR A THREE-LAYER FLOW OF SHORT FIBER-CONTAINING MELTS IN EXPANDING PIPE DIES

S.R. Doshi, J.M. Dealy, J.M. Charrier, Dept. of Chemical Engineering, McGill University, Montréal, Québec, Canada H3A 2A7

Short fiber-reinforcement of thermoplastics has become a popular method of gaining cost effective property advantages in injection molded articles. Its use in extruded engineering products such as pipes, has been limited, however, due to the problems associated with the surface finish and to the strong axial fiber orientation developed during processing. It has been demonstrated that the use of a suitable expanding channel die can promote a preferential hoop orientation of fibers in the core region of the extruded pipe; a strong axial orientation, however, is inevitable near the surface. A coextrusion process in association with the expanding channel geometry has now been demonstrated to be a practical solution to both the problems of fiber orientation control and surface finish. A theoretical analysis of the flow of the three-layer melt in the expanding channel die is used in conjunction with a model for flow/orientation relationships to predict the fiber orientation at the die exit. The analysis is used to examine the effect of rheological and processing parameters on the fiber orientation distribution. Experimental results are also presented to support the theoretical predictions.

15h45 (11/6)

## THE FIBRE CONTENT DISTRIBUTION OF COMPRESSION MOLDED LONG FIBRE-REINFORCED THERMOPLASTIC PRODUCTS

Hidetsune HOJO, E-Gon KIM and Kiichi TAMAKAWA, Department of Mechanical Engineering II, Tohoku University, Sendai, Japan.

The separation of the matrix and the fibre during the molding process of long fibre-reinforced thermoplastics, is caused by the flow of the molding process, and the product is non-homogeneous. Hence, on the design of products, it is very important to calculate the distribution of fibre content resulting from the separation in relation to the molding-process variables.

A theoretical equation on the separation has been derived on the basis of solid-liquid two phase-flow by the present investigators. Here the coefficient of separation has been proposed.

In this paper, fibre is represented by a circular cylinder and a sphere of the same volume, and the imaginery fibres are set up in an initial charge state. After the molding flow states are obtained, the imaginery fibres' separation distances are derived from the separation equation. The coefficient of separation may also be obtained from the composites' viscosity, and the fibre content distribution is also calculated, using the same method. The effects of molding-process variables on the distribution are also presented. The material used in the experiments is a stampable polypropylene composite sheet. The experimental results applied to compression molding are in good agreement with this theoretical consideration.

16h20 (11/7)    THE MODELING OF MOLD FILLING IN RESIN TRANSFER MOLDING,
R. Gauvin, M. Chibani, Department of Mechanical Engineering,
École Polytechnique de Montréal, P.O. Box 6079, Succ. A,
Montréal, Qué. Canada H3C 3A7.

One method of producing medium and large FRP parts is the Resin Transfer Molding
(RTM).  It offers important advantages over more labor intensive processes such as hand
lay-up and spray-up tehcniques. However, one of the major difficulties with RTM is to
properly design the mold and to locate the injection port in such a way that the mold will
be filled completely without excessive pressure.  Cavity pressure is the most important
parameter to minimize leakage problem at the parting line, to reduce mold deformation and
to assure a good quality part.  Very little data exist in the literature to correctly
predict the pressure distribution in the cavity during mold filling.  In an attempt to
solve this problem, a simplified model applicable to unidirectional flow is proposed.  It
is based on Darcy's law for flow of liquids through a porous media.  In this case, the
liquid is an unsaturated polyester resin flowing through a porous fiberglass mat or woven
roving reinforcement.  The model is used to obtain the permeability of various reinforce-
ments.  The permeability is evaluated using the concept of porosity which is a function of
the glass content and of an experimental factor which is a characteristic of each type of
reinforcement, mat or woven roving.  Effects on the proposed model of parameters such as
glass density, surface density of the reinforcement and number of reinforcing layers are
examined.  The set-up used to collect permeability data is described and results for
various reinforcements and combination of reinforcements are presented.

16h45 (11/8)

BONDING PHENOLIC PLASTIC PARTS TO FIBERGLASS
REINFORCED COMPOSITE STRUCTURES USING AN EPOXY RESIN
WITH POLYAMIDE CURING AGENT AS A PRIMER.
Howard Novak
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701 Columbia Boulevard
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Often irregularities and voids in the fiberglass reinforced composite surface structure
prevent adequate wetting and adhesion of the viscous B-stage structural adhesive film
during the bonding - final cure cycle.  Also voids and pores trapped between the adhesive
film and phenolic parts generate gas and contribute to a porous, frothy adhesive
bondline.  The use of radiographic analysis and shear testing of prototype and production
hardware confirm the above deleterious condition.  Small quantities of condensed surface
moisture emanating from ambient air impingement on cool structural adhesive film, cause
additional deterioration of the adhesive bondline.  This paper outlines the proper use of
the wet film, low viscosity, epoxy primer in conjunction with the B-stage film adhesive for
simultaneous cure, and describes the effective strengthening of the adhesive bondline
between phenolic plastic parts and fiberglass reinforced composite structure.  In addition,
improvements in adhesive material usage and fixturing improvements are also discussed.
Data is presented showing the significant improvements in repeatability of adhesive
bondline shear strengths during production hardware sampling.

# SYMPOSIUM No. 12: POSTER PAPERS
## (CHAIRMEN: B. FAVIS AND T. VU KHANH)

(P/1)

RELATION BETWEEN COMPOSITION, PROCESSING AND MECHANICAL PROPERTIES
OF RIM-NYLON BLOCK COPOLYMERS

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The Netherlands

The anionic polymerization of $\varepsilon$-caprolactam initiated with a rubbery prepolymer which contains two or more terminal initiator groups results in the formation of nylon-6 block copolymer. The mechanical properties of these block copolymers depend not only on the composition of the material but also on the processing conditions.
The influence of the amount of rubber phase and of the molar mass of the rubber component on toughness and stiffness of the block copolymers is investigated. Besides, it appears that the temperature of the mold and the temperature of the two streams from the machine to the mold have a very important influence on the polymerization rate and on the properties of the polymer. This relations will be explained by the morphology and the cristallinity.
Furthermore, some information will be given about the influence of the dosing rate on the properties of the end product.

(P/2)

ELEMENTS OF MICRORHEOLOGICAL MODELLING, R.J.J. JONGSCHAAP,
Twente University of Technology, Dept. of Applied Physics,
Rheology Group, 7500 AE Enschede, The Netherlands.

In order to describe the relationship between the rheological behaviour of polymeric liquids and their microstructure many molecular theories have been developed. These theories are based upon various concepts like bead-spring chains, entanglements, transient networks, reptation motion and anisotropic friction.
After a brief review of some of these theories and concepts the possibility of achieving some kind of integration between them will be discussed. Starting with some cases that have been reported in previous publications: the combination [1] of the transient network model with the bead spring model and [2] of the repation model and the transient network model, further possibilities will be discussed.
Progress in this field is important from a theoretical and a practical point of view as well. Theoretically it is important to recognize certain common elements in different types of theories and in applications it may be usefull to apply in one type of theory certain well established concepts of an other one. The combination of the transient network and the reptation model, for instance offers the possibility of using the special kinetics of the repation motion in the transient network model and conversely, to use certain kinds of non-affine motion, developed in transient network theories in the reptation model.
1) R.J.J. Jongschaap, H. Kamphuis and D.K. Doeksen
   Rheol. Acta 22, 539 (1983)
2) R.J.J. Jongschaap, H. Kamphuis
   Soc. of Rheology Meeting, Blacksburg, Virginia (1985).

(P/3)　　　　THE FLOW BEHAVIOR OF POLYACRYLATE AND POLYMETHACRYLATE
SOLUTIONS; Li Wenduan, Xia Chanagfu, Zhang Jiehui, Wei He, Xu
Xi (Polymer Research Institute, Chengdu University of Sci. &
Techn., China)

A series of high molecular weight homopolymers and copolymers of alkyl acrylates and alkyl methacrylates were prepared. The solubility, flow behavior, drag reduction effectiveness and resistance to degradation in drag reduction use in relation to composition, molecular weight and its distribution, size of side groups, and structure sequence of the polymers were studied by IR, DTA, GPC, NMR, high-speed stirring and closed-loop pipeline test. The friction coefficient (f) of these polymers in kerosene solution bears a relation to Reynold's number (Re) and Re at the very onset of drag reduction (Reo): $f = 0.079 \, Reo^{-0.25}(Reo/Re)^n$. There is a threshold value of shear stress ($\tau_{wm}$) above which the drag reduction will increase no longer. The maximum drag reduction achievable increases with increase of concentration, while the value of $\tau_{wm}$ is independent of the concentration.

(P/4)　　　　A critical evaluation of integral constitutive equations in simple
flows, R.D. Wesson, A.C. Papanastasiou , and J.O. Wilkes,
Department of Chemical Engineering, The University of Michigan,
Ann Arbor, Michigan 48109

The numerical stability and accuracy of single-term and two-term entegral constitutive equations in simple, homogeneous shear flows, and in non-homogeneous extensional flows is examined. The predicted shear and normal stresses, the Weissenberg number and the recoverable shear at the point of Newton iteration divergence are related to analytical results. The significance of the local rate of strain as well as the spectrum of relaxation times on the numerical stability and accuracy are discussed in detail. The results are extrapolated to behavior of integral equations near singularities.

ON THE USE OF END EFFECTS FOR POLYMER MELT CHARACTERIZATION

(P/5)

L. Choplin, Department of Chemical Engineering, Université Laval,
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and
P.J. Carreau, Department of Chemical Engineering,
Ecole Polytechnique, Montreal, QC, CANADA, H3C 3A7

Polymer melt flow through capillary or slit dies is characterized by very high excess pressure drop (end effects), which is composed of an excess pressure drop at the entrance of the die and an excess pressure drop at the exit of the die. The total excess pressure drop has been shown to be due to the sum of the excess viscous dissipations at the entrance and at the exit. The energy dissipated in excess results from the combination of the transient shear and the transient shear and the transient elongational character of the flow field in the entrance and the exit regions of the die, and is strongly dependent of the non linear viscoelastic behavior of the polymer melt.
In the past, the large excess pressure drop for polymer melts in dies was attributed to the storage of elastic energy and related to the recoverable shear. Our comprehensive study on end effects has shown that the storage of elastic energy does not contribute at all to the total excess pressure drop in the die. Hence, end effects have to be seen only as a measure of the energy dissipated in excess in the die on account of the particular kinematics existing at the entrance and at the exit.
Any correlation involving end effects which includes the recoverable shear (or the Weissenberg number) evaluated in the fully developed flow region in the die must be used with caution.

(P/6)

MOLECULAR ORIENTATION IN COMBINED EXTENSIONAL AND SHEAR FLOWS,
J.P. Santerre and J.J. Picot, Dept. of Chemical Engineering,
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A converging flow cell was constructed to study various combinations of extensional and shearing strain rates up to 400 and 700 reciprocal seconds respectively. Laser Dopplar Anemometry and Birefringence were used to measure strain rates and molecular orientation. Analysis of results show that orientation can be predicted for this 2-D flow provided an accurate rheological model is available.

(P/7)

DETERMINATION OF RHEOLOGICAL PARAMETERS IN MELT SPINNING PET BASED ON VELOCITY AND TEMPERATURE PROFILES AND FREEZE POINT TENSION DATA, H.H.George, Westfield Consulting Group, 523 Clark St. Westfield,NJ 07090, USA.and M.H.G.Deeg, Celanese Research Co. 86 Morris Avenue Summit, NJ 07901, USA

Historically, models of the melt spinning process have been used to calculate temperature,velocity and stress profiles from the process conditions and an assumed extensional viscosity function. In this work the procedure was reversed using measured temperature and velocity profiles and a single tension measurement at the freeze point a rheological spinning function is calculated. This function is essentially the extensional viscosity but by this technique it is measurable only in a restricted region of the temperature – deformation rate plane due to the nature of the spinning process. Estimates of the spinline heat transfer coefficient are also made.

(P/8)

EFFECTS OF RUBBER PARTICLE MORPHOLOGY ON YIELD AND FRACTURE IN HIGH IMPACT POLYSTYRENE

Clive B. Bucknall and Ivana K. Partridge, School of Industrial Science,
Cranfield Institute of Technology, Cranfield, Bedford MK43 0AL, England

Relationships between structure and mechanical properties are studied in a series of high impact polystyrene (HIPS) polymers. The series includes materials having single-core-shell, double-core-shell and multiple-inclusion rubber particles, with a median particle diameter varying from 0.2 to 1.8μm. Analysis of electron micrographs shows that the volume fraction of composite particles, $\emptyset$ increases from 0.17 to 0.44 with increasing particle size, at a fixed polybutadiene concentration. The volume fraction was also varied by melt blending the HIPS with polystyrene, in order to separate the effects of $\emptyset$ from those of the particle size. Measurements were made to determine the effects of these two parameters upon yield behaviour in tension and compression, kinetics of tensile creep, and fracture behaviour of HIPS. Influence of strain rate and post-yield behaviour in these polymers are also considered.

(P/9)

X-RAY STUDY OF POLYETHYLENE DURING DRAWING,
D. T. Grubb, Department of Materials Science, Cornell University, Ithaca,
New York 14853.

High modulus polyethylene fibers and tapes can be obtained by tensile deformation in the solid state to high draw ratios. X-ray diffraction shows that almost perfect orientation is achieved by a draw ratio of 10x, although the modulus is still quite low at that point. Thus modulus develops as a fully oriented highly crystalline structure is rapidly stretched by 2-3x. Microscopic mechanisms for this process are difficult to imagine, and models for modulus development tend to ignore the presence of crystals. A synchrotron X-ray source has been used to obtain WAXD patterns *during* the drawing process from 10-25x total draw ratio. These are remarkably little different from the patterns which are obtained when the drawing is stopped. This shows that only a small fraction of the crystals in the fiber can be broken up or otherwise disordered *at any one instant of time* during the drawing process.

(P/10)      SPACE-TIME DISTRIBUTION IN FILLING A MOLD, I. Manas-Zloczower, J.W. Blake, and C.W. Macosko, Department of Chemical Engineering and Materials Science, University of Minnesota, Minneapolis, MN 55455

The residence time of a fluid particle in mold filling is total time spent in the mold. Displaying curves of constant residence time in the mold gives the space-time distribution during the filling process. A simple method to calculate space-time distributions is presented. Applications to mold filling in reaction injection molding (RIM) are illustrated


(P/11)      A STUDY ON POLY(VINYL CHLORIDE) BLENDS WITH CHLORINATED POLYETHYLENE AND ACRYLIC RESIN, Xu Xi, Zhang Liwu and Li Huilin, Polymer Research Institute, Chengdu University of Science and and Technology, Chengdu, Sichuan, The People's Republic of China.

By means of Brabender plasticoder, dynamic viscoelastometer, tansmission electron microscope, scanning electron microscope and others, the effects of the composition of blend and processing conditions by which it is prepared on the compatibility, mechanical properties, processability as well as the rheology of the blends of PVC/CPE/ACR were studied. The experimental results show that the impact resistance and processability of PVC are improved significantly by blending it with CPE and ACR(PVC/CPE/ACR = 100/5-20/1-10). With increase of CPE content in the blend, the impact strength increases, but the tensile strength lowers. CPE/ACR (1/1) is incompatible, PVC/ACR compatible while PVC/CPE/ACR is partially compatible. CPE may prevent PVC from gelling, while ACR makes PVC more fusible. Based on these results the mechanism of toughening by CPE, the action of ACR and the morphology change of the blends are discussed.


P/12)       THE MELT RHEOLOGY OF CHLORO-POLYETHER AND POLYEPICHLOROHYDRIN BLENDS; Lu Liming, Li Kebin and Li Shijing (Dept. Polym. Mat. Sci. Eng., East China Inst. Chem. Techn., Shanghai, PRC)

In the present work, the coupled chloro-polyether/polyepichlorhydrin (P/R for short) blends which contain diamine acting as an interfacial coupling agent of 0.3% and the P/R blends without coupling agent were prepared (the blending ratios P/R: 100/0, 90/10, 80/20 and 70/30) and the melt rheological properties of the blends have been studied. It was found that the coupling agent greatly changed the rheological behavior of P/R blends. Both the coupled and uncoupled blends are pseudoplastic with the pseudoplastic character of the former stronger than that of the latter. The viscosity of coupled P/R blends decreased with rubber content at low content and increases with rubber content at high content, while the viscosity of uncoupled P/R blends decreases linearly with rubber content over all the range of experimental composition. Both the coupled and uncoupled P/R blends obey the principle of temperature and composition superposition. $E_T$, which reflects the dependence of viscosity on temperature, slightly depends on rubber and coupling agent content. $E_\phi$, which reflects the dependence of viscosity on rubber content, depends on the structure and composition of P/R blends. Finally, a model has been proposed to describe and predict the melt rheological behavior of P/R blends: $\eta = a/[1 + (\tau/b)^{m-1}]$, where $\eta$ is viscosity, $\tau$ is shear stress, and a, b and m are parameters. Both the coupled and uncoupled P/R blends obey this model.


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(P/13)　　　　　　　　　　HIGH PERFORMANCE PRODUCTS FROM GEL LIKE SPHERULLITES
OF POLYETHYLENE, T.Ohta, F.Okada, Research Center,
Toyobo Co. Ltd., Katata, Otsu, Shiga 520-02, Japan.

The aim of this presentation is to provide newer polymer processing method on the advanced high performance products in excess of Kevlar.

It is characterized by super drawing of a pressed sheet, which obtained by pressing an accumulated material of gel like spherullites formed from semi dilute solution of polyethylene (1983, EP 141418). This method is based on the finding of the following facts, that is;

1. Gel like spherullites, including much solvent of about 90%, are formed by cooling a semi dilute solution of UHMW-PE.
2. By pressing an accumulated material of gel like spherullites as to be able to remove a solvent properly from them, an accumulated material of lamella is obtained, where lamella surface orient in parallel to the surface of a pressed sheet.
3. The above pressed sheet have super drawability and an uniaxial drawn article having a tensile strength of 4.0 GPa and a tensile modulus of 200GPa can be obtained.

The pressed sheet in this method can be easily drawn with a die, so that it becomes possible to produce a large diameter monofilament ( 1.0 mm$\phi$) having strength of 2GPa and modulus of 100GPa. Such monofilament can be obtained neither by die drawing of melt extrudates nor by gel spinning and drawing.

(P/14)

BLENDS OF PDMS/SEGMENTED POLYURETHANES.
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Mixtures of polydimethylsiloxane (Dow Corning PDMS, $\eta$ = 1000 cs) and a segmented polyurethane (Upjohn Pellethane, 2102-80A) were compression molded into sheets. Dynamic mechanical and dielectric relaxation spectroscopy of the mixtures were performed to determine phase behavior for blends containing 0 to 10% PDMS. Contact angle and ESCA measurements confirm that polydimethylsiloxane occurs preferentially at the surface as expected. Stress-strain and tear strength data will also be reported.

(P/15)

EFFECT OF STOICHIOMETRIC RATIO ON EPOXY CURING
KINETICS VIA DYNAMIC MECHANICAL SPECTROSCOPY.
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Dynamic mechanical spectroscopy has been utilized to study the curing kinetics of epoxy networks. Shell Epon 828 and Magnolia 360-L have been mixed at different stoichiometric ratios, and heated from room temperature to the isothermal reaction temperature of 129°C for 2 hours for B-staging. The change in mechanical properties (i.e. E' and tan $\delta$) from B to C stage of cure was monitored by isothermal (148°C) dynamic mechanical measurements. Temperature-frequency scans were acquired before and after C-staging to determine the effect of stoichiometric ratio on the glass transition temperature (Tg) and modulus. A 10 wt.% reduction of either epoxy or amino reactants results in a significant decrease in Tg. Subsequent C-stage reaction time must be increased when stoichiometric ratio is varied.

(P/16)     BLENDING OF THERMOPLASTICS AND ELASTOMERS IN AN INTERNAL
MIXER: FLOW VISUALIZATION, INFLUENCE OF ROTOR DESIGN AND
MIXING CONDITIONS ON PHASE MORPHOLOGY, Kyonsuku Min, Polymer
Engineering Center, University of Akron, Akron, Ohio, 44325

The blending of elastomer and thermoplastics in an internal mixer has been investigated. Flow visualization of blending elastomers and thermoplastics has been carried out using a modified model internal mixer with the front and transverse glass windows. The designs of rotors are varied from simple two roll mill type to single screw type as well as kneading disks. It is found that a change of flow fields in an internal mixer create different phase morphologies of blends.

The effects of temperature, blending time and rheological properties on flow behavior and morphology are described.

(P/18)     THEORETICAL AND EXPERIMENTAL STUDY OF THE POLYMER PLASTI-
CIZATION IN THE RECIPROCATING SCREW OF AN INJECTION-MOLDING
MACHINE, E. Wey, B. Vergnes, J.F. Agassant, Centre de Mise
en Forme des Matériaux, UA CNRS 852, Ecole des Mines de
Paris, Sophia Antipolis, 06560 Valbonne, France.

In a first time, experimental studies were performed to observe and to measure the behaviour of the polymer during the plasticization process. Melt pressure was measured along the barrel and melt temperature along the screw. After rapid cooling, the screw was extracted from the barrel and samples taken out to observe the evolution of the melt/solid repartition at different intervals of time during the injection cycle.
In a second time, a global thermomecanical approach of the plasticating process was carried out. It is divided into two parts :
- During the screw rotation, the process is analyzed like an instationnary extrusion : the classical computations of the extrusion process (solid conveying, melting, pumping ..) were modified, extended to the instationnary case and connected together to provide a complete description of the phenomena.
- When the screw remains stationnary, the heat conduction from the barrel induces a change in the melt film thickness between the solid bed and the barrel, as well is in the temperature of the melt pool and the solid bed.
Theoretical and experimental pressure and temperature evolutions are in good agreement. The evolution of the melt/solid repartition during the injection cycle is well described by the model.

(P/19)     PET FIBER OBTAINED FROM PSEUDO-GEL STATES; M. Ito and K.
Tanaka, Department of Chemistry, Science Univ. of Tokyo; Tokyo,
Japan.

In this paper use discuss the drawing behavior of poly(ethylene therphthalate) films obtained from pseudo-gel states which were prepared from 14/W/W Poly(ethylene terphthalate) (PET) in Nitrobenzen. The PET films were drawn by a two stage drawing process involving first solid state coextrusion with polyethylene polyoxymethylene and then conventional tensile drawing at 170-240C. The draw efficiency was evaluated by the tensile properties of the drawn products. The maximum draw ratio was DR=11.4, i.e. 2X higher from the hitherto reported values and the modulus and strengh values of the draw fibers were 17 GPA and 0.4 GPA. These values are slightly lower from the values of the heat treated draw fibers (DR=6) which were prepared from commercially as spun fibers. The results suggest that heat treatment is necessary for improving the performance of the drawn films from pseudo-gel intermediate.

(P/20)

DEVOLATILIZATION OF A RESIDUAL POLYSTYRENE/WATER MIXTURE IN A TWIN SCREW EXTRUDER; A.M. Catani and W. Hofer*, National Research Council Canada Industrial Materials Research Institute, 75 Mortagne Blvd., Boucherville, Qué. J4B 6Y4, Canada and* Werner & Pfleiderer Corporation, 663 E. Crescent Ave, Ramsey, N.J. 07446, U.S.A.

Polymer devolatization (DV) is a process operation during which, volatiles contaminants such as unreacted monomer, solvent or water are removed. Amongst currently used equipment there are the twin screw extruders having water or steam injection unit to induce foaming. The foam-enhanced DV produces high mass transfer rates enabling removal of large amount of volatiles especially when a vacuum system assist the extruder. Processing laboratory tests on the co-rotating ZSK-30 twin screw extruder with appropriate screw modifications and venting, indicates that it is possible to remove all the water (38-40%) from a residual polystyrene paste-like mixture. This work was part of an investigation to recuperate from commercial slurries, sufficient polystyrene for salable purposes.

(P/21)

AN EXPERIMENTAL AND NUMERICAL INVESTIGATION OF PEROXIDE INITIATED DEGRADATION OF POLYPROPYLENE IN A SINGLE SCREW EXTRUDER, C. Tzoganakis, J. Vlachopoulos, A.E. Hamielec, Department of Chemical Engineering, McMaster University, Hamilton, Ontario, Canada, L8S 4L7, and J.J. Godfrey, USS Chemicals, Technical Center, Monroeville, PA 15146, U.S.A.

The peroxide initiated degradation of high molecular weight polypropylene is known to produce products with tailor-made properties. Experiments were carried out in a single screw extruder using different levels of initiator concentration. Dramatic changes in melt flow index and molecular weight distribution were noted. The results were compared to numerical simulations using either simple plug flow models or more sophisticated finite difference and finite element methods.

(P/22)

MODELING FOR COMPUTER INTEGRATED SYSTEMS IN POLYMER PROCESSING
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In recent years there has been a rapid growth in the development and usage of computer assisted technologies in the polymer processing industry.

Polymer processing involves many steps, ranging from product design and manufacturing to mechanical behavior under service conditions. The inherent interdependence between these different steps is more evident with an integrated approach which includes many aspects of modeling and simulation.

This paper will review the basics behind the integration and relationship with computer modeling as seen from the individual components characteristics and requirements.

Also it will discuss the role of the key parameters such as material properties and the mathematical representation of the problem and their effects on the desired final results. Finally, applications related to injection molding of some industrial parts will be presented.

(P/23)        THE EFFECT OF PROCESSING ON THE FINAL PERFORMANCE AND FINE STRUCTURE OF PET FIBRE, Hu Xuechao, Zhang Yu, Din Zuomin, Shao Huili and Qian Baojun, China Textile University, Man-made Fibre Research Association, 1882 West Yan- An Road, Shanghai, China.

A new method (on line heated processing) for producing PET fibre has been developed. By this method it is possible to produce PET fibre which can be used in textile industry without any further process. A comparison of final performance of this type fully orient- ed yard (FOY) and PET fibre produced by traditional POY-DY processing (FDY) has been made. These two samples were examined by WAXD, DSC, TMA, Polarizing Microscope and Density gra- dient etc. The aim of this work is to investigate the structure of this new product and the mechanism of this new processing.

(P/24)        LUBRICATION APPROXIMATION FOR THE ANALYSIS OF VISCOELASTIC FLOW; by Bruce Caswell, Brown Univertisty, Providence, RI, 02912, U.S.A.

The lubrication approximation is developed relative to directions intrinsic to the flow instead of the usual developoment in which directions reside in the coordinate system. The aim of this work is to develop stress approximations which are valid in pure shearing deformations and which approach reasonable and well-behaved systems as the flow departs from pure shearing. For example, for extrusion flow a simple model is given in which the stress tensor is exact in the purely shearing domain and which approaches Newtonian behaviour as the free surface develops. The theory of small disturbances superposed upon pure shearing is used to obtain the leading terms in the equation of motion.

(P/25)        COMPOUNDING INDUSTRIAL POLYMERS: EFFECTS OF THE MIXER TYPE ON MELT RHEOLOGY, DISPERSION AND TEXTURE IN MODEL POLYBLEND AND POLYALLOY, by A.P. Plochocki, Polymer Processing Institute at Stevens,Castle Point, Hoboken, NJ 07030, USA; Z. Tadmor, Department of Chemical Engineering, TECHNION, Haifa, Israel; and P.S. Hope, Polymer R&D, BP Chemicals Ltd., Grangemouth, Scotland, UK, FK39XH.

Representative commercial grades of polyethylene (LDPE) and polystyrene, selected on the basis of melt viscosity and elasticity ratio functions, are used at 2/1 (LDPE/PS) ratio for studying the multiphase melt mixing process in main types of industrial mixers. Specimens of the polyblend and of a corresponding polyalloy are quantitatively analyzed with respect of phase morphology, its melt-flow and the mixing process sensitivity. Minor phase domain size for the polyblend was found to be in satisfactory agreement with predictions based on melt rheology of the component polymers and interface tension (SIMULBLEND software). The research program is encompassing six industrial mixers and the results for three mixers are currently evaluated: we report here preliminary results for a twin (corotating) screw compounder (BP) and batch distributive and continuous distributive (PPI) laboratory mixers only. Phase morphology was analyzed with electron microscopy and an image analyzer on "as received", and after-capillary-flow samples. The morphology of the polyblend/alloy is disperse. It is finer and less susceptible to flow segregation in the polyalloy than it is in the polyblend. In function of the mixing history the mean size of the minor phase domain and melt fluidity change. The changes are small for polyalloy and much more pronounced for the polyblend.

# OPTIMIZATION OF RUBBER EXTRUDERS
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The product qualities of rubber extrudates are closely combined with the operating parameters of the extruder itself. The extruder can be divided in two sections: feed zone and conveyor zone. Both zones have been intensively investigated at the IKV.

The paper shows the main influence-parameters for both screw sections. So e.g. effects of viscosity, different feeding zone or conveyor-zone geometries, screw and barrel temperatures will be discussed. The analysis of the thermodynamical processes in both zones were the point of departure to process models which allow the description of them. These models will be presented, they allow a qualitative or even a quantitative (conveyor zone) prediction of the process under different conditions. So optimizations concerning the process parameters or concerning the screw geometry could be done.

The paper will show, how useful the different models are under different conditions. In this sense the boundaries of each theory will be discussed. Nevertheless the semi-empirial optimization by modeltheory (scale-up) will be presented. The paper will gave practical hints for the use of this theory for rubber extruders.

Practical examples show some aspects of optimization under different conditions either for processors of rubber or for machinery constructors.

(P/28)

STYRENE/BUTYL ACRYLATE COPOLYMERIZATION WITH LAYER MORPHOLOGY: KINETICS AND VISCOELASTIC PROPERTIES
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Styrene (S)-Butyl Acrylate (BA) copolymers with layer morphology have been synthesized using an emulsion polymerization process. The kinetic parameters studied include: monomers composition, initiator content, feeding time and monomer addition sequence. The final product consists of a homopolymer nucleus surrounded by concentric shells of copolymers with different composition; the initial composition is quite rich in the monomer that forms the nucleus while the process ends with an enriched layer of the second homopolymer. Since the middle copolymer layers tend to increase the compatibility among the original homopolymers, we expected to have a set of core-shell products with completely different properties. However, the experimental results showed that this was not the case. The composition effect on the viscoelastic properties shows on one hand that an increase in the BA content lowers the elastic response of the final product. On the other hand, the elasticity increases with increasing copolymer content. As the initiator content present in the reaction media increases, the viscosity of the core-shell products decreases due to the existence of a media flooded with free radicals. If the BA is first added, a graft polymerization is favored due to the polar nature of this homopolymer and therefore the molecular weight level increases.
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(P/29)

THE FLOW OF AN UPPER-CONVECTED MAXWELL FLUID IN A
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Technology, Cambridge, MA  02139

The interaction between shear and elongation in the flow of visco-
elastic fluids is studied in the porous tube problem, where fluid is
injected into or sucked out of the tube through the wall.  The degree of
shear/elongation interaction is controlled by varying the amount of slip
on the wall via a slip coefficient $\beta$.

For the upper-convected Maxwell fluid, exact similarity forms for the
velocity, stress and pressure exist.  The resulting ordinary differential
equations are solved by three methods:  perturbation analysis, a rescaling
technique which transforms the boundary value problem into an initial-value
problem, and finite differences.  In the suction case with no slip on the
wall, a simple pole exists at De=0.263; this is directly related to the
simple pole for pure elongational flow at De=0.25.  In injection with no
slip, the finite difference calculations reveal a limit point at De=0.073.
Using grids that vary from 30 to 1000 nodes, this limit point is shown to
be stable with grid refinement and the solution to be oscillation-free.

(P/30)

FLOCCULATION OF CARBON BLACK IN FILLED RUBBER COMPOUNDS, )
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It has been found that appreciable carbon black flocculation can occur in filled
rubber stocks during storage or vulcanization in the absence of shear.  The kinetics of
this flocculation process was studied by means of low strain dynamic mechanical property
and electrical conductivity measurements.  The results showed the rate of flocculation
to be governed by the type and concentration of carbon black, polymer macrostructure,
mixing history and annealing temperature.  A mechanism responsible for the formation of
this carbon black network structure was proposed and the resulting changes in the physical
properties of vulcanizates prepared from these rubber compounds were elucidated.

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