



# Symposium 9

## Morphology and Structure Development



## Control of shish-kebab morphology in polymers crystallized under shear

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The current consumption of polymers is enormous which is expected to have a further sustainable growth throughout this century. This tendency is partially caused by an industrial demand on high standard polymers with predetermined properties. The majority of these materials are semicrystalline and inevitably these crystals are oriented by flow during processing. Optimising properties, to either minimise use or maximise benefits, needs an understanding of how flow-induced orientation competes with crystallisation. Two different morphologies can be found in crystallized polymers: spherulites forming at quiescent conditions and shish-kebabs appearing under shear. Critical examination finds that the longest chains play a catalytic role in the formation of shish-kebabs recruiting other chains into the formation of this morphology. The conventional wisdom is that the longest chains in an ensemble stretched by shear flow form the “shish” upon which the bulk of the material crystallises as “kebabs”. A universal parameter for the formation of shish-kebab structures, the specific work of flow, and a method by which it may be measured for any given ensemble of polymers are provided in this work. The magnitude of the specific work required to create shish-kebab structures depends on both the chemical structure of the polymer and its molecular weight distribution as these both affect the longest relaxation time and has profound implications for the design of polymer processing equipment. Model linear-linear hydrogenated polybutadiene blends as well as industrial low-density polyethylene have been investigated by both small-angle X-ray scattering and birefringence methods. The critical parameters responsible for the formation of shish-kebab structure in these polymers have been established and measured. The proposed approach is simple, elegant and can be easily implemented in industrial laboratories to test commercial materials before processing in real industrial applications.

S09-921

## The Effects of Additives on Material Properties and Shrinkage Characteristics

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The paper is concerned with the improvement of the predictive capability to include the effects of additives in the flow-induced crystallization (FIC) model presented previously in PPS-23. In this work, material-specific FIC parameters obtained experimentally for samples with different colors are provided as the input for the simulation. A two-phase model to calculate total stress (FENE-P for amorphous and rigid dumbbell for crystalline phase) is adopted, and Schneider's rate equation is used to describe the evolution of structures (spherulites and oriented shish-kebabs) during crystallization. The experiments required to obtain the model parameters, mainly utilizing the Linkam Cell, Dynamic Scanning Calorimetry (DSC), Thermo-Mechanical Analyzer (TMA) and Steady Shear Parallel Plate Rheometer, are discussed. An isotactic, unfilled PP from Borealis is used as the sample. Two types of colorants with different particle structures and nucleating potentials were mixed to the base polymer with a concentration of 0.8% for each colorant. With the simulation program we predict the shrinkage data and also the morphology distribution in the injection molded product. It is found that different structures of the colorants have significantly different effects on the crystalline morphology, the crystallization rate enhancement, the viscosity behavior and the shrinkage of the molded part.



## Saturation of flow effects on spherulitic and oriented crystallization

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It is well known that fast flow of a crystallizing polymer melt induces the formation of shish-kebab structures. Saturation of this effect has been observed and related to the depletion of long chains, which are oriented and stretched by the flow and form the threadlike precursor of the shish [Keller & Kolnaar 1997, Somani et al. 2000, Kornfield et al. 2002]. A similar saturation is observed in the effect of flow on the number of pointlike precursors, which, when nucleated, grow into spherulites. A model has been developed, in which the creation of pointlike precursors is enhanced by stretch of the contour paths of the long chains. A maximum number density of flow-induced pointlike precursors is introduced to account for the saturation. By comparing model predictions to microscopic observations of the spherulitic morphology, it is shown that this maximum number density depends on the Weissenberg number. Longitudinal growth of precursors is introduced in the model. Since long chains may be used for the creation of new pointlike precursors or incorporated in growing threadlike precursors, changes in the two saturation processes are expected. Oscillatory shear rheometry is a useful tool to monitor the effects of flow on spherulitic and oriented crystallization. Depending on the previous flow history, either both saturation processes can be distinguished or the saturation of pointlike precursor creation is hidden by the onset of threadlike growth. These observations are discussed from the modeling point of view. References: A. Keller & H.W.H. Kolnaar, *Materials Science and Technology* 18 (1997) R.H. Somani et al., *Macromolecules* 33 (2000) J.A. Kornfield et al., *Ind. Eng. Chem. Res.* 41 (2002)

S09-1350

## THE DETERMINATION OF THE RELEVANT PARAMETERS OF POLYMER CRYSTALLIZATION FOR PROCESS MODELING

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In polymer science, the process-microstructure-properties relationships is of great industrial and academic interest. Especially, because the operating conditions that produce thermo-mechanical environments in processing conditions are complex, it is necessary to know the origin and subsequent development of specific crystallized morphologies, i.e. spherulite, shish-kebab, transcrystallinity zone and teardrop-shaped spherulite, under various conditions, i.e. isotherm, anisotherm and shear. Recently, a mathematical model describing crystallization kinetics has been developed at CEMEF and implemented into the finite element Rem3D<sup>®</sup> code for injection-molding [1]. It is based on the phenomenological assumptions of Avrami; moreover, it enables us to predict the microstructure development, for example the distribution of spherulites size. Nevertheless, it requires a reliable determination of the crystallization parameters, namely transformed volume fraction, growth rate, activation frequency, density and size of crystallized entities. This present work is approached as a multi-criteria optimization problem, where the aim is to experimentally capture and to analytically extract the relevant parameters of crystallization. The studies concern two different polymers, a homopolymer polypropylene iPP and a polyether-block amide PEBA<sup>®</sup>. Experiments are investigated by means of polarized light microscopy and small-angle light scattering. The treatment of data by classical method or using inverse genetic algorithm method to extract the parameters necessary to our model is discussed. Finally, molding simulation will be presented as an illustration. [1] J. Smirnova, L. Silva, B. Monasse, J.-M. Haudin, J.-L. Chenot, *Eng. Comput.* 2007, 24, 486. Keywords: Crystallization, Polymers, Process Modeling.



## Non Adiabatic Thin-Film (Chip) Nanocalorimetry for Fast Cooling and Heating (MK/s)

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To study the kinetics of processes on a millisecond time scale thin-film nanocalorimeters based on commercially available microchips from Xensor Integration, NL, were constructed. The gauges consist of a submicron silicon nitride membrane with a film-thermopile and a film-heater which are located at the central part of the membrane. Controlled fast cooling is possible in addition to fast heating and AC-mode operation at non adiabatic conditions. The calorimeter was used to study isothermal crystallization after fast quenches. Crystallization of iPP, nucleated iPP and iPP based nanocomposites was investigated with ms time resolution. The calorimeter was also used to study the melting of isothermally crystallized PET. Our results on melting at rates as high as 2,700 K/s in combination with DSC and HyperDSC™ give evidence for the validity of a melting-recrystallization-remelting process for PET at low scanning rates (DSC). At isothermal conditions PET forms crystals, which all melt within a few dozens of K slightly above the crystallization temperature. There is no evidence for the formation of different populations of crystals with significantly different stability (melting temperatures) under isothermal conditions.

S09-161

## Polymorphic Crystallization of Beta-Nucleated Polypropylene in Pipe Extrusion – Comparison between Simulation and Experiment

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In order to meet the increasing requirements in new market segments as well as to overcome the growing competition of other materials the polymorphism of PP can be used. Special nucleating agents are added to induce the beta-modification which leads to an improved longterm strength and elevated impact resistance of the final product. The present work aims at verifying the assumed influence of processing/cooling conditions on the morphology by simulating the cooling behavior of an extruded pipe with a common FE-program (Abaqus/CAE 6.5) and evaluating the resulting fraction of  $\chi$ -modification. Many existing theoretical approaches describing the crystallization behavior require an expensive and time-consuming material characterization. To offer the operator an inexpensive estimation of the crystallization behavior, the used model bases on a single (CCT) test. First comparisons of the simulated values with WAXD-measurements on produced pipes show a qualitatively good agreement. The discussed model is able to display the different behavior at the inner and outer layer of the pipes.



## **Integrative Materials Modelling of Semi-Crystalline Thermoplastics Parts**

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The general aim of the Cluster of Excellence “Integrative Production Technology for High-Wage Countries” is to overcome the actual contradictions between value- and planning-orientation as well as between scale and scope in production technology. One important aspect of this approach is the development of virtual production systems to increase simulation suitability and thereby to reduce development times and costs as well as to optimize the utilization of material. Related to materials technology in general and especially to semi-crystalline thermoplastics this general aim requires the coupling of process simulation and structural analysis. This necessity arises because of the dependence of the inner properties of injection moulded parts on the processing conditions. So a prediction of inner properties and their integration into material models suitable for plastics leads to a more accurate and material saving design of polymer parts. At IKV software has been developed which allows the prediction of locally determined inner properties like degree of crystallisation, spherulite diameter and molecular orientation resulting from process parameters and geometry. By using mapping algorithms this data can be transferred and thus used in FE-models for structural analysis. Parallel to this, a user-defined material model has been developed and implemented as a subroutine into commercial FEA-software. This model describes the mechanical material behaviour including its dependency on the actual load case as well as on the local distribution of inner properties. Thereby the material model is being calibrated for every finite element according to the predicted inner properties. The modelling and simulation activities go along with intensive material characterization and validation by microscopic, calorimetric and mechanical analysis. The paper includes all aspects mentioned above and gives a prospect on future works in this field of materials technology.

**S09-343**

## **Crystallization of electron beam crosslinked UHMWPE**

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Ultra high molecular weight polyethylene (UHMWPE) is known for its high wear resistance and notched impact strength as well as a low sliding friction as required for total joint arthroplasty and friction bearing technical applications from off-shore fenders to conveyor belts. Often crosslinking is performed by e.g. electron or gamma irradiation to further reduce wear and improve thermo-mechanical properties. Despite the extraordinary large chain length of UHMWPE (molar mass 2-6 10<sup>6</sup> g/mol) compared to that of HDPE (molar mass 0.05-0.25 10<sup>6</sup> g/mol) a high degree of crystallization of about 50 % can be obtained which is somewhat less than the 60 to 80 % of HDPE. However, the effect of crosslinking on crystallisation has not yet been elucidated well. There are two possibly contradictive effects: Irradiation will lead to the formation of radicals and consequently, shorten the chain molecules, which should result in an increase in chain mobility and an enhancement of crystallization. On the other hand, a spatially crosslinked structure will show a lower molecular mobility and therefore a hindered crystal formation. In the present study, the crystallization behaviour of crosslinked UHMWPE as prepared at different electron beam irradiation dose of 0, 50, 95 and 110 kGy at 120°C and subsequent annealing at 150°C for 5 hours was investigated by synchrotron wide angle X-ray diffraction as well as DSC. It has been shown an enhancement of crystallization with an increase in the crosslink density due to an increasing irradiation dose. According to swelling experiments the molar mass between neighbouring crosslinks decreases from 57,000 to 3.170 g/mol with the irradiation dose from 0 to 110 kGy. The crystallization rate as determined from the crystallization peak temperature increases significantly with crosslinking, whereas the degree of crystallinity decreases slightly.



## Squeeze Flow Induced Crystallization of Isotactic Polypropylene.

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In the field of flow induced crystallization investigation, many experimental devices are devoted to shear flow because this is much easier to design and to use. Nevertheless, in many of processing systems, uni- or bi-axial elongational flows take place. From a rheological point of view these types of strain are known to produce more molecular orientation. Thus, some experimental devices allowing a controlled elongational deformation and the following of the crystallization process are needed. In this work, a simple experimental methodology was proposed to analyze polymer crystallization induced by biaxial elongation flow. The basic suggestion is to use the gap control system of a shearing hot stage (CSS450 from Linkam) to produce some squeeze flow while following the crystallization process by polarized light microscopy. The method was applied to an isotactic polypropylene which exhibits a substantial crystallization kinetics enhancement due to the squeeze compared to quiescent conditions crystallization. Moreover, despite a relatively short squeeze flow duration, the kinetics enhancement is as important as for longer shear treatments. In terms of crystalline morphology, like for shear flow induced crystallization, the squeeze flow promotes the nucleation so that the spherulites number is much higher than without any flow. However, it seems that the squeeze flow tends to produce some raw nuclei. Furthermore, from X-rays measurements, it was shown that the squeeze flow leads to remarkably generate some beta crystalline phase. Nevertheless, for the present experiments, no real orientation of the crystalline phases (alpha and beta) was obtained. Hence, the feasibility of using such a system to study the effect of bi-axial elongation on the crystallization was shown in the present work.

S09-468

## FLOW-INDUCED CRYSTALLISATION OF POLYETHYLENE AND POLYPROPYLENE MELTS

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Isothermal experiments have been carried out in a Multipass Rheometer (MPR) for polyethylenes (PE) and polypropylenes (PP) in order to understand the physical processes that govern the flow-induced crystallisation of polymers (FIC) in complex flows. The polymer melt was cooled down to the desired temperature and then crystallisation was induced by moving the pistons of the Multipass rheometer and forcing the material to flow within a narrow well defined test section geometry. The MPR enables precise flow and shear rates, similar to those encountered in industrial processing (apparent wall shear rates up to 104 s<sup>-1</sup>), and can also generate several types of flow, due to interchangeable mid-sections of different geometry (capillary, slits of different sizes, cross-slot). The formation of either spherulites or fibrous entities were visualised optically (through quartz windows) or detected by means of X-ray diffraction (through a Berillium capillary). The key observation for FIC of HDPE was that fibrous crystallisation occurred during the piston movement. The fibrous crystals formed locally in the high shear stress zones of the flow near the wall of the slit. PP had a broader operating window for FIC. In the case of PP, flow was found to enhance spherulite crystallisation kinetics and also induce fibrous crystallisation, both during and after flow cessation. Qualitative diagrams showing the crystal morphology for isothermal FIC MPR experiments as a function of temperature and wall stress were created for both polymers and represent the starting platform on which the modelling work will develop. The results help to clarify current conflicts between previously published FIC results on PP (e.g. Zuidema et al., *Macromol.Theory Simul.* 10: 447-460) and PE (e.g. Saquet et al., *J. Mat. Sci.* 35: 5247-5253) where some studies involve FIC during flow and others FIC after flow. [1]  
<http://www.cheng.cam.ac.uk/research/groups/polymer/MPR/index.html>



## Volumetric rheology of polymers: The influence of shear flow cooling rate and pressure on the specific volume of iPP homopolymers

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Polypropylene as a commodity polymer has a high market share and therefore a huge data set for simulation and processing parameters are available. However, the relationship between rheology, processing conditions and the main properties determining macroscopic shrinkage (i.e. specific volume) is still not understood in sufficient detail to predict the resulting dimensions of a product. Since specific volume is the key parameter for the final shape of a product, e.g.: Injection moulding, a custom designed dilatometer was used for the quantification of the influence of shear, pressure and cooling rate on specific volume. The fully automated dilatometer achieves cooling rates up to 100 °C/s, elevated pressures up to 100 MPa and shear rates up to 200 s<sup>-1</sup>. In this study three different iPP homopolymers grades, different in molecular weight and molecular weight distribution, were investigated. Isotactic polypropylene iPP1 had a molecular weight of  $M_w \sim 310$  kg/mol and a PDI of  $M_w/M_n \sim 3.4$ , iPP2 a molar mass of  $M_w \sim 376$  kg/mol and a molecular weight distribution of  $M_w/M_n \sim 6.7$  and finally the molecular characteristics of iPP3 were  $M_w \sim 466$  kg/mol and  $M_w/M_n \sim 6.6$ . Experiments at different cooling rates were performed at elevated pressures in the range of 10 MPa to 60 MPa and cooling rates of 0.1 °C/s and 1.5 °C/s. Shear experiments at elevated pressures in the range of 10 MPa to 60 MPa, a cooling rate of 1.5 °C/s and a constant shear rate of 67 s<sup>-1</sup> applied at two different temperatures of 143 °C and 164 °C respectively. Dependent of the molecular characteristics of the materials, cooling rates and shear flow pronounced effects on the temperature indicating the transition in specific volume  $T_c$  and the rate of transition were found. In order to investigate the crystalline morphology, additional ex situ measurements were performed with optical microscopy.

S09-534

## Crystallization of UHMWPE at the melt/flat substrate interface - the role of entanglements

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## Precursors, crystallization and melting in sheared bimodal HDPE melts

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Flow induced crystallization is an important issue for polymer processing. Flow can induce metastable precursors with very low or no crystallinity that can direct the whole crystallization process. Flow induced precursors (FIPs) are active in the early stages of crystallization enhancing the kinetics and promoting the formation of oriented shish kebabs. To enhance the formation of FIPs in shear flow, we make use of a specially synthesized blend of low and high molar weight (LMW and HMW) linear HDPE. Remarkably, we found that, at 142°C, just above the equilibrium melting temperature  $T_m^0$ , shear flow can induce needle-like precursors that are clearly detectable with X-ray scattering. At this high temperature, FIPs fulfilling the (demanding) requirements for stability can crystallize and form a suspension of shishes without kebabs. The others have a limited lifetime and dissolve back in the melt. The dissolution timescale of subcritical precursors matches the disengagement time of HMW suggesting that the early FIPs are HMW rich. Analysis of the flow conditions indicate that FIPs arise with the stretching of the network of HMW molecules but only if a critical total strain is exceeded. FIPs and shishes generated with shear at 142°C can be used as seeds for the nucleation of the rest of the molecules. On cooling, the onset of crystallization can shift up to 132°C depending on the flow conditions. Bulk crystallization starts with nucleation of kebabs at high temperature and, in some cases, proceeds, at lower temperature, with nucleation of randomly oriented lamellae that decrease the degree of orientation of the morphology. We observe that ~0.5% of shishes is sufficient to template a fully oriented morphology where the low temperature nucleation of randomly oriented lamellae is suppressed.

S09-766

## The Effect of Structure and Processing Conditions on Efficiency of Specific Nucleation in Polypropylene

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The work deals with the efficiency of  $\beta$ -nucleating agent NJ Star NU 100 based on N,N'-dicyclohexyl-naphthalene-2,6-dicarboxamide in isotactic polypropylene (iPP). Several grades of iPP differing in melt flow indexes (MFI) from 0.3 to 1 200 g/10 min were used as a virgin materials. The nucleating agent was immixed into them in two concentrations, 0.01 and 0.03 wt. %. The specimens were prepared from all virgin materials and blends via compression-moulding using various conditions; the processing temperature varied from 200 to 220 °C. Polymorphic composition of prepared specimens was analyzed using wide-angle X-ray scattering. Polypropylene with 0.03 wt. % of  $\beta$ -nucleating agent crystallizes predominantly into  $\beta$ -phase while neat iPP into  $\alpha$ -phase, both independently on MFI and processing temperature used. However, the formation of  $\beta$ -phase in iPP with 0.01 wt. % of the nucleator is strongly influenced by processing temperature. The compression-moulding at 200 °C leads to the predominant formation of  $\beta$ -phase while the materials processed at 220 °C crystallizes almost solely into  $\alpha$ -phase. This significant change in crystallization behaviour caused only by increase/decrease of processing temperature can be ascribed to partial solubility of NJ Star NU 100 in the polypropylene melt. The extent of nucleator dissolution increases with the final temperature of processing leading to a decrease in its efficiency. Moreover the solubility seems to be dependent also on the molecular structure of the polypropylene. In the case of processing temperature of 210 °C it is evident that the lower is MFI, the higher is the tendency of iPP to crystallize into  $\alpha$ -phase. These results exemplify strong relationship between the initial concentration of the nucleating agent and the final temperature of heating on one side, and the crystallization, the polymorphic composition, and the supermolecular structure of the samples on the other.





## Specific mechanical work as universal parameter for the formation of shish-kebab structure?

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The morphology of semicrystalline polymers strongly affects their physical properties. Therefore control of the structure on different length scales is technologically important. Changes in structure and properties are mainly associated with the flow-induced transition from a relatively isotropic, spherulitic morphology to a highly oriented, shish-kebab morphology which increases stiffness and strength. This morphological transition is induced by flow and is very sensitive to the molecular characteristics of the polymer, particularly those of the longest chains. In this presentation a universal parameter for the formation of shish-kebab structures, the specific mechanical work, and the method by which it is measured are discussed. We refer to a previous study (1) where, for different shear conditions, the transient response of PB-1 during and after flow has been monitored by birefringence and turbidity. The combination of a sandwich-type shear cell and the different probing techniques allows for an accurate determination of the transition to highly oriented shish-kebabs. This transition is characterized by both a characteristic upturn in the birefringence during flow, and a sharp increase in the crystallization kinetics as obtained from characteristic crystallization times. It is shown that the critical shear-rate for the formation of the oriented structure falls off with increasing shear time, which indicates that the total amount of flow is an important parameter. Here the suggestion by Janeschitz-Kriegl (2) that a specific amount of work is required to form shish kebabs is applied. For the 'constant-shear' experiments in this study the specific mechanical work can be obtained in a very easy way. Results confirm that the oriented structures only form if more than a certain amount of work has been performed on the melt. 1. Baert J., Van Puyvelde P., Langouche F., *Macromolecules*, 2006, 39, 92152. Janeschitz-Kriegl H., Ratajski E., Stadlbauer M., *Rheol Acta*,

S09-792

## Relationship between morphology of UHMWPE reactor powders and their ability to compaction and gel formation

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Aiming at elucidation of relationships between morphology of UHMWPE reactor powders and their ability to compaction and gel formation, a complex study of UHMWPE nascent morphology and its influence on the nascent particle merging under pressure, and the process of particle dissolution was carried out with by WAXS, SEM, FTIR, DSC, light scattering and thermoluminescence techniques. The investigated lab-scale UHMWPE reactor powders were synthesized by slurry polymerization in heptane on supported Ti/Mg catalytic systems (I) and on a highly active Ziegler-Natta catalyst particle of colloidal sizes modified by an organic compound (II). A commercial UHMWPE (Stamylan) (III) was studied for comparison. The individual particles (50-400 nm) appeared to be the clusters consisting of the smaller particles (subparticles) of almost spherical shape with the sizes less than a micron. The subparticles have a complicate inner structure of a lamellar type. In powders I and III, they are connected by fibrils of 50-100 nm in diameter, which unite them in strong 3D constructions. The length of the fibrillar units, their amount and degree of subparticle connectivity vary in the powders synthesized on various catalytic systems. In powder I, the fibrils are almost absent. It is found that compactability depends on the amount of fibrils in the reactor powders, which play a negative role in producing a mechanically coherent material. Despite the fact that polymer has first to be dissolved at high temperature in order to form a gel at cooling, and, consequently, a synthesis-induced memory has to be destroyed, the investigated reactor powders are gelled in various ways. A role of tie molecule amount, conformational defects and molecular mobility in a process of dissolution and gelation, of which the data were obtained by DSC, FTIR, thermoluminescence and light scattering is discussed. The work was supported by RFBR (06-03-32707; 06-03-0811-ofi) and SPb Scientific Centre grants.



## PVDF surface functionalization and its effect on the crystal phase transition

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We investigated the effect of the surface functionalization on the crystal phase change of poly(vinylidene fluoride) films. The stretched and poled PVDF films were used for this study. Ion-beam and plasma treatment were employed for the surface modification of PVDF. The surface treatments induced some changes of chemical composition as well as the morphology of PVDF surface. It had a significant influence on the interfacial adhesion with thermally deposited metal electrodes on the PVDF. Surface modifications played a pivotal role for both the determination of interfacial strength between PVDF and electrodes and the change of crystal structure in the PVDF film. While the amount of  $\beta$ -phase crystal in PVDF decreased with the treatment time increase, the interfacial adhesion increased with the modification time. In this research, we were able to find the optimum treatment condition for both enhancing the adhesion and retaining piezoelectric structure.

S09-1033

## Flow-induced crystallization of polymers: Saturation in nucleation

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Both the molecular characteristics of the polymer and the applied thermo-mechanical history applied to the polymer influence the crystallization kinetics of the material. Quiescent crystallization of isotactic polypropylene (iPP) leads to the formation of isotropic crystallites or spherulites. Application of flow will, when strong enough for a long enough time, accelerate crystallization by the formation of extra point-like precursors. When flow is even strong enough to stretch the molecules, threadlike precursors will form from which oriented structures will develop. Based on rheological characteristics of polymer molecules several flow regimes were identified and an attempt was made to relate the flow regimes to the enhanced point nucleation and fibrous nucleation as observed in flow induced crystallization (FIC). The transition between the regimes is marked by two critical Weissenberg numbers, related to the orientation and stretch of the longest molecules. To actually create the extra precursors (point- or threadlike) the flow time also has to be sufficiently long i.e. a certain amount of strain or work has to be applied. A saturation in threadlike precursors has been observed when the flow time is increased, arising from the depletion of long chains. In our study, in which the crystallization process is monitored using rheometry, also a saturation of the number of flow-induced point-like precursors, from which spherulites grow, is observed. In the flow regime where threadlike precursors can form, the saturation of point-like precursors can disappear by the onset of growth of threadlike precursors. These results are used to develop a model which describes the formation of flow-induced precursors including the saturation effects observed in experiments.



## Flow-induced formation of microfibrillar phase in polyolefine blends

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The work focuses on microfibrillar-phase formation in polymer blends during extrusion through a die with semihyperbolic-converging channel. For these purposes, three polyethylene/polypropylene blends with mixing ratios (wt./wt.) 80/20, 70/30 and 60/40 were prepared. Final structure and properties of extruded blends were examined using wide-angle X-ray scattering and tensile testing. It is demonstrated that the formation of microfibrillar-phase morphology is achieved in all blends. Structure and properties of these microfibrillar-phase composites are strongly influenced by mixing parameters.

S09-1277

## Structure evolution of amorphous and semicrystalline polymers during uniaxial stretching as observed by WAXS

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The understanding of the structure evolution during deformation of polymers [1-3] and the identification of active deformation mechanism [4] is an essential route to establish structure-mechanical properties relationships and to develop accurate constitutive models. In this work the structure evolution of PET and PP during stretching was assessed by wide-angle x-ray scattering. Both polymers had initially different morphological states and distinct mechanical behaviours. Rectangular tensile specimens were stretched in a miniaturised home-developed stretching device at different strain levels under an X-ray synchrotron source (A2 polymer HASYLAB, DESY, Germany). All polymers showed similar trends of evolution of the level of molecular/crystalline phase orientation: after a rapid increase for the initial strains (elastic region), a threshold value is reached just after yield point, thereafter orientation remaining constant. For amorphous PET, the increment on the molecular orientation was accompanied by the development of a highly oriented mesophase. For initial semicrystalline PET, deformation led also to a slight increase on the degree of crystallinity. The initial low crystallinity PP evidenced a heterogeneous deformation and at necking the lamellar structure was disrupted with a significant reduction of the degree of crystallinity. Initially high crystalline PP showed a significant reduction on the deformation capabilities, no necking and little evolution of the crystalline phase. Modelling of these behaviours is a challenging task, but structure and its evolution needs to be considered in any constitutive model. [1]Mahendrasingam A, Blundell DJ, Martin C, Fuller A, MacKerron DH, Harvie JL, Oldman RJ, Riekel C, Polymer 41(2000) 7803[2]Davies RJ, Zafeiropoulos NE, Schneider K, Roth SV, Burghammer M, Riekel C, Kotek JC, Stamm M, Colloid Polym Sci, 282(2004) 854[3]Martins CI, Cakmak M, Macromolecules, 38(2005) 4260[4]Lin L, Argon S, J Mat Sci, 29(1994) 294



## Structure-property relation in isotactic polypropylene with non-lamellar crystals

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The morphology and reorganization of mesomorphic non-lamellar crystals of isotactic polypropylene (iPP), produced by controlled rapid melt-crystallization at cooling rates between 80 K s<sup>-1</sup> and 1000 K s<sup>-1</sup>, and subsequent annealing above 400 K, was quantitatively investigated by atomic force microscopy. Mesomorphic nodules of size of about 20 nm at ambient temperature transform on heating to monoclinic crystals at about 350 K, with the crystal morphology being unchanged. Further heating to 433 K increases the crystal size to 40-50 nm. The crystal structure/morphology affects the thermal, mechanical and optical properties, as is concluded e.g. from the analysis of the glass transition temperature (T<sub>g</sub>), of the modulus of elasticity and of the transmittance of light. We observed a strong increase of T<sub>g</sub>, if lamellar crystals get thinner and get replaced by nodules, and then only slightly with decreasing size of nodules, with the latter achieved by increasing the cooling rate from 100 K s<sup>-1</sup> to 1000 K s<sup>-1</sup>. Similarly, the dependence of modulus of elasticity on the cooling rate shows two distinct regions associated with different crystal morphologies. It decreases strongly initially with increasing the cooling rate, likely caused by a decrease of the crystallinity and of the thickness of lamellae and remains at low level where nodules are present. Annealing of nodules further demonstrates the impact of the crystal morphology on these application relevant properties. Screening test regarding optical properties indicate increased transmittance of visible light in preparations with non-lamellar crystals, in comparison to preparations with lamellar crystals.

S09-160

## Evolution of microstructure in liquid crystalline polymers across their phase transition from isotropic to ordered state

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Kinetics of the ordered (nematic/cholesteric) nucleus growth in the melted liquid crystalline polymers across their isotropic to ordered phase transition was investigated experimentally under cooling. The ordered phase entities in the form of droplets revealed in the optical images during the isotropic phase separation were treated statistically. The resulting frequency distributions of the droplet area were described analytically using the model of reversible aggregation. This model was inspired by the application of equilibrium thermodynamics of irreversible processes and gives a generalized description of microstructure in melted and frozen liquids. Analysis of the mean droplet diameter evolving with time across the phase transition allowed identification of two regimes involved in the phase ordering. Within the first regime, nuclei of the ordered phase appear spontaneously and subsequently grow, whereas within the second regime, their size increases because of nucleus coarsening. Since thermodynamic ensembles of droplets are self-similar across the phase transition, both regimes were quantitatively described using the universal scaling function. The power index found, being compared with the theoretical predictions, allowed clarification of molecular mechanisms responsible for both nucleus growth and nucleus coarsening in the liquid crystalline polymers studied across their phase transition.



## Photodegradation of Polypropylene Containing Nucleating Agents

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The work discusses the effects of polymorphism of isotactic polypropylene on its photodegradation behaviour. The starting polymer was modified by a specific  $\alpha$ -nucleating/clarifying agent, 1,3;2,4-bis(3,4-dimethylbenzylidene)sorbitol, by a specific  $\beta$ -nucleating agent, N,N'-dicyclohexyl-naphthalene-2,6-dicarboxamide, or their combination. Both the nucleating agents are commercially available. The samples of thickness 0.2 mm, were prepared via compression moulding. Differential scanning calorimetry revealed that the modification of isotactic polypropylene by a specific  $\beta$ -nucleating agent caused predominant formation of the trigonal  $\beta$ -phase. With virgin samples modified by  $\alpha$ -nucleating agent and combination of both nucleating agents and also with neat polypropylene only monoclinic  $\alpha$ -phase was detected. Thus the  $\alpha$ -nucleating agent possesses higher nucleating efficiency as compared to  $\beta$ -nucleating agent. The samples were exposed to UV-irradiation in the interval from 0 to 240 hours. The differences in morphology were reflected in different photooxidative behaviour. Infrared spectroscopy showed that neat polypropylene was the most sensitive to the photooxidation and the sample modified solely by the  $\beta$ -nucleating agent was the least sensitive. The remaining two samples exhibited an intermediate sensitivity, moreover quite similar. According to results from differential scanning calorimetry UV-exposure led to gradual changes in crystallization mechanism specifically asserting in individual materials. This behaviour was ascribed to homogeneous nucleation of partly degraded macromolecules. The polypropylene containing solely  $\alpha$ -nucleating agent possesses the fastest change of crystallization mechanism; the crystallization temperature significantly decreased after only 24 hours irradiation. Thus, possible changes of the nucleating agent itself during UV-exposure were also discussed.

S09-189

## Photodegradation of $\beta$ -Nucleated Polypropylene: The Effect of Structure Parameters

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The main aim of the work was to observe the influence of melt flow index (MFI) on photooxidative degradability of neat and  $\beta$ -nucleated polypropylene. The concentration of 0.03 wt. % of specific  $\beta$ -nucleating agent NJ Star NU 100 based on N,N'-dicyclohexyl-naphthalene-2,6-dicarboxamide was immixed into five commercial grades of polypropylene differing in melt flow index from 0.3 to 1200 g/10 min. Then, compression moulded films prepared from both the neat and  $\beta$ -nucleated materials were exposed to UV-irradiation for several exposure times. The photodegradation kinetics observed via infrared spectroscopy and expressed by carbonyl index was significantly slower for all  $\beta$ -nucleated polypropylenes. This result proved already published lower degradability of  $\beta$ -nucleated polypropylene. Melt flow index of the materials slightly influenced the photooxidation kinetics independently on the presence of  $\beta$ -nucleating agent; the carbonyl index of the material with the lowest MFI increased markedly at the beginning of irradiation as compared to the others materials. However, after prolonged irradiation time, the increase retarded. The evolution of the crystallinity and  $\beta$ -phase content in irradiated samples were studied using wide-angle X-ray scattering. The crystallinity of all samples under study increased at the beginning of irradiation and at prolonged UV-exposure time remained stable. The  $\beta$ -phase content in nucleated samples did not change dramatically during irradiation. Differential scanning calorimetry revealed that the crystallization temperature of all irradiated samples increased at the beginning of irradiation, however, after UV-exposure prolongation it dramatically decreased. The effect of MFI was not unambiguously observed.



## Surface Chain Orientation during Crystallization Induction Period Studied with Polarized FTIR-ATR

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Thermo-induced surface orientation behaviors were studied in situ by Fourier transform infrared spectroscopic (FTIR) measurements along with attenuated total reflection (ATR) and transmission methods during the cold crystallization of melt-quenched amorphous poly(pentamethylene 2,6-naphthalate) (PPN) film. The chain in the crystalline phase formed during the cold crystallization process was found to orient parallel with the film surface with a naphthalene ring perpendicular to the film plane. By observing the isothermal crystallization process via polarizing optical microscopy and wide-angle X-ray diffraction methods, it was revealed that PPN shows very slow crystallization kinetics, even when crystallized at the temperature associated with the fastest crystallization rate. Furthermore, the crystallization induction period was longer than 150 minutes, during which time a significant amount of crystalline phase was not to be formed. The chain orientation at the surface during the crystallization induction period was again measured via polarized FTIR-ATR spectroscopy. It was found that the preferential surface orientation occurs during the early stage of the induction period and no further orientation was observed during the subsequent crystallization process. Rapid local ordering that occurred during the crystallization induction period, especially at the surface, appears to be followed by gradual packing of the locally-ordered chain to form the crystalline phase.

S09-315

## Morphological Distribution of Injection Moulded Isotactic Polypropylene in the Presence of Pigments: A Study Using Synchrotron WAXS

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The morphological distribution of injection moulded iPP in the presence of Cu-phthalocynine and ultramarine blue was investigated using the synchrotron WAXS. The results show that under the shear conditions the Cu-phthalocynine can induce the higher degree of crystallinity than the ultramarine blue. The WAXS image patterns show that the Cu-phthalocynine can effectively enhance the molecular orientation of iPP in the shear region whereas the ultramarine blue cannot. In the presence of Cu-phthalocynine, the anisotropic feature is observed in a broader range. Since the Cu-phthalocynine cannot induce the branched shish-kebab structure without flow, the observation implies that the weak flow is sufficient enough to induce the shish and subsequently the branched shish-kebab structure when the Cu-phthalocynine is added. The effect of ultramarine blue on the formation of branched shish-kebab, however, is not significant. An intricate balance between shear flow and local supercooling is also believed to control the crystallization. In the presence of Cu-phthalocynine, the thickness of crystalline lamellae is increased. However, the thickness is only slightly affected by the ultramarine blue in the shear region and decreased in the core region. Since the crystallization in the presence of colorants would be also influenced by other factors such as fold surface enthalpy and even surface slippery, the effects of the colorants on the thickness of crystalline lamellae are still open to debate.



## High performance differential scanning calorimetry (HPer DSC): A powerful analytical tool for the study of the metastability of polymers

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The crystallization and melting behavior of polypropylene (PP), polyoxymethylene (POM) and polyamide-6 (PA6) has been investigated by means of varying the cooling and heating rates using a high performance differential scanning calorimeter (HPer DSC). The influence of the sample mass and scan rate on thermal lag has been sorted out and the importance of making proper corrections is stressed. By varying the cooling rates from 5 to 250 °C/min in combination with one particular heating rate (10 and 300 °C/min have been used) reorganization and especially recrystallization effects in a PP sample have been examined. Recrystallization of the PP can be avoided by using a high heating rate (300 °C/min). The influence of incorporating a stabilizer acting as a comonomer in the POM chain on the kinetics of the crystallization and melting behavior is studied. The influence of the maximum heating temperature in the melt on crystallization of POM and of POM with stabilizer is investigated by self-seeding experiments using high heating and cooling rates. Furthermore, the melting behavior of PA6, where several transitions take place during heating which are up to now not fully understood, is discussed subsequent to cooling at 5–300 °C/min. Throughout it has been made clear that it is important to have the capability of applying proper combinations of low/high and cooling/heating rates in order to examine the metastability of polymer systems and the related kinetics of transitions, to scrutinize the phenomena seen and to arrive at the right explanations.

S09-479

## Effect of Surfactant Adsorption and Drying Procedure on the Dispersion of Organoclay in Polymer Matrix

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Cationic surfactant, hexyltriphenylphosphonium bromide (HTP) was selected to modify montmorillonite clay (Cloisite Na+) to investigate the effects of surfactant adsorption and drying procedure on the formation of PBT/clay nanocomposites. A series range of surface coverage ratios from 0 to 3.0 CEC of adsorbed HTP to MMT were studied by the UV/vis spectrophotometer and X-ray diffraction (XRD). It was found that the adsorption behaviour of the clay surface was highly depended on the surfactant concentration and a maximum adsorption of HTP to MMT was achieved at ~1.7 CEC HTP. The intercalation of surfactant in clay galleries also varied with the surfactant concentrations as the interlayer spacing remains at 1.76 nm when HTP was below 1.0 CEC and it increased to ~2.0 nm after ~1.7 CEC of HTP. The FEGSEM characterisation of the clay powder (HTP-H) obtained by heat drying and followed by milling, and the freezing dried clay powder (HTP-F) as shown in Fig. 1, displayed that the heat dried organoclay followed by milling was compressed into large and relative hard particles, while freezing dried organoclay formed loose particles consist of thin multi-layer silicates. Both clay powder HTP-H and HTP-F were melt compounded with PBT polymer in the Haake internal mixer, and the obtained PBT/clay composites were analysed by XRD and TEM, respectively. The different adsorption resulted from different surfactant concentrations, 1.5 CEC and 1.7 CEC HTP-MMT revealed that higher surfactant adsorption which possesses larger interlayer spacing would be easily intercalated. On the other hand, the effect of drying procedure has shown that the freezing drying was much easier to the formation of PBT/clay nanocomposites compared to that heat dried and milled organoclay, as the dispersion and the degree of intercalation of HTP-F powders was greater than that of HTP-H within PBT matrix.



## Polypropylene/Organic Functionalised Organoclay Nanocomposites with Improved Mechanical Properties and Thermal Stability

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A functionalised organoclay was prepared by surface treatment of commercial organoclay (Cloisite 30B) with silane coupling agent, 3-aminopropyltriethoxysilane (APS), which was subsequently melt compounded with polypropylene (PP) and maleic anhydride grafted polypropylene (MAPP) in a Haake internal mixer. The FTIR, TGA and XRD analysis of the functionalised organoclay APS-30B showed that the chemical interactions were enhanced by the formation of Si-O-Si bond between the silane coupling agent and the organoclay. The thermal decomposition onset temperature of the organoclay was increased by ~20°C upon the silane treatment, although no changes in the interlayer spacing was observed. The effects of the APS on the dispersion of organoclay in PP/30B nanocomposites and its resulting mechanical properties were studied by XRD, TEM and tensile test. It showed that thermal degradation occurred in the organoclay 30B during the melt compounding, resulting in poor mechanical properties. However, APS treated organoclay/PP nanocomposites exhibited much improved thermal stability and mechanical properties of ~50% increases in Young's modulus, which is probably due to the strong interaction of the coupling bonds between PP matrix and the organoclays. Meanwhile, the investigations on the effects of different amounts of APS on the properties of APS treated organoclay/PP nanocomposites showed that an optimum amount for better mechanical properties was at 3%-5 wt.% of organoclay. The excessive APS may prevent the mechanical performance due to the blocking effect on the organoclay surface and self-condensed APS at the boundaries of PP matrix and the organoclays.

S09-578

## PROPERTIES-MORPHOLOGY-PROCESSING RELATIONSHIPS IN POLYMER-BASED CLAY NANOCOMPOSITES

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Recently, there is a growing interest to a new class of polymer-based materials called nanocomposites. These materials, where low amounts of a filler are dispersed at a nanometric scale, may present unique properties without significant changes in the density, the processability, the transparency. Among the different nanofillers that can be potentially used, organo-modified layered silicates are used as nanofiller precursors. Under certain conditions, in fact, the tactoids of the silicates can break into lamellae with a thickness falling in the nanometric scale. The aim of this work is to develop a model that could describe polymer clay nanocomposites. In particular we tried to interpret them as polymer blends where the organoclay represents the dispersed phase in a polymeric matrix. The tuning of these models can be an invaluable tool to describe and to predict the behaviour of these class of materials. Unfortunately, very few attempts are available in the literature in this sense. It has been investigated the validity of Wu's equation (usually used for polymer blends) in the case of nanocomposites systems to find a model that could give the relationships between processing conditions and the final morphology of the nanocomposite. We also investigated a method to relate processing conditions and rheological properties of nanocomposites.





## Investigation of the effect of orientation on properties of polyamid copolymer

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Packaging industry needs different types of materials fitting the different requirements. One of the important processing technologies is the vacuum forming. Complex deformation occurs in this process, and it influences the structure of the material. It is especially important in the case of crystalline polymers as the crystallisation usually occurs in oriented samples. Our research was carried out on vacuum formed Pebax<sup>®</sup> materials. Mechanical and thermal properties were determined as function of the orientation of the samples. We determined the crystallisation kinetics of the material in isothermal and in non isothermal conditions. It was found that the change of the modulus and the yield stress with the orientation is more or less follows the Hennig-rule. Thermodynamic melting point was determined by Hoffman-Weeks method. It was found that the Avrami-equation can describe the isothermal crystallisation kinetics in very wide range.

S09-761

## Strings microstructures in sheared suspensions of spheres in viscoelastic liquids

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Solid suspensions are widely used in industrial application. Examples are the manufacturing of filled polymer composites, paints, and coatings. The addition of particles leads to a change in the rheological properties of the fluid as well as in the flow fields. Many experimental results show that particles suspended in a non-Newtonian fluid can arrange themselves into various structures. In particular it is reported that the formation of particle strings or cluster depend on the imposed flow and on the nature of the suspending fluid. This work is focused on the investigation of string formation in a simple shear flow. In such a flow, experimental observations show that the particles align along the flow direction and then they chain one to each other. In addition, a cessation of individual particle rotational motion is found, when they come into contact. We have implemented a finite element code to simulate the behaviour of such a suspension in order to verify the absence of rotation and the stability of these structure formations. The rigid-body motion is imposed on the particle surface through constraints, i.e. the force and torque-free conditions are automatically satisfied. The analysis is carried out for a newtonian fluid and for different viscoelastic medium in order to study the impact of the nature of the fluid on the structure formation.



## Polymorphic transformation in polybutene-1: temperature influence

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The work directs attention towards the influence of annealing temperature on polymorphic transformation in isotactic polybutene-1 (PB-1). Polybutene-1 possesses a peculiar crystallization behaviour and polymorphism being not currently fully understood. Polybutene-1 crystallizes from melt into the unstable form II. Depending on temperature and pressure conditions PB-1 recrystallizes into the thermodynamically stable form I upon thermal ageing. For the purposes of present work, three different polybutene-1 materials, two homopolymers and ethylene-copolymer were processed using compression moulding and injection moulding to prepare samples for further analyses. These were characterized by differential scanning calorimetry, wide angle X-ray scattering and tensile testing. Then, the samples were annealed at five different temperatures -22, 6, 22, 40 and 60 °C in time interval from 0 up to 48 days at ambient pressure. It has been observed that temperature directly influences the transformation rate from form II into form I. At temperatures 6 and 22 °C the transformation rate was fastest, while at -22 °C the rate was slowest. The difference between ethylene-copolymer and homopolymers was observed in the increased transformation rate for ethylene-copolymer PB-1. The morphology change is consequently reflected by the extensive evolution of mechanical properties.

S09-772

## AFM STUDY OF MORPHOLOGICAL REORGANIZATION OF MESOMORPHIC CRYSTALS IN ISOTACTIC POLYPROPYLENE.

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The atomic force microscope (AFM) has been used to investigate morphological reorganization of mesomorphic crystals in isotactic polypropylene from the solid state. Samples were crystallized in non-isothermal mode at high cooling rate. Height, phase and amplitude images were recorded, using the tapping mode, during the subsequently annealing in the range temperature 40-60°C. Mesomorphic domains originally obtained by melt crystallization were followed during growth size.



## Synthesis of Uniformly Sized Molecularly Imprinted Microspheres and Nanoparticles for Primidone: Influence of Cross-linker:Functional Monomer Ratio and Cross-linker Type on Morphology and Selectivity

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Uniformly sized molecularly imprinted polymers (MIPs) were prepared by miniemulsion polymerization method using methacrylic acid (MAA) as the functional monomer, ethylene glycol dimethacrylate (EGDMA) and trimethylpropane trimethacrylate (TRIM) as the cross-linker agent, primidone (antiepileptic drug) as the template molecule and azobisisobutyronitrile as the initiator. MIPs with controlled physical shapes with different size ranges can well satisfy various application purposes. The results showed that varying the TRIM:EGDMA ratio allows the particle size of the MIP beads to be changed, whereas the favorable binding property of the MIP beads remains intact. The particle size and morphology were analyzed using scanning electron microscopy. The amount of cross-linker agent is a key to forming a cavity in a polymer network. If the density of cross-linker agent is low in the polymerization, lack of cross-linker agent can not fix template molecule from three-dimensional molecular imprinting. The load of primidone and the selectivity of MIPs with different cross-linker agent: functional monomer ratios were analyzed by UV spectroscopy. We believe that the results presented in this work, should be valuable for future research towards development of drug delivery and new separation. References [1] Keiichi Yoshimatsu, Kristina Reimhult, Anatol Krozer, Klaus Mosbach, Koji Sode, Lei Ye, *Analytica Chimica Acta*. 2007, 584, 112-121. [2] Jun Haginaka, Hiromi Tabo, Chino Kagawa, *Journal of Pharmaceutical and Biomedical Analysis*. 2007, 6375, 1-5. [3] Dorothea Vaihinger, Katharina Landfester, Iris Krauter, Herwig Brunner, Gunter E. M. Tovar, *Macromol. Chem. Phys.* 2002, 203, 1965-1973.

S09-842

## INVESTIGATING ON THE PORE MORPHOLOGY OF POLYMERIC SCAFFOLDS PREPARED BY THERMAL INDUCED PHASE SEPARATION

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Thermally induced phase separation (TIPS) is a versatile technique for the preparation of microporous membranes (Song, 1994). Since its development in the early 1980s, much attention has been focused on its applicability to insoluble polymers at room temperature and its utility for morphology control by playing on a closed set of variables. This technique is based on the principle that a single homogeneous polymer solution at high temperature is converted into two-phase separated domains composed of a polymer-rich phase and a polymer-lean phase via thermal energy removal by controlled cooling procedure (Van de Witte, 1996). After the removal of the solvent, a microporous structure can be obtained by sublimation, evaporation or solvent/not solvent exchange. During the TIPS process the phase transitions may proceed by the combination of liquid-liquid phase separation and solidification mechanisms involving the crystallization of the solvent, the vitrification or the gelation of the polymer. The final structure of the scaffolds depends on the competing phase transition between the liquid-liquid phase-separation and solidification processes (Schugens, 1996). In this work, a comprehensive morphological study of biodegradable polycaprolactone scaffolds obtained by different binary systems has been performed in order to emboss the potential of the TIPS technique to develop tailored porous scaffolds with high oriented porosities. Song, S. W.; Torkelson, J. M. *Macromolecules* 1994, 27, 6389. Van de Witte P, Dijkstra PJ, van den Berg JWA, Feijen J. - *J Membr Sci* (1996) 117: 1-31. Schugens C, Maquet V, Grandfils C, Jerome R, Teyssie P. - *Polymer* 1996; 37:1027-1038. Schugens C, Maquet V, Grandfils C, Jerome R, Teyssie P. - *J Biomed Mater Res* 1996; 30: 449-461.



## Evaluation of microstructure –adhesion properties correlation in polyurethane adhesives

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Segmented polyurethanes consist of hard and soft segments exhibit special properties using in adhesives in order to various applications. In otherwise blending and co polymerization has also been considered in last two decades. As the polyols have different chemical structure, various polyurethanes with different properties could be synthesized. In the present work we applied blends of an ether type and HTPB(hydroxyl-terminated polybutadiene) prepolymers to synthesize of polyurethane adhesives and adhesion compared with pure ether or HTPB type ones. In this way, elastomeric polyurethanes based on Toluene diisocyanate (TDI) and 1,4-butanediol (BD) and two kinds of type polyols were synthesized. In the first step polyols were reacted with -NCO groups then obtained prepolymers mixed; in thesecond step chain extender was added. Differential scanning calorimetry (DSC), dynamic mechanical analysis (DMTA) and Fourier transform infrared spectroscopy (FTIR) have been used to analyze phase separation and microstructure- macro mechanical properties of the samples. Mechanical testing was carried out to determine T-peel strength and tack resistances of synthesized adhesives. Also lap shear strength of the various adhesives was measured on aluminum and Glass substrates. Results showed interesting and reasonable correlation between structure and adhesion properties of polyurethane adhesives.

S09-888

## Cone Calorimetry and Condensed Phase Structural Changes in Flame-Retardant Butyl Acrylate Methyl Methacrylate Copolymer Composites

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Flame-retardant (FR) behaviour of composites made with poly(butyl acrylate-co-methyl methacrylate) (BAMMA) copolymer has been investigated by thermogravimetry (TG) and cone calorimetry. Composites were prepared with talc, magnesium hydroxide and zinc borate, FRs that act in both the condensed and gaseous phase in the vicinity of the combustion zone. The hydrated fire retardants decompose with evolution of water, via an endothermic reaction that cools the substrate. Magnesium oxide formed is retained in the composite and it can act as an insulating barrier, limiting diffusion of combustible volatiles entering the gas phase. Zinc borate is used to improve the FR properties through smoke suppression and char promotion. Cone calorimetry is a valuable method to evaluate the relative fire hazard performance of polymer compositions. The TG thermogram of BAMMA exhibited one mass loss step at 423°C. Addition of water releasing components caused decomposition to occur at lower temperatures and created a further char degradation stage. This TG curve indicated that the char residue retained volatile components from polymer degradation. BAMMA exhibited an ignition time of 20 s, with heat release rate increasing rapidly with a peak at ~1000 kW•m<sup>-2</sup> as the polymer combusted. Addition of talc (50 %wt) caused increased ignition time (40 s) and two peak HRRs, both at ~300 kW•m<sup>-2</sup>. The changes in shape of the HRR curve indicated initial char formation and secondly a char degradation. The addition of FR reduced further the HRR, with greatest reduction occurring for composites containing a higher proportion of magnesium hydroxide, which was attributed to an endothermic contribution on conversion to its oxide. A reduction of the smoke extinction area was observed, which was caused by reduced fuel entering the combustion zone because of entrapment of volatiles on particle surfaces thereby limiting diffusion. The relationship and synergy of the composite system will be further discussed.



## Development of Branched Polymers by Ultrasound-Assisted Melt Mixing Process with Multifunctional Agents

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The chain structure of polymeric molecules is an important characteristic of polymers. Well-defined architectures of branched polymers are essential in order to understand fundamentally the relationship among chain-branched structure and several physical properties. Ultrasound-induced polymer scission is a useful route which can either be used as a post-processing step or can be used during ultrasound-induced polymerization. In this study, we intended to apply the transformation of molecular structure from linear to branched one during melt processing of polymers. Compared with the previous approaches, here we are introducing a new and reactively simple method by imposing ultrasound and a multifunctional agents (MFA) to produce branched structure. The transformation of molecular structure was confirmed by the measurements of rheological properties of the modified polymers. After the ultrasonic irradiation of polymer chains together with MFA, increase in complex viscosities and shear-thinning behavior were observed. The Cole-Cole plot and measurement of extensional viscosities revealed the characteristic features of branched structure with well-defined extensional behavior. It was expected from this study that we may be able to provide information associated with the development of a viable process of polymer modification.

S09-1001

## Correlation of Morphology and Mechanical Properties in Rubber Modified Polypropylene

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The objective of this work was to develop and investigate impact modified polypropylene (PP) binary blends based on conventional thermoplastic elastomers, namely ethylene vinyl acetate copolymer (EVA) and ethylene propylene diene monomer terpolymer (EPDM) having higher impact resistance than PP. Non linearity of variation of mechanical properties as a function of blending ratio was investigated, achieving the role of morphology of dispersed phase, domains size, domains size distribution and its number density which results in different mechanisms of rubber impact toughening. Thus the studies enabled us to establish a correlation between the morphology and mechanical properties in a systematic manner to find out different phenomena, responsible for properties modification in impact toughening of PP blends.



## Calendering of rubber - contribution to the improvement of the quality of rubber sheets

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The calendering process is used to transform a polymer melt into films and sheets by squeezing it between pairs of co-rotating rolls. The quality of the calendered sheet is determined by the three-dimensional flow field in the gap between the two rolls. One well known problem is defects, which are caused by gas entrapments in the calendered sheets with a thickness greater than approximately 0.8 mm, depending on the rubber type. Dimensions, concentration, space distribution and circularity of gas entrapments in the calendered rubber sheets depend on maximum nip pressure, which is a function of the process parameters. The aim of this contribution is to investigate the movement of the gas entrapments in the polymer melt forced through the calender roll gap. In this region the viscoelastic material is highly accelerated. Such flow field generates high stresses as a result of material stretching. It causes the pressure to be anisotropic in the direction of the velocity vector in the flow field. This, in turn, determines the migration of the gas entrapments from the main flow stream to the region of lower stresses. This phenomenon is termed the Uebler effect. A laboratory standard four-roll inverted-L calender is used for the experimental setup. The occurrence of the gas entrapments in the material bank and in the roll gap is investigated using X-ray tomography. The X-ray tomography is a non-destructive measurement technique in which the measured object is not influenced or altered.

S09-1065

## Characterization of crystalline and amorphous regions of HMSPP films.

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The introduction of long chain branching and/or some crosslinking into isotactic polypropylene (iPP) backbone changes drastically its melt properties. Rheological properties of the melt are strongly affected by molar mass and distribution of molar mass, and the presence of long-chain branching or crosslinking. This characteristic enhances the density of entanglement, changes the elongational flow of polymer melts which play an important role in many processing operations like film blowing and thermoforming. Therefore, several approaches have been developed to make branching and modified polypropylenes. High melt strength polypropylene (HMSPP) is one of the new materials that exhibit these properties. It is now established that long-chain molecules can crystallize into a two-phase structure: periodic arrangement of crystalline lamellae and amorphous interlayer. Whether, short and long branching is incorporated into polypropylene chain, how the influence of these changes in the morphology of HMSPP films? In this way, we studied the morphology of HMSPP films processed by thermopressing. Morphological changes were analyzed by sorption measurements, differential scanning calorimetry (DSC) and wide-angle X-ray diffraction (WAXD). The results obtained from these analyses were to get morphological aspects related to the distribution and organization of the amorphous and crystalline phase.



## Relationship between the Morphology and Mechanical Properties of Compatibilized and Un-compatibilized HIPS/PE Blends

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The main objective of the present work was to study the relationship between the morphology and mechanical properties as well as the fracture behavior of compatibilized and un-compatibilized HIPS/PE blends in air and under an aggressive environment (sun flower oil). The tensile properties of the samples were measured according to ASTM D-638. Essential Work of Fracture (EWF) tests were conducted to measure the essential specific work of fracture ( ) and non-essential specific work of fracture ( ). Environmental Stress Cracking Resistance (ESCR) of the samples was investigated using a special modified tensile creep test. The microstructures of the HIPS and HIPS/PE blends as well as the morphology of fractured surfaces of the ESCR and EWF test samples were studied using SEM and TEM techniques. It was found that, the variation of the tensile properties of HIPS (yield stress, tensile strength and elongation at break) is strongly affected by the PE content and its morphology in the HIPS matrix and therefore by the compatibilization process. The results showed, although the ESCR of HIPS decreases with incorporation of PE, but an effective compatibilization of this blend can increase its ESCR even higher than HIPS. The essential specific work of fracture of compatibilized HIPS/PE blends was higher than un-compatibilized HIPS/PE blends and pure HIPS, while its non-essential specific work of fracture was higher than un-compatibilized blend and lower than pure HIPS. The different properties of compatibilized and un-compatibilized blends and HIPS, in ESCR and EWF tests, were attributed to the different mechanisms of fracture in these materials. The different mechanisms of fracture were justified using morphological studies performed on fracture surfaces of each sample. Different mechanisms of fracture were related to the different microstructure of the samples.

S09-1089

## Early stages of photodegradation in polybutene-1

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The work deals with initial stages of photodegradation in commercial- available polybutene-1 (PB-1). For these purpose, thin PB-1 films were prepared by compression moulding. Then the samples were exposed to UV light in a SEPAP 12/24 irradiation device. The structure changes were observed via rheometry, FTIR analysis and wide-angle X-ray scattering. During initial exposure, an unexpected competition between chain scission and crosslinking of PB-1 chains was observed.



## The role of physical factors in photodegradation of polypropylene

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The paper is focused on the role of physical factors such as thickness or mode of processing in photodegradation of isotactic polypropylene. Specimens were prepared by compression moulding or injection moulding. Subsequently, they were exposed to UV radiation in accelerated ageing device. The extent of degradation was determined by FTIR and ATR. Degradation profile was observed by micro-infrared spectroscopy. It is demonstrated that the degradation changes are influenced by processing history and dimension of the specimens.

S09-1168

## Effect of melt rheological behavior of blend components on morphology and mechanical properties of PC/ABS blends

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Effect of melt linear viscoelastic properties and blend ratio on morphology and mechanical properties of PC/ABS blends were studied. The influence of MAH-g-ABS compatibilizer concentration (1, 3, 5%wt) was also investigated. The blend samples containing 35, 50, and 65 %wt ABS were prepared by melt mixing in an internal mixer at temperature of 220 °C and rotor speed of 120 rpm. The SEM micrographs of the samples in which PC phase was etched by NaOH showed matrix-dispersed type morphology for the sample containing 35 %wt PC as dispersed phase, while the sample with 35% wt of ABS showed the co-continuous type morphology, similar to that observed for the sample with 50%wt of each blend component. These results could be explained in terms of melt viscoelastic properties of blend components in conjunction with the concept of droplet break up process. The Newtonian behavior of PC with lower viscosity compared to ABS facilitated the droplet break up of PC minor phase leading to the matrix-dispersed morphology whereas the droplet break up process could hardly take place for ABS minor phase, due to its high melt viscosity and elasticity. It was demonstrated that presence of MAH\_g\_ABS compatibilizer, due to its preferential affinity towards ABS phase could have different effects on mechanical properties, in particular, impact strength of the blend samples depending on their blend ratio and morphology.





## Crystallization behavior of poly(lactic acid)

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Calorimetry and polarized optical microscopy are commonly adopted techniques in the study of polymer crystallization. Calorimetry allows the determination of the evolution of the crystalline degree through the latent heat of crystallization. Information about the evolution of morphology inside the sample cannot be obtained by this technique. On the other hand, optical microscopy allows the direct determination of the evolution of morphological characteristics of the sample, which in quiescent conditions essentially mean number of nuclei and spherulite dimensions (radii). Despite of the fact that both techniques provide data about the same phenomenon, it is still under discussion which is the appropriate relationship linking the resulting data. The aim of this work is the study of crystallization kinetics of poly(lactic acid) (PLA), by coupling the two techniques in simultaneous measurements through a novel transparent single cell system from Linkam SI. In addition to the complete biodegradability, PLA is made from the abundant natural recyclable polymer, with excellent plasticity, processibility, and biocompatibility. Lactic acid-based polyesters are well-known biodegradable polymers that can be used not only for biomedical applications, but also in packaging and consumer goods. The physical and mechanical properties of crystallizable PLA are largely dependent on its solid-state morphology and level of crystallinity: the microstructure of PLA is dramatically changed from amorphous to highly crystallized state as crystallization proceeds. However, the crystallization rate of PLA is extremely slow in comparison with commercial thermoplastics. It is clear from literature studies that a simple way to fasten the crystallization rate of PLA has not been found yet. However, structural change can be achieved by controlling molding or annealing condition during fabrication process, in which PLA parts are retained under conditions of fixed temperature and time.

S09-1217

## Nucleation effects in iPP: from fiber reinforced composites and microcomposites to nanocomposites

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Crystallization of i-PP has recently been reinvestigated due to the increasing technological interest towards the new generation of composites in which the polymer is in the form of filaments, powder or film, and particularly - towards nanocomposites. Nanocomposites based on PP represent a special challenge for industry because of their commodity status. The morphology of iPP developed during the crystallization from the melt is greatly dependent on cooling rate, in nonisothermal regime, and on undercooling, in isothermal regime, and it is significantly affected by heterogeneous nucleation caused by the presence of different nucleators/additives. The aim of this paper is to compare the nucleating activity of differently treated glass and carbon fibers (1, 2), used for production of bulk iPP-based composites with those induced by  $\alpha$ - and  $\beta$ -nucleating agents, as well as by organo-modified nanoclays. For this purpose, bulk composites were produced by compression molding of maleic anhydride modified iPP, and nanocomposites – by melt mixing and lately developed latex technique (3, 4). The process of crystallization of iPP in fiber reinforced composites, nanocomposites and in the presence of nucleating agents was followed by DSC and PLM. Both neat maleic anhydride modified iPP, iPP reinforced with differently treated fibers and iPP filled with organoclay were found to crystallize into spherulitic morphology. XRD analysis of the samples crystallized under different conditions has revealed the presence of  $\alpha$ ,  $\beta$  and, in some cases –  $\gamma$ -crystalline phase. The different nucleating activity for the fibers/fillers/nanoclay was evaluated by induction time of crystallization, crystallization onset temperature and half-time of crystallization, interfacial energy parameters method, and the basic energetic parameters of crystallization were also determined.



## Effect of synthesis method on morphology and phase separation in thermoplastic polyurethane elastomers based on polyol-blends

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Thermoplastic polyurethane elastomers are immiscible in thermodynamic point of view and two phases structure has been seen in these kinds of materials. Segmented polyurethanes consist of hard and soft segments exhibit special properties using in various applications. Blending and co polymerizations have also been considered in last two decades to prepare new materials in this field. In the present work we applied two kind's polyols; an ether type and HTPB (hydroxyl-terminated polybutadiene) to synthesize of thermoplastic elastomer polyurethanes (TPU) and properties have been compared with pure ones. Also two different methods were chosen to prepare TPUs. In the first method at first step polyols were mixed, and then reacted with -NCO groups, in the second step chain extender was added. In the second method at first step polyols were reacted with -NCO groups then mixed; in the second step chain extender was added. Microstructures and phase separation phenomena in obtained TPUs have been investigated to evaluate morphology. In this way, TPU based on Toluene diisocyanate (TDI) and 1,4-butanediol (BDO) and two kinds of polyols were synthesized. Differential scanning calorimetry (DSC), dynamic mechanical analysis (DMTA), Atomic Force Microscopy (AFM) and Fourier transform infrared spectroscopy (FTIR) have been used to analyze phase separation and microstructure-macro mechanical properties of the samples. Mechanical testing was carried out to determine T-peel strength, lap shear strength of the various TPUs. Results showed interesting and reasonable correlation between structure -morphology TPUs.

S09-1284

## Studies on Structure-Property Relationship in Polypropylene /Carbon Nanofiber Composites

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The novel properties of carbon nanofibers (CNF) have generated scientific and technical interest in the development of nanofiber-reinforced polymer composites. The performance of these composites depends largely on the matrix–CNF interface, which determines the way loads can be transferred from the polymer to the CNF and their dispersion behavior. The dispersion of CNF in matrix presents great challenges due to their extremely small dimensions, high surface areas, and high surface energies. The functionalization of CNFs could enhance their chemical compatibility with the matrix and hence dispersion and interfacial properties are expected to improve. In this research, nanocomposites of oxidized carbon nanofiber (o-CNF) and Polypropylene (PP) were prepared in Haake rheomix and their morphological, thermal, electrical and mechanical properties were compared with those prepared with untreated CNF. Torque rheometry showed a similar processing behavior for both types of nanocomposites. The morphology developed in nanocomposites was investigated by X-ray diffraction (XRD) and scanning electron microscopy (SEM). Both oxidized and untreated CNF-filled nanocomposites were crystallized in  $\alpha$ -monoclinic form as confirmed by XRD. SEM images showed well-dispersed CNF in PP matrix in both cases. The differential scanning calorimetry (DSC) showed an increase in crystallization temperature in both types of nanocomposites, indicating their role as nucleation sites in PP matrix. Thermogravimetric analysis (TGA) indicated an increase in thermal stability which is independent of oxidation of CNF. The electrical conductivity, however, decreased in o-CNF nanocomposites. This may be due to the fact that, oxidation process damaged graphitic structure of CNF and caused less number of  $\pi$ -electron available for electron transport. In case of o-CNF based nanocomposites, the aspect ratio is reduced due to oxidation and consequently, caused a reduction in tensile and dynamic mechanical properties.



## Rheological properties and shear induced crystallization of model polyethylene blends

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In this work a polymer model blend system has been studied to investigate the flow-induced crystallization phenomenon. A low molecular weight polyethylene copolymer (LMWPE), containing 2 mol % hexane with Mw ~50000 and polydispersity ~2, was used as solvent. An ultra high molecular weight polyethylene homopolymer (UHMWPE) with Mw ~5-6\*10<sup>6</sup> and polydispersity ~9, miscible in the LMWPE matrix, was used as the crystallizing component. The model blends, LMWPE/UHMWPE 100/0, 99.8/0.2, 99/1, 98/2, 95/5, 90/10 and 85/5 w/w, were prepared by solution blending. The linear dynamic oscillatory melt rheology of these blends at T=140°C showed a strong influence of the UHMWPE content on their viscoelastic behaviour, reflecting a modified time scale relaxations. To separate the different relaxation processes involved, the relaxation spectrum, h(t), was calculated. At this regard a novel methodology, based on the relationship between h(t) and the Molecular Weight Distribution (MWD) function generalized to properly describe polydisperse samples with some narrow structure in MWD, was applied. It relies on the use of the double reptation mixing rule and the Generalized Exponential function (GEX) describing the MWD. A good agreement between the viscoelastic properties and the model predictions was found, which allowed to extend the experimental data range in a reliable way. The validity of the methodology was also confirmed by comparing the complex viscosity predictions at lower frequencies with the steady shear viscosity values at very small shear rates. The shear flow induced crystallization of model polyethylene blends was investigated by using a modified Linkam CSS-450 shearing stage for in-situ WAXD and SAXS measurements. The temperature of the experiments was 128°C. A short shear duration (5s) was used for different shear rates. The relaxation times were related to the X-ray scattering results to analyze the flow-induced crystallization based on the topology of the polymer.

S09-1362

## Non-lamellar crystal morphology of isotactic polypropylene: A comparative study by AFM and TEM

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The morphology of crystals, formed at the surface and in the bulk of rapidly cooled and subsequently at elevated temperature annealed films of isotactic polypropylene (iPP) was analyzed by transmission electron microscopy (TEM) and by atomic force microscopy (AFM). Both techniques show a lamellar geometry of crystals after melt-crystallization at 12 K s<sup>-1</sup>, and a nodular geometry after melt-crystallization at 750 K s<sup>-1</sup>. The morphology of crystals is independent on the position of the investigated film of thickness of 100 μm, suggesting (a) that the crystallization at the surface is not affected by the use of a glass substrate for preparation, and (b) that the temperature-gradient during primary crystallization is sufficiently small to ensure identical structure at the surface and in the bulk. AFM suggests a larger size of crystals than TEM, in particular if the absolute size of objects approaches the dimensions of the used tip of the AFM. If the absolute size of objects is distinctly larger, then AFM and TEM yield nearly identical dimensional information.



## Effect of comonomer type and content on the crystal structure and morphology of statistical copolymers based on isotactic polypropylene

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The effect of the comonomer type and content on the crystal structure and morphology of propylene-based statistical copolymers are analyzed by X-ray techniques, atomic force microscopy, calorimetry, and polarizing optical microscopy. In this investigation, butene-1 and ethylene were used as comonomers. Beside the analysis of the degree of crystallinity, and of transition temperatures, we put special emphasis on evaluation of the effect of the condition of crystallization on the internal structure, shape and size of crystals. In particular, we are interested in gaining knowledge about conditions for formation of non-lamellar crystals which in case of the isotactic homopolymer form on cooling at a rate faster than about 102 K s<sup>-1</sup>. Furthermore, we attempt to study the thermodynamic stability of such mesomorphic domains, which is done by special annealing experiments.

S09-1392

## Effect of Flow on Crystallization: Nucleation and Growth Rates During Steady Shear Flow

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The reason for the intense interest in crystallization of flowing polymer melts, when even quiescent crystallization is not yet completely understood, is its immense technological relevance to polymer processing. In fact, the study of polymer crystallization enhanced by flow implies the possibility of controlling the final morphology and the resulting mechanical and functional properties of semi-crystalline polymers. Despite numerous studies investigate on the effect of shear on crystallization, the description of the evolution of morphology in shear conditions is still challenging. In particular, the great part of the published papers analyze the effect of a step shear on the crystallization and only in few papers the effect of a steady shear treatment on the crystallization is analyzed. In this work, the effect of imposed steady shear flow on morphology and the kinetics of isothermal crystallization of an iPP has been studied, in particular, measurements of nucleation and growth rates of spherulites during steady shear flow were performed by means of a Linkam Shear Cell coupled with an optical microscope. Furthermore, the evolution of crystallinity under shear conditions, calculated combining nucleation and growth rates values, was compared with data obtained by means of in situ wide-angle X-ray diffraction performed in the A2 beamline at the Hamburger Synchrotronstrahlungslabor at the Deutsches Elektronen-Synchrotron in Hamburg (Germany). Experimental data have shown that under flow the number of activated nuclei increases with time, whereas under quiescent conditions for the resin analyzed it was function only of temperature. Furthermore, also the growth rate was found to increase significantly by effect of the flow. An attempt was made to determine the parameter which better describes the effect of flow on crystallization kinetics. Some theories will be discussed in comparison to the experimental data of nucleation rate in low shear experiments.



## SOLIDIFICATION OF POLYMERS AND METAL PARTICLES AT HIGH COOLING RATES

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We present the capabilities of a new calorimeter device, positioned between DSC and ultrafast scanning techniques regarding scanning rate range. Solidification of isotactic Polypropylene and Sn metal samples was studied by means of the newly developed method. For polymers crystallization kinetics was studied at cooling rates  $40..10^4$  K/s within the temperature range 250..500 K. At rates faster than 400 K/s iPP does not crystallize on cooling, that allows to investigate isothermal crystallization at any temperature between glass transition and melting temperature. Sn supercooling effect was studied for cooling rates  $10..10^5$  K/s and compared with DSC and ultra-Fast single sensor calorimeter data covering the range from  $10^{-3}$  to  $10^7$  K/s.