Symposium 7

Rheology & Rheometry

S07-209

The Rheotens Test – A Useful Guide to Polymer Processing at Free Surface Conditions

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The drawability of polymer melts is of great importance for many polymer processing applications. The Rheotens test, which is a prototype industrial flow, assesses the elongational properties of polymer melts and results in an extension diagram, which presents the drawdown force of an extruded filament as a function of the drawdown velocity. The experiment is fast and easy to perform with high sensitivity and good reproducibility, and is therefore widely used in industry. The existence of Rheotens mastercurves and grandmastercurves allows a direct and quantitative comparison of the elongational behaviour of different polymer melts under the action of an imposed drawdown force. This can be used to investigate how structural differences of the macromolecular chains influence the material properties of a polymer. For example, we found that different production technologies (tubular versus autoclave reactor) for the polymerisation of low density polyethylene result in changes of the tensile force/drawdown speed diagram. Furthermore, exceptions from temperature invariance are indicative for (temperature-dependent) wall slip in the capillary die, or flow induced crystallisation. Also, the rupture stress of polymer melts, which is relevant for processing applications, can be determined by Rheotens experiments from the force and draw ratio at rupture. The rupture stress is found to be lower for linear polymers than for branched ones. The apparent elongational viscosity calculated from Rheotens curves depends on the prehistory and therefore on processing conditions, while the true uniaxial elongational viscosity is measured starting from isotropic samples. A comparison of the two viscosities clearly shows that preshear reduces the level of elongational viscosity considerably. This is of importance for many processing applications, which are dominated by elongational flow, and links polymer melt rheology to industrial applications.

S07-297

Rheological Properties of Ionic Liquids

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Ionic liquids (il) found wide spread use in many technologies as phase change materials for heat transport, as electrolytes support in solar sells, or as solvents for polymers. While application data for properties like viscosity and conductivity are available for many ionic liquids, not much is known about the molecular dynamics (rheological properties) behind these material parameters. At the example of a widely used ionic liquid, 1-Butyl-3-methylimidazolium tetrafluoroborate (BMIBF4), we investigate its dynamic behaviour by various rheological experiments. First, we establish a measurement protocol, which allows us to perform temperature sweeps. These measurements reveal the extreme sensitivity il's viscoelastic properties to heating and cooling rates. Secondly, in wide temperature and frequency ranges we measure the complex shear modulus and derive limiting properties such as plateau modulus and Newtonian viscosity at high and small frequencies. Finally, we compare our results with the most recent theory on dynamic behaviour of ionic liquids [1] and discuss observed peculiarities in materials behaviour in the context of this theory. Moreover, we compare the rheological properties of different ils among themselves and with theory. Doing so, we gain insight into the structural properties of these liquids, too. 1. S. Odinaev, I. Odjimamadov, The Relaxation Theory of Electroelasticity and Dielectric Properties of Ionic Liquids, Mod. Phys. LettersB, 15 (2001), 285-290.

S07-569

Rheo-DSC: combining the worlds of rheology and thermal analysis

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In this presentation, we will present a unique new experimental device that couples rheological measurements with thermal measurements in one single unit. This allows to perform these measurements simultaneously on the same sample under exactly identical conditions. The latter has the advantage that heat effects, generated for instance during crystallization or during a curing reaction, are identical during the rheological and the thermal measurement. This is not the case when such measurements are performed using conventional DSC and rheological experiments. We will present the new experimental set-up and discuss two different case studies. The first case study deals with the crystallization of polymers in which the main issue discussed will be the correlation between the viscosity and the degree of crystallinity. It will be demonstrated that the device has some advantages with respect to the conventional measurements. Secondly, the curing of an epoxy will be discussed.

S07-1120

Rheological behavior of polymer melts in equibiaxial elongational flow using a modified lubricated squeezing flow technique

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Despite its technological significance, the rheological behavior of polymer melts in equibiaxial elongational flow is largely unexplored and, consequently, is inadequately understood. The simple reason for this is that methods for generating equibiaxial elongational deformations are either very complicated or not reliable. The most widely accepted method for generating rheologically controlled, equibiaxial elongational flow is the rotating clamp method, or MultiAxiale Dehnung (MAD), developed by Meissner. However, the extremely complicated nature of the MAD rheometer has resulted in a relatively limited set of experimental data. A promising method that has been used with some success is known as Lubricated Squeezing Flow (LSF), where a polymer melt is squeezed between lubricated surfaces. Unfortunately, uncontrolled lubricant thinning limits the LSF technique to rather modest strain levels. Here we report the first direct comparisons of data obtained with the LSF and MAD techniques. We find that the data obtained using LSF deviate from the MAD data at Hencky strains of less than one, and display behavior that could easily be mistaken for strain hardening. For the past few years, we have been developing a modified LSF technique that involves the continuous injection of lubricant through porous metal plates. We report the first measurements of transient equibiaxial elongational viscosity obtained using the modified LSF technique and make comparisons with data from the MAD rheometer.

S07-101

Rheological characterization of PTT / MMT nanocomposites

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This work has as main objective to evaluate the changes in dynamic rheological properties generated by the addition of a nanoclay and a terpolymer as a compatibilizer in nanocomposites of poly(trimethylene terephthalate), PTT, and organophilic montmorillonite, MMT. These materials were processed in a Haake rheometer, using a 5 wt% of the nanoclay and 5 wt% of the compatibilizer. The materials structures were characterized by X-ray diffraction (WAXS) and by scanning electronic microscopy (SEM). The rheological properties were measured in a controlled strain ARES Rheometric Scientific rheometer using a 25mm plate-plate geometry and at a temperature of 240ºC. WAXS results showed formation of intercalated structures in the nanocomposites without the compatibilizer agent (sample 1). On the other hand, complete exfoliation of the platelets of the nanoclay was achieved with the addition of the terpolymer (sample 2), although the morphological results indicated formation of two phases in these last nanocomposites. The shear viscosity of all nanocomposites decreased with time, indicating that these materials were suitable of degradation after long periods of time. The measurements of the storage modulus G´ and the loss modulus G´´ as a function of frequency of sample 1 indicated that these nanocomposites developed a percolated network structure. However, the dynamic behavior of the nanocomposites which contain the terpolymer (sample 2) was quite different. In this case, G’’ was always higher than G’, showing that the viscous behavior of the PTT matrix was dominant. This can be an indication that, even if the nanoclay was exfoliated, it was located only in the compatibilizer phase. This structure will be analyzed further by transmission electronic microscopy (MET).

S07-165

Linear and non-linear viscoelasticity of polydisperse star/linear polymer blends

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It is well known that polydispersity and branching have important and, at the same time, hardly predictable effects on rheological and processing properties of industrial polymers. In the literature, much experimental and theoretical work has been done in order to address this problem and a number of important results have been obtained, especially for polydisperse linear polymers and monodisperse, well-defined, branched polymers. Industrial polymers are instead, in many cases, contemporarily polydisperse and branched. Their viscoelastic behaviour is, of course, much more complex with respect to the model systems usually investigated in the literature. When polydispersity and branching are both present, many different relaxation processes are indeed active at the same time and their corresponding kinetics are expected to reciprocally influence each other. In this work, we aim to elucidate the viscoelastic behaviour of a class of such complex materials.A set of polydisperse star/linear polybutadiene blends characterised by different composition and arm average molecular weight has indeed been prepared on purpose for this study. Linear “parent” polymers were synthesized in a pilot-scale continuos reactor via anionic polymerisation. A coupling agent was introduced in a second stage in order to obtain the blends.Light scattering is used to determine the molar mass distributions of the samples and the results are correlated with the linear viscoelastic characterisation in the frame of the existing tube theories. The non-linear rheological response is analysed with special attention to the time-strain separability and to the damping function at short and long times. The different responses to uniaxial extensional flow are also investigated.

S07-194

The Role of Molecular Architecture on Rheological Properties and its Effect on Film-Casting Performance

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The rheological and processing (film-casting) characteristics of a well-characterized series of metallocene catalyzed long-chain branched HDPE resins are studied. A critical analysis of the combination of jump (step) strain and uniaxial extension to obtain the model parameters for the McLeish-Larson multi-mode pom-pom model is presented. Incorporated in the rheological study is an analysis of a new encapsulation technique designed to overcome material failures in extensional flow seen at strains higher than two units using a LLDPE stabilizer sheath. The effect of long-chain branching and ultimately strain-hardening is evaluated on the cast film process. Evaluation with respect to film width profiles, edge-bead profiles, and rheological response is investigated. Increases in strain-hardening behavior promote a reduction in film necking and conversely an increase in film thinning.

S07-275

A Mesoscopic Tube Model of Polymer/layered Silicate Nanocomposites

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Rheological behaviors of suspensions of completely exfoliated silicate lamellae in polymer melts are investigated. Due to polymer-polymer and polymer-plate interactions, macromolecules of the polymer melt are effectively confined into tubes formed by other macromolecules and the plates. A mesoscopic rheological model of the suspension is constructed by combining a mesoscopic rheological model of polymer/layered silicate nanocomposites [H. Eslami, M. Grmela, and M. Bousmina, J. Rheol., in press (2007)] with a mesoscopic rheological model of melts composed of reptating macromolecules [H. Eslami, and M. Grmela, Rheol Acta, in press (2007)]. Responses to oscillatory, transient and steady shear flows are calculated and compared with available experimental data.

S07-331

IUPAC Guideline for rheological characterisation of polyamide melts

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This investigation is the result of an IUPAC project of the Subcommittee on Structure and Properties of Commercial Polymers. Members of several industrial organizations, universities and institutes cooperated, to make comparative measurements, with the aim to formulate a guideline how to measure the rheological properties of polyamide 6.The measured rheological properties of PA6 depend strongly on the sample preparation method, humidity regulation and time-temperature history during the measurement and last but not least the kind of rheometer being used. The results of the investigation show the changes in molecular weight during the different kinds of rheological measurements due to hydrolysis and amidisation reactions.A guideline is introduced, which can be used to make comparable rheological measurements. Such comparable measurements are of course important not only for patent applications, but also to determine the rheological properties which are being used for FEM simulations on the processing behaviour of polyamide.

S07-557

Characterization of the onset and development of different melt instabilities in LDPE-LLDPE blends

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It is known that a suitable blending of LDPE and LLDPE can reduce undesired melt instability phenomena: achieving this reduction will give rise to a widening of the processability window of these materials. In this work a series of LDPE-LLDPE blends of different compositions has been prepared by melt blending in a corotating twin screw extruder. These have been characterized first by capillary rheometry in order to get the apparent flow curve. Secondly a careful morphological analysis of the surface of the extruded polymer jets was carried out by means of Scanning Electron Microscopy (SEM): this in order to detect the very early stages of the small scale melt instabilty at low shear rates and to follow the subsequent evolution as long as the shear rate was increased. With this experimental procedure it was possible to evaluate the shear rate ranges corresponding to different flow regions: smooth extrudate surface (absence of instability), sharkskin (small scale instability produced at the capillary exit), stick-slip transition (instability involving the whole capillary wall) and gross melt fracture (i.e. a large scale ""upstream"" instability originating from the entrance region of the capillary). One can finally get a quantitative map in which it is possible to make an assessment of the flow type at a given shear rate and blend composition. A preliminary discussion and interpretation of the data can be addressed.

S07-637

A transient rheology study of the PET-PEN-Montmorillonite clay nanocomposite

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PET-PEN nanocomposites were prepared by an extrusion process with an organic modified montmorillonite clay, the viscosity of all blends diminished as compared to the system with no clay added. A rheological study was conducted to study the complex structure formed by the polymer matrix-clay interaction. Instantaneous relaxation stress curves are presented for the systems PEN, PEN-PET and PET-PEN-1phr clay. A Fourier Transformed (FT) frequency response was obtained from the relaxation curves and compared to the linear oscillatory data. FT data shows an extended frequency region. The results were modeled by a rheological equation which accounts for the formation-destruction dynamics of the structure during flow. Relaxations times spectra are presented and compared for both rheological test instantaneous stress relaxation and linear oscillatory flow. Additional studies of TEM microscopy and capillary rheometry are presented where evidence of a slip layer in capillary flow was observed for the system with clay added.

S07-767

SHEAR AND ELONGATIONAL RHEOLOGY OF HIGH ASPECT RATIO NANO-PARTICLE FILLED POLY (ETHER ETHER KETONE)

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Nanoparticles with a high aspect ratio, such as carbon nanofibres (CNFs) and carbon nanotubes (CNTs), have attracted significant interest, as they promise, and indeed show remarkable mechanical and physical properties. In combination with their low density, they are ideal candidates as nanofillers for high-performance polymer composites. For such nanocomposites, understanding the rheology and microstructure is of key importance for processing. This study therefore aims at investigating the influence of aspect ratio, degree of dispersion and weight fraction of the nanoadditive on shear and elongational. Three different types of nanoparticles are considered: vapour grown carbon nanofibres (VGNF), multi-walled carbon nanotubes (MWNT) and single-walled carbon nanotubes (SWNT). Nanocomposites with different weight fraction of the nanofillers were melt-compounded by twin-screw extrusion, using semi-crystalline poly(ether ether ketone) (PEEK) as matrix system. Dynamic shear measurements at low frequencies reveal that both the viscosity and the storage modulus increase with nanofiller content, more significantly for CNTs (7 orders of magnitude) as compared to CNFs. However, above a critical concentration of the nanofiller, the storage modulus becomes almost independent of the frequency, suggesting the onset of solid-like behaviour of these nanocomposites. The observed higher percolation threshold for CNFs (between 10-15 wt%) as compared to multi-walled nanotubes (between 0.5 – 1 wt%) was discussed in terms of length degradation and dispersion of nanofibre/tube in the PEEK matrix. Additionally, the elongational rheology measurements were performed using a Rheotens apparatus. Interestingly, both melt strength and drawability increase with nanofibre content; in contrast, the addition of CNTs promotes a higher melt strength, while the drawability significantly decreases at the critical loading. Moreover, an increasing elongational viscosity was detected at low extensional rates

S07-784

Oscillatory shear rheology of iron silicone filled polypropylene composites

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Linear viscoelasticity of unfilled polypropylene (PP) and PP filled with micro sized soft magnetic powder (FeSi6.8) was investigated. Wide range of powder weight fraction is examined, namely zero up to 95.1wt.-%. With the aid of shear rheology, linear viscoelasticity is measured using oscillating plate system in wide temperature and angular frequency ranges. All investigated materials show the typical shear thinning behaviour of polymer melts. The influence of the filler particles on the rheological behaviour of the compounds can be characterized by complex viscosity, shear storage modulus G` and shear loss modulus G`` versus angular frequency. At constant temperature, an increase in filler content enhances complex viscosity and shifts the meeting point (G`=G``) and the elastic behaviour of the material (G`>G``) to higher angular frequencies. The slope of G` and G`` varies with increasing temperature from 1.35 to 1.68 and from 0.84 to 0.97, respectively. Also the rheological behaviour is always observed between gels and polymeric melts especially in the low temperature domain. As expected, increasing temperature results in the decrease of complex viscosity for constant filler contents. Complex zero viscosity as well as complex viscosity increases dramatically at all examined temperatures at almost 67wt.-% filler content. At such a threshold percentage, the spherical FeSi particles start to interact with each other either by friction or mutual interfacial rolling. Increasing filler content enhances complex zero viscosity up to ten times compared to that of the unfilled PP. Master curves of time-temperature superposition show different behaviour of normalized complex viscosity versus reduced angular frequency for all investigated materials depending on the filler content. Also, an increase in filler content extends the reduced angular frequency range up to seven times compared to unfilled PP.

S07-788

Micro-rheological Study of a Main Chain Thermotropic Liquid Crystalline Co-polyester Containing a Small Amount of Fully Exfoliated Nanoclay

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An exfoliated blend of nanoclay in a main chain thermotropic copolyester (TLCP) with flexible spacers is prepared. The nanoclays used in this study were organo-clays with lateral dimensions of 15-25 nm. The TLCP used in this study was a copolyester of hydroxybenzoic acid (HBA), hydroquinone (HQ) and sebacic acid (SA), HBA/HQ/SA. The combined wide angle x-ray diffraction and transmission electron microscopy analysis show that the nanoclay particles were uniformly dispersed inside the TLCP matrix in a fully exfoliated state. Vibrational spectroscopic studies using NMR and FTIR show that there exists hydrogen bonding between the nanoclay and the TLCP molecules. Micro-rheological studies carried out using both mechanical rheometry and optical shearing apparatus show that the presence of the small amount clays significantly affects the rheological behavior of the TLCP both in the linear and non-linear responses. In the LVE region, the dynamic storage modulus shows a low frequency plateau followed by a pseudo-terminal response to that of an isotropic polymer melt, and the storage modulus of the composite is higher than that of the pure TLCP at low frequencies. In the non-linear region, both the hybrid and the pure TLCP show flow aligning characteristics with positive first normal stress difference at all shear rates tested. However, the hybrid shows a negative second normal stress difference whereas the pure TLCP exhibits a positive second normal stress difference. Our results suggest that the presence of nanoclay enhances the unidirectional flow aligning characteristics without in the meantime causing any nematic shielding effects.

S07-819

Mechanical Instabilities in the Capillary Rheometry of Polymer Melts

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During the extrusion of polyethylene (PE) melts mechanical instabilities appear with increasing shear rate. The mechanical instabilities are visible as surface distortions of the extrudate. For certain regions of the shear rate the mechanical instabilities show characteristic behaviors and are classified as, i.e. shark-skin, stick-slip or melt-fracture. During the extrusion pressure fluctuations appear in the die. Those fluctuations correlate with the mechanical instabilities. The topic of this work is to optimize the detection of the pressure fluctuations and afterwards to apply several ways of mathematical analysis of the pressure data. We investigated the mechanical instabilities of PE melts via a commercial capillary rheometer (Goettfert-Rheotester 2000). We observed at different temperatures and shear rates for several industrial PE melts the time dependent pressure. By this we studied the correlation between the appearing mechanical instabilities and the time dependant pressure. For an improved measurement of the pressure in the capillary die we had to manufacture a special measurement die. This slit die contained three high sensitive piezoelectric pressure transducers (increment:10^-2 bar at ~200 bars) to record the time dependant pressure (increment 10^-4s). The fast data acquisition of our setup (100,000 pts./s) allowed us to improve the signal to noise ratio of the pressure signal via oversampling. For the analysis of the pressure data we used mathematical tools as the Fourier-transform and the autocorrelation function. From this we have found characteristic measures for the different mechanical instabilities. The characteristic peak in the FT-spectrum appears for shark- skin at 5 - 15 Hz, for melt-fracture between 1-5 Hz and for stick-slip below 0.1 Hz.

S07-955

Melt flow rate testing of moisture sensitive plastics

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The current melt flow rate method (ISO 1133) does not adequately cover the measurement of materials that degrade or further polymerise at the melt flow rate test conditions. Materials such as PET, PBT and PA containing absorbed water tend to degrade, sometimes rapidly, at processing temperatures. This will result in poor repeatability and reproducibility of melt flow rate results. The ISO Plastics Melt Rheology committee (TC61/SC5/WG 9) is currently developing a modified melt flow rate method for reliable measurement of moisture sensitive materials, e.g. PBT and PET, thereby providing an alternative to intrinsic viscosity measurements. The modified method controls more tightly the time-temperature history experienced by the material and thus the resultant variability in measured properties due to degradation. Results on a range of moisture sensitive materials are presented, demonstrating the effect of moisture content and temperature on measurements. Repeatability of measurements of melt flow rate were up to 10% (1 standard deviation). The results of an intercomparison are also presented. The need to tightly control the sample preparation (e.g. drying) and sample handing procedures is highlighted as being critical to reliable measurements of such materials.

S07-1002

High Strain Rate Rheometry of Polymer Melts

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With the increased use of micro-scale and thin-walled injection moulding processes, wall shear strain rates experienced by polymer melts flowing through the gate region can be greater than 106 s-1. This is outside the region of conventional flow characterisation and therefore there is a need to characterise polymers at extremely high processing rates. A modified high-force all-electric moulding machine has been used in air-shot mode with capillary dies fitted at the nozzle to examine the rheology of a number of commercial polymers at uncorrected strain rates of up to 6x106 s-1. shear and extensional flow properties were obtained through the use of long and orifice (close to zero land length) dies of the same diameter. A range of polyethylene, polypropylene and polystyrene melts have been characterised to examine the effect of molecular weight and chain branching. Wall slip behaviour of two grades of HDPE has been examined at high strain rates, and the effect of a hyperbranched PMMA has been studied.

S07-1300

A STUDY OF THE RHEOLOGY, PROCESSING AND FLOW INDUCED MESOSTRUCTURES OF GLASS BEAD FILLED POLYSTYRENE

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This paper presents some recent results, both experimental and theoretical, on the effects of the addition of glass beads to the linear and non-linear rheology, and hence melt processability, of a commercial polystyrene. The addition of the glass beads also leads to interesting structural aspects such as chaining of the glass beads and cavitation, particularly in non-linear extension. The beads were coated with a commercial coupling agent prior to blending using a solvent procedure. First, a set of linear rheological measurements were carried out on both the pure PS and glass bead/PS blends. Time-temperature superposition was used to obtain the complex viscosity behaviour over a wide range of frequencies for all samples. The presence of the glass particles was found to raise the viscosity. The increase was found to be predicted satisfactorily by the empirical Kreiger- Dougherty relationship, plus a novel horizontal shift factor for the frequency. This second factor adjusts for the enhanced strain in the matrix due to the presence of the rigid glass beads, and hence the earlier onset of shear thinning. Non-linear measurements, in both shear and extension, were also carried out. The use of the same shifting factors gave good agreement at small strains in both cases, but divergence occurred at higher strains. Currently this is thought to be due to two distinct effects. First, the presence of the glass beads affects the development of molecular orientation during flow, reducing the overshoot in non-linear shear and the amount of strain hardening in non-linear extension. Second, post analysis of the samples from the extensional tests, showed the presence of cavities in the PS matrix; this may be the major contributor to the strain hardening reduction. Results will be presented showing a comparison between experimental results and theoretical predictions for extrusion, and in particular the effect of the glass particles on die swell.

S07-100

Rheological properties of PTT/MMT nanocomposites after twin-screw extrusion

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This work shows the importance of the rheological characterization on the choice of the best processing conditions of nanocomposites obtained by melt intercalation. Nanocomposites of poly(trimethylene terephthalate), PTT, and organophilic montmorillonite, MMT, were processed in a twin screw extruder at 120 rpm by two methods. The first sample of nanocomposite, called direct nano, was processed by mixing directly 95 wt% of PTT and 5 wt% of MMT, which were feed together at the feeding zone of the extruder. The other sample, called dilute nano, was obtained in two steps. First a masterbatch of 75 wt% of PTT and 25 wt% of MMT was processed. Then this masterbatch was diluted in the polymeric matrix PTT giving rise to a nanocomposite of 5 wt% of MMT. The materials structures were characterized by X-ray diffraction (WAXS) and by rheological properties, which were measured in a controlled strain ARES Rheometric Scientific rheometer using a 25mm plate-plate geometry and at 240ºC. WAXS results showed formation of intercalated structures in all the nanocomposites samples. Rheological tests showed that the PTT matrix degraded after re-processing. The steady and dynamic rheological results of the two types of nanocomposites were quite similar and showed that the materials had well dispersed structures and formation of a percolated network structure (pseudo-solid behavior). Based on all these characterization the method 1 (direct nano) was chosen as the more efficient way of processing PTT / MMT nanocomposites, because in these materials the degradation degree of PTT was the lowest and a good dispersion degree of the nanoclay in the polymeric matrix was obtained.

S07-168

DETERMINATION OF THE MOLAR MASS DISTRIBUTION FROM RHEOLOGICAL MEASUREMENTS AND SIZE EXCLUSION CHROMATOGRAPHY: A COMPARATIVE STUDY

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The way from molar mass distribution (MMD) to material functions is definite in principle, whereas the reverse calculation is ill-posed. Although the molar mass range accessible by size exclusion chromatography (SEC) could be successfully extended towards higher molar masses, the determination of MMD from rheological data poses a good alternative solution to SEC. In general it can be said that it is possible to determine the high molecular regions more accurately by rheological measurements, but the calculations sometimes pose problems, because of the used mixing rules. Furthermore is the determination of more complex distributions like those of bimodal samples or blends not trivial. These inconveniences are the reason why SEC is normally the preferred method. The aim of this study is to find the limits of both methods and to verify their applicability for different systems.Since the way from the MMD to the modules is definite, we calculate them with a software package provided by the rheometer producer (Rheoplus from Anton Paar) and with an Excel program which is exactly based on the BSW-Model and the mixing rule of Schausberger. For the determination by chromatographic methods we use a high temperature SEC with a mixed bed column and a refractive index- as well as a viscosity detector. The molar mass distribution is afterwards calculated with universal calibration. In this way the molar mass is determined as a result of the separation according to the hydrodynamic volume of the solute particles. Finally we will compare the measured modules with the ones calculated from the distributions. The MMD determined with the aid of SEC will be compared to the one calculated from the modules.

S07-199

Automation and High Throughput Screening in Rotational Rheometry for Polymers

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Reduced time for product development cycles is leading to an ever-increasing request for rheological measurements. One way for reducing the time the user needs to be present for preparing and running a test is to employ a sophisticated control of the rheometer and an intuitive user interface for the software. With such an approach the test itself can be pre configured and is running fully automatically including the analyzing of the data. However, still the sample loading before and the cleaning of the fixtures after the test is needed, which often takes the longest time and during which the rheometer sits idle. In addition loading and cleaning requires frequent interaction by the user when multiple samples are to be run. Therefore a fully automated, robotically operated rheometer was developed. The full functionality, modularity and accuracy of the rotational rheometer are available, which means the modern principles of high-throughput screening are brought to full function on the rheometer. The basic rheometer setup remains as modular as before including the ability to run all test modes the rheometer offers with the difference that the high-throughput rheometer now performs all measuring steps automatically. In addition, the standard and proven environmental chambers of the rheometer are available. The rheometer itself runs by the standard rheometer software and the measurement data and analysis results can be transferred to a monitoring database. The sample loading and the cleaning of the geometries is assisted by a sample preparation unit and a cleaning station, respectively. The sample throughput is further maximized by the use of multiple geometries allowing the simultaneous rheological measurement by the rheometer and the cleaning of the geometries at the cleaning station by the robot. The high-throughput rheometer and its special adaptation to polymer melts are described and discussed.

S07-282

Determination of the Degradation rate of Polypropylene Homopolymer by means of Rheology

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Polymeric materials, in either the solid or molten state, undergo both physical and chemical changes when heat is applied to them, thereby causing undesirable changes in their properties. Thermal decomposition of polymers, in the absence of oxygen, usually takes place through chain scission reactions. This is especially true in the molten state. A new rheological method was developed to determine the thermal degradation process of polymer melts. Low frequency oscillation measurements were carried out at elevated temperatures as a function of time. Some creep measurements were also done at specific periods during the degradation process. The measured rheological data were used to calculate the changes of free volume. It was shown that the degradation of polypropylene exhibits two regions with different rates. Stabilisers decrease the rate of decomposition in the first region, with no effect on the second.

S07-323

Study of the wall slip effects in a HDPE/calcium carbonate micro-composite by capillary rheometer

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In this work, the wall slip effects exhibited by a high-density polyethylene (HDPE)/calcium carbonate (CaCO3) micro-composite are investigated by means of a capillary rheometer, and compared with those of the neat polymer. Given the intrinsically complex nature of the particulate composite in the melt state, which is a suspension of rigid particles in a polymer melt, the applicability of various theoretical models to the study of the behaviour of the composite is explored.The particulate composite examined, at 30 wt.% of uncoated CaCO3 particles, prepared via melt compounding in presence of calcium stearate (1.5 phr), exhibits an optimal balance between stiffness and toughness and it is therefore considered an ideal candidate for the production of high-perfomance pipes. The experiments for the wall slip analysis are carried out by a capillary rheometer (by Ceast SpA, Torino, I), which operates at constant-piston-speed, using circular dies of two different diameters and various length to diameter ratios. Shear rates ranging from 10 s-1 to values close to the onset of oscillating flow are explored. The results indicate that wall slip effects occur during the flow of the composite whereas they practically do not take place for the neat polymer. For the particulate composite, the Mooney technique, widely used for polymers, appears to be ineffective at separating the slip and viscous flow components. This is tentatively attributed to processes that make the wall slip velocity dependent on the diameter of the die. The wall slip effects are then studied by using the Jastrzebski data analysis scheme, which is typically applied for two-phase, not polymeric systems. The effect of test temperature on the wall slip phenomena of the composite is also explored.

S07-400

Rheology and Processing of Carbon Nanofiber filled Polypropylene Nanocomposites

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Carbon nanofibers (CNFs) have attracted more attention due to their one-dimensional structure, excellent electrical and thermal conductivity, together with their excellent mechanical properties. The processability of carbon nanofiber filled polypropylene nanocomposites was analyzed through rheological studies and torque rheometry. Carbon nanofiber (CNF) reinforced polypropylene (PP) nanocomposites were prepared in a DSM microcompounder. The melt rheological analysis of the nanocomposites was performed in a Bohlin Gemini 200 parallel plate rheometer at different temperatures and a frequency range of 0.05 to 50 Hz. The influence of frequency, temperature and nanofiber content (ranging from 0% to 8%) on complex viscosity, storage and loss modulii and damping behavior was investigated. A shear thinning behavior at high frequencies was observed for all the compositions. Both the viscosity and modulus increased significantly at low frequencies for CNF loading more than 2wt%, suggesting an onset of pseudo-solid-like behavior due to the formation of interconnected network of CNFs (rheological percolation). The crossover frequency approached to lower value with CNF loading which indicated higher relaxation time due to restrictions imposed by CNFs during flow of nanocomposites. Dispersion of CNFs in polypropylene matrix during processing was studied w.r.t. CNF content, residence time and processing temperature. Torque rheometry, morphology development and electrical resistivity were correlated to study the dispersion of CNFs during compounding. Increasing CNF loading from 2% to 5% resulted in 8 order of magnitude reductions in surface resistivity, which indicated an electrical percolation threshold at 3.5 wt% of CNF. Lower rheological percolation threshold as compared to electrical percolation threshold is due to the fact that denser CNF network is required for electrical conductivity, while a less dense CNF network can impede the motion of polypropylene chain.

S07-483

Melt Rheology and Extrudate Swell of Organobentonite-filled Polypropylene

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Melt rheological properties and extrudate swell of organobentonite- filled polypropylene nanocomposites were studied by using a capillary rheometer in a shear rate range of 50-8000 s-1 and a temperature range of 190-210C. The nanocomposites exhibited shear-thinning behavior and the viscosity was well-described by the power law in this shear rate region. The addition of organobentonite enhanced the pseudoplasticity, i.e. increased the shear thinning behavior. With increasing organobentonite concentration, the shear stress/viscosity increased, while the power law index (n) decreased, and this effect is more significant at higher filler concentrations (>3 wt%). The dependence of melt shear viscosity on temperature obeyed the Arrhenius-Eyring expression, and the activation energy (Ea) decreased with increasing shear rate. Extrudate swell is a non- linear function of shear rate, while it is a linear function with shear stress and/or temperature. With increasing organobentonite concentration (>3 wt%), the extrudate swell clearly decreased, which is attributed to the limitation of the elastic recovery of the polymer chains by highly oriented silicate layers.

S07-489

Anomalous Rheological Properties and Extrusion Processability of Polyethylene Blends

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The rheological properties of the binary blends composed of a linear polyethylene (HDPE or LLDPE) and a branched polyethylene (LDPE) are studied. It is found that some blends show enhanced oscillatory shear moduli than the individual pure components, suggesting that the relaxation mechanism with long characteristic time is generated in a molten state. Further, they show higher zero-shear viscosities. The anomalous rheological behavior is observed for not only the blends with autoclave LDPE but also those with tubular LDPE, although the deviation from the linear additive rule is more prominent for the blends with autoclave one. Moreover, the anomalous behavior is observed irrespective of the number of short-chain branches in linear polyethylenes, which affects the miscibility with LDPE. The drawdown force, defined as the force needed for the extension of a polymer melt from a capillary rheometer, is also evaluated to comprehend the rheological information under the elongational flow and found to be quite sensitive to the anomalous behavior. The binary blends of autoclave LDPE and tubular LDPE, however, do not show any anomalous behaviors.

S07-498

Vertical orientation of extruded polypropylene containing unique nucleating agent

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Relation between structure and properties are studied for a polypropylene (PP) film containing unique nucleating agent. It is found that appropriate operating condition at T-die processing gives vertical orientation of PP molecules to the flow direction. This anomalous behavior is attained by the orientation of needle-like crystals of the nucleating agent to the flow direction and the strong nucleating ability for PP crystallization. The mechanical anisotropy of the film is completely different from that of a conventional PP film.

S07-511

Consitutive model for HIPS in the thermoforming range

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Within their thermoforming range amorphous polymers are deformed while they are in their rubbery state (i.e., above glass transition temperature).In this range their mechanical behavior results of a combination of hyperplasic, viscous and anelastic components. Roughly speaking constitutive model should account for very specific and coupled temperature and strain rate effects and for the combination of some irreversible strain and heperelasticity.This study first build an exhaustive data base obtained in monotonic and non monotonic tension over a wide range of strain rates and temperatures. Particular attention is paid to the relevance of local strain measurements.Based on these experimental data a revisited network model will be presented that allow modeling strain rate and temperature dependence as welle as loading unloading loops.This "visco hyperlestic" models allows 3D modeling in a thermodynamical frame and should allow easier numerical modeling though some physical aspects should be assessed now.It makes it possible to reproduce experimental hysteresis while unloading, loops while reloading as well as linear viscoelasticity at low strain.Paper will also stress on the necessary quality of experimental measurements.

S07-512

Influence of thermal and shear rate degradation on the rheology and processability of reprocessed ABS in injection molding process

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The effects of reprocessing on the processability of two ABS grade thermoplastic polymers has been investigated. Reprocesing in an injection molding process of a low viscosity ABS and a high viscosity ABS grade has been done changing operating temperatures and shear rates, DOE techniques were applied to plan experiments and later analysis. The flow properties of virgin and reprocessed materials have been evaluated by capillary rheology. Experimental results clearly indicate a qualitatively different behavior of the two polymers upon reprocessing. Low viscosity grade shows a reduction of viscosity upon increasing the number of processing cycles, thus confirming the degradation of this polymer. High viscosity grade, conversely, shows an increase of melt viscosity as the number of injection molding cycles is increased. It has been confirmed that applied shear rates in injection molding process affect to material behavior such as applied temperatures.

S07-573

Novel Instrument for Superposition Rheometry

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Many fluids consisting of multiple phases change their structure when subjected to shear. One of the phases might disaggregate, orient itself, be sheared or stretched, which influences the viscosity or elasticity of the material. This change of structure can be observed with the oscillating resonator described below, since the oscillation has tiny shearing amplitude (about 0.1 micron at the surface), thereby not affecting the structure. The presented parallel superposition rheometry is performed by the combination of a standard rheometer with a resonator. In a cone and plate or plate-plate geometry, the resting plate is exchanged here with a mechanical resonator performing rotational oscillations. This resonator is the core of a highly sensitive method to measure the viscosity and elasticity of a fluid. It makes use of a mechanical resonator vibrating at one or several of the resonator's eigenfrequencies. By bringing the resonator into contact with a fluid, such that the former induces a sinusoidal shear in the fluid, an increase in the damping of the system occurs. Observing the damping with a phase locked loop allows the determination of the mechanical behaviour of the fluid. The resonant frequencies are given by the design of the resonator and can be set to any frequency between 50 and 1000 Hz. A mechanical model of the resonator consisting of impedances has been derived. Therewith, fluids with low viscosities such that the shear wave decays within the gap can be measured as well as highly viscous fluids, where a shearing takes place throughout the gap. The sensitivity of the presented resonator allows the measurement of fluids with viscosities between 0.1 mPas and 10 Pas.Complex viscosity measurements of PIB in decalin are presented. This solution shows a highly shear rate dependent behaviour. Its effect on the parallel superposition modulus G is shown with the help of this new instrument.

S07-626

Development of New Milling Machine for Making Amorphous Rice Flour

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The novel milling machine for making amorphous rice powder have been developed without adding any water. This hand made machine is consist of two mortar and a ring type heater. By using this machine, amorphous rice powder can be easily obtained without any water. The properties of rice flour such as crystallinity, gelatinization temperature, rheological properties was investigated in term of WAX,DSC, steady shear viscosity. It is clarified that rice flours obtained from our milling machine were completely amorphous and it is easy to control crytallinity of starch changing conditions such as temperature, water contents of rice and so on.

S07-640

RHEOLOGICAL BEHAVIOUR OF POLYOLEFIN – BASED NANOCOMPOSITES IN ISOTHERMAL AND NON-ISOTHERMAL ELONGATIONAL FLOW

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The knowledge of the rheological behaviour of the polymer melts is very important to assume their processing performance. In particular, many polymer processes, as film blowing, fiber spinning, thermoforming, etc., require the understanding of the extensional rheology of the melts. Now, the nanocomposites are not only a subject of the academic research but they are beginning to live up to their promise and in some applications this class of materials is starting to replace the conventional composites or the pure polymers. However, the addition of a filler to a polymer can worsen the processability of the material and therefore, it is necessary to evaluate all the rheological properties and in particular the behaviour under extensional flow of nanocomposites, in order to consider a possible use of these new materials for film blowing applications. In this work, the rheological behavior in shear and isothermal and non-isothermal elongational flow of polyolefin based nanocomposites was investigated. All the rheological properties have been measured in order to qualitatively correlate these values with the morphology of these systems and considering a possible use of these materials for film blowing applications. The nanocomposite has been prepared by melt compounding in a co-rotating twin screw extruder, using low-density polyethylene and poly (ethylene-co-vinyl acetate) (EVA) as matrix and Cloisite 15A and Cloisite 30B as nanofillers at 5% wt/wt. A larger strain-hardening effect in isothermal elongational flow is shown by the nanocomposites compared to that of the pure matrix. Moreover, the force measured in non-isothermal elongational flow again rises with the presence of the nanofiller, while the drawability is only slightly lower than that measured for the pure matrix.

S07-643

COMPRESSION STRENGTH AND DEFORMATION OF THE OVOALBUMIN MACROMOLECULES WITH BIOMEDICAL APLICATIONS FORMED AT DIFFERENT CONDITIONS OF CONCENTRATION, IONIC FORCE, PH AND TIME OF AGING

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The ovoalbumins are proteins that are widely used as emulsificant agents or binding agents in the industry, independently of its nutritional properties. Nevertheless, due to their protein origin, ovoalbumins present a range of rheological responses (i.e. texture attributes) depending on concentration, ionic force, pH and aging time, this is caused mainly by denaturation or structural changes that occur at the conditions to which they are exposed in most of the industrial processes where these proteins are employed. The present work studies the effect on rheological properties in uniaxial compression tests of the gels prepared with ovoalbumin at different conditions (pH, ionic force, protein content), in order to look for alternatives or improvements in processing as well as provide a better understanding of these materials based on their mechanical response. Ovoalbumin gels were prepared by heat treatment at constant pH and inonic force. In the rheological response a peak rupture force was observed at high content, as well as an increase in Young modulus (i.e. high firmness). The ionic force showed to increase with the value of the rupture force as ions are added up to a maximum of 50 mM ion concentration after which the force diminishes, similar results were observed by changing the alkalinity, rupture force increases with pH and reaches a maximum at a value of 9.1. Finally, the effect of the storage time presented a maximum in the mechanical response of the gels at fixed conditions of ion content (50mM NaCl) and pH (i.e. 7) at 7 days of storage, this is thought to be caused by an increase in the acid content (~0.15% w/v). This results help to identify, in this type of macromolecules systems, which conditions offer better advantages in biomedical applications.

S07-653

Development of viscosity measuring system for polymers

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Injection moulding is one of the most widely used technique producing complex final product in one manufacturing step. Maintaining and improving of the quality of the plastics product requires detailed knowledge of the cavity filling process. Polymer melts are non Newtonian fluids therefore their viscosities, addition to temperature, pressure and molecular weight, depend on the deformation rate. The main object of this research was to develop a special injection mould that is suitable for the determination of the viscosity of the polymer melts. The injection speed and the measured pressure difference between two flow lengths were used in the calculation. The flow curves were also determined by MFI instrument. It was found that the spiral mould is a suitable method for determination of the viscosity of the polymer melts. The rheological characterization of materials was successful with this method in high shear rate range, between 100 s-1 and 20 000 s-1.

S07-655

RHEOLOGICAL STUDY OF MIXTURES OF MALTENES AND/OR ASPHALT WITH STYRENE-BUTADIENE-STYRENE TRI-BLOCK COPOLYMER

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In recent years the thermo-mechanic properties of the tri-block copolymers have been widely studied, the thermoplastic nature of the styrene-butadiene-styrene copolymers (SBR) at high temperatures and their ability to form a network at low temperatures explain the preference for these kinds of materials to modify the asphalts. Blends of asphalt with copolymers form multiphase systems. Such systems contain a phase rich in polymer, a phase rich in asphaltenes not adsorbed in the polymer, and a phase formed by maltenes. In this work, the asphalts AC-20 (Salamanca, México) are separated in maltenes and asfaltenes. In this sense, the role of maltenes is as important as the role of asphaltenes in determining the viscoelastic response. The rheological behavior in this type of materials determines the level of modification that the system needs in order to obtain a critical concentration and this also leads to a better understanding of the role of the maltenes in the properties of blends with SBR. The rheological measurements were performed in a AR2000 controlled-stress rheometer, using parallel plates (diameter = 25 mm; gap = 0.5 mm). The viscoelastic properties, storage modulus (G’) and loss modulus (G’’) were determined through small amplitude oscillatory shear flows at frequencies ranging from 0.1 to 600 rad/s at different maletenes and/or asphalts contents and at different temperatures (25, 40, 50, 60, 70 and 80 ºC). The results indicate that the copolymer content has an important effect on the rheological behavior of these blends, where a viscous behavior predominates over the elastic character, G´´>G´ in all the cases studied. The results of this study help to identify which of these conditions offer better advantages in industrial applications.

S07-659

Rheological properties of poly(dimethylsiloxane) filled with clay

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In recent years, polymer/clay nanocomposites have received much attention because they often exhibit a remarkable improvement of the properties when compared with virgin polymer or conventional micro- and macro-composites. In general, layered silicates have a layer thickness about 1 nm and a very high aspect ratio (e.g. 10–1000). Only a very small amount of layered silicate loadings can already result in pronounced improvements of properties such as stiffness and strength, increased dimensional stability, improved flame retardancy and decreased gas permeability. The rheological behavior of suspensions is one of the most sensitive indicators to analyse the particulate microstructure in molten polymers. Understanding the rheological properties of nanocomposites melts is not only important in gaining fundamental knowledge of the processability, but is also helpful in understanding the structure–property relationships in these materials. The linear and nonlinear rheological properties of 4 wt% clay (white hectorite) filled poly(dimethylsiloxane) (PDMS) were investigated systematically here. The material was prepared by dispersing clay into PDMS by ultrasound-assisted mixing. The linear viscoelastic properties showed the plateau moduli in the low frequency region, which revealed the presence of a space-filling network of clay platelets. In addition, the clay nanocomposites exhibited time-dependent characteristics and flow history dependency, indicating its thixotropic naturel. The structure evolution, i.e., buildup at rest and breakdown under flow, was investigated by using a series of transient flow protocols.

S07-833

Study of the nonlinear dynamics of triblock copolymers when subjected to fiber-spinning experiences.

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Tri-block copolymers show a not trivial behavior in flowing conditions, in view of their intrinsic molecular anisotropy. The scenario is further complicated by the occurrence of phase transitions from different meso-phases occurring as physical parameters change. These peculiarities might be further magnified when dealing with Rheotens experiments, where flow instabilities at high take-up velocities occur. From a mathematical point of view, the onset of such instabilities is a so-called Hopf bifurcation. In this work, Rheotens experiments are conducted on linear styrene-isoprene-styrene (SIS) tri-block copolymers samples varying the take-up velocity in a wide range of values also covering the occurrence of instability phenomena. Melt strength is measured during the experiences. The take-up velocity is set to be constant in every experiment, thus the melt strength is supposed to attain the regime conditions. The process is assumed to be isothermal and the procedure was repeated at different temperature values. The results are then analyzed by resorting to typical tools of nonlinear time series analysis and bifurcation theory (Neural Networks and Normal Form theory). The goal is to carry out an empirical model able to correlate the process dynamics to the process parameters (extrusion velocity and temperature) and characterize the actual bifurcations.

S07-946

Physico-mechanical properties of coordination crosslinked gels

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It is coordination crosslinked gels will be derivated in weak solutions of polymers at the expense of interplay of macromolecules functional groups and transient metals ions. The originating of strong clusters of a spatial grid is most brightly exhibited in change of flow characteristics of systems. In the given activity the researches of gellation of aqueous solutions derivative of cellulose - sodium carboxymethyl cellulose (Na-CMC), oxyethyl cellulose (OEC), and sodium lignosulfonate (Na-LST) were conducted at the presence of ions Al3+, Fe3+, Cr3+, Cr2O72-, Co2+, Ni2+, Cu2+, Zn2+. For this purpose the viscous properties of systems up to and moduluses of elasticity after the moment of formation of gel were measured. Was established, that the seaming of solutions Na-CMC and OEC at the presence of two and tervalent ions takes place practically instantaneously. However modulus of elasticity G of a system reaches an equilibrium value within several day. Is rotined, that the process of seaming in systems Na-CMC - salt of tervalent metal is reaction of first order on concentration of an ion, and G reaches 1-2 kPa. In remaining systems of value of a modulus of elasticity do not exceed 0.5 kPa and in the greater degree depend on concentration of polymer, than from concentration of crosslinking agent. The solutions Na-LST are structured only at the presence of ions of a hexavalent chromium Cr2O72-, and process is characterized by the brightly expressed induction period. During some time after cooking the viscosity of systems practically does not vary, then it is sharply (on some orders) is augmented, the system loses flow state, and the gel with minimum G is reshaped, which one grows in time up to achievement of an equilibrium value. The given process can take from one about several months, and the modulus of elasticity of these gels reaches 3-6 kPa and more.

S07-956

Recent and future developments in ISO standardisation

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The ISO committee ISO TC61/SC5/WG 9 Plastics Melt Rheology is responsible for developing standards on polymer melt rheology in ISO.Standardized methods currently covered by this committee are:ISO 1133: 2005 Plastics - Determination of the melt mass-flow rate (MFR) and the melt volume-flow rate (MVR) of thermoplasticsISO 11443: 2005 Plastics - Determination of the fluidity of plastics using capillary and slit-die rheometersISO 20965: 2005 Plastics - Determination of the transient extensional viscosity of polymer melts [tensile drawing method]ISO 16790: 2005 Plastics - Determination of drawing characteristics of thermoplastics in the molten state [fibre-spinning method]ISO 17744: 2004 Plastics - Determination of specific volume as a function of temperature and pressure (pvT diagram) - Piston apparatus methodThe current activities of the polymer melt rheology committee and the mechanisms for standardisation will be described. Potential proposals for new work items include standardisation of in-process rheological measurements and calibration of oscillatory and rotational rheometers.

S07-1050

Rheological Characterization of Reactive Extrusion Process Based Polypropylenes

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The aim of this contribution is to compare rheological behavior of three different samples of metallocene catalyzed polypropylene [virgin (linear) metallocene polypropylene (mPP), and (branched) mPPs prepared through reactive processing with (0.01 wt %) and without peroxide]. For their rheological description in different flow situations (shear and elongational) the eXtended Pom-Pom (XPP) and PTT-XPP models were used. A rotational rheometer (ARES 2000) with the SER Universal Testing Platform were used for the measurement of dynamic data (storage G' and loss G'' moduli) and uniaxial extensional viscosity. It was shown that both processed (branched) mPPs (with and without peroxide) exhibit distinct behavior in uniaxial extensional viscosity (appearance of strain hardening) in comparison to the virgin (linear) mPP. The XPP and PTT-XPP models proved their usefulness for a branching level quantification based on the measurements of steady shear and elongational viscosities. On the other hand, poorer models predictions of the transient extensional viscosity indicate absence of an H branching for the processed mPPs.

S07-1151

Rheological Study of Branched Polypropylene Prepared by Electron Beam Irradiation

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Introducing of branched structure into linear polypropylene was investigated by studying of the rheological behavior of modified polymers. Electron beam irradiation method was applied for sample preparation. Branched polymers were prepared by irradiation of polymer in presence of different concentration of TMPTMA. Irradiation has been done under air and nitrogen atmospheres. Homopolypropylene and its copolymer were used as linear precursor. The presence of branched structure in modified polymer was confirmed by rheological measurements and MFI test. The obtained results showed a competition between degradation, grafting, branching, crosslinking and monomer homopolymerization reactions. The level of branching and the predominated reactions were adjusted with changes in level of monomer and irradiation dose. Analysis of these data also indicted that branching reaction occurred efficiently in solid state modification. Extent of crosslinking reaction was measured by solvent extraction with xylene.

S07-1183

Rheological properties of quaternized polysulfones

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Polysulfones and their derivatives present interesting properties that led to a wide spectrum of industrial and environmental applications. Quaternized polysulfone combines the characteristics of polysulfone (good thermal and chemical stability, mechanical strength) and those of the polyelectrolytes. It is well known that polyelectrolytes are polymers with ionizable groups that dissociate in polar solvents. The presence of charged groups in hydrophobic polysulfones may affect their solution properties.The objective of this paper is to evaluate the effect of the chemical structure on the rheological properties of polysulfones and quaternized polysulfones with different ionic chlorine content (PSFQ). The rheological functions, i.e. dynamic viscosity, shear rate, elastic shear modulus and viscous shear modulus were obtained in different solvents, concentrations and temperatures, with a Bohlin Instrument CS 50, using the cone and plate measuring system (4 degrees/40 mm). The used solvents were selected as a function of the ionic chlorine content of PSFQ (proton-acceptor), which dictates the solubility in the N,N-dimethylformamide (DMF) (proton-donor), methanol (Me) (proton-donor), or DMF (proton- donor)/water (proton-acceptor), Me (proton-donor)/water (proton-acceptor), DMF (proton- donor)/Me (proton- donor). The observed behaviour regarding the variation of shear stress with shear rate was justified through consideration of multiple association equilibria generated by the specific interactions, via hydrogen bonding.

S07-1212

Solidification behaviour of an iPP during film casting experiments

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The crystallization of a polymer melt, taking place during transformation processes, has a great impact on the process itself, mainly because it causes a large increase in the viscosity (hardening). Knowledge of the hardening kinetics is important for modeling and controlling the transformation processes. A number of researchers have investigated the rheology of crystallizing materials. The most critical point in the experimental work on rheology during crystallization is that the evolution of the crystallinity, csi.g(t), and of the hardening evolution, Gamma(t), a “Normalized Rheological Function” (NRF), are usually determined during two different experiments, carried out on two different devices. The target function, the hardening behavior Gamma(csi.g), is obtained by elimination of the time. Unluckily, the material behavior strongly depends on the temperature. Therefore, if the two experiments were carried out under even small temperature differences, the results can be completely wrong.Recently [1] some of us proposed a novel technique which allows simultaneous analysis of several runs, even if they are not carried out at same temperatures. The hardening function, obtained by this technique, predicts the hardening of the iPP to be due to an intermediate level of crystallinity (more than 20% to obtain a doubling of the melt viscosity), a result which is in contrast with a part of the literature. In this work, starting from well characterized film casting experiments (being measured the width, the velocity, the temperature and the crystallinity along the draw direction), the hardening of the material was drawn from a simple model of the process, and it was compared with the hardening predicted after the technique pointed out in [1], as well aswith hardening predicted by other approaches from literature.

S07-1280

Effect of hydrocarbon oil on melt rheology and morphology of SEBS triblock copolymers

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The effect of addition of hydrocarbon oil on the rheology of triblock copolymer (styrene- ethylene-/butylenes-styrene, SEBS) was studied in this paper. The rubbery plateau modulus observed at the room temperature decreased with increasing the oil concentration. SEBS/oil blends showed rapid decrease of E’ as well as neat SEBS. Above Tg of both phases (PS and PEB) SEBS showed power-law relationship of G’ at low frequency regions. The power-law index was smaller than the value observed at terminal region for linear flexible chain, resulting from the formed immiscible morphology. G’ curve of SEBS-50 indicated frequency-independency at low frequencies. For temperature sweep test, SEBS with oil showed extremely sudden decreasing at a critical temperature during heating process. This suggests that the microphase separated structure disappeared and the both phases were mixed homogeneously above the critical temperature. It was found that the ODT temperature was dependent on the oil content. The morphological change of the SEBS compound was studied by AC-mode atomic force microscopy with a oscillating probe tip.

S07-1335

On the interplay between the viscoelastic and the structural relaxation behaviour of amorphous glassy polymers

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Polymer glasses are rheologically complex materials as their viscoelastic response is a function of the kinetics of a structural variable. Experimentally, to overcome such complexity, several loading protocols have been established over the years, yet resulting in a number of unsolved intricacies. From a theoretical point of view, we tackled the problem by coupling the structural relaxation kinetics with the constitutive equation for linear viscoelasticity written in the reduced time domain. In this paper a further reliability of the approach was substantiated. Simple geometrical descriptions and thermodynamic rules motivated the need of coupling constitutively the viscoelastic and the structural relaxation phenomena, actually representing the novelty of our theory. It will be shown analytically that, in the reduced time domain, the dimensionless bulk compliance coincides with the memory function appearing in the modified KAHR equation, so that the bulk viscoelastic functions can be extracted directly from the experimental PVT data. The thermal/mechanical loading sequence named Protocol I was discussed with a series of simulated data including those inaccessible by real experiments. The classical "volume implosion" phenomenon was replicated in both tensile and compression mode of loading.

S07-1393

Relaxation Patterns of Long, Linear, Monodisperse Polymers: BSW Spectrum Revisited

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Predictions of theories for the dynamic moduli of long, linear, monodisperse polymers are summarized and compared with experimental observations. Surprisingly, the predicted scaling of the relaxation spectrum with the 1/2 power for intermediate relaxation times is not found in the experiments. Instead of this, scaling with a power of about 1/4 extends up to the longest relaxation modes. This is expressed in the empirical relaxation time spectrum of Baumgaertel-Schausberger-Winter, denoted as "BSW spectrum". We compare the BSW spectrum with those from Doi and Milner & McLeish, which are based on the dynamics of reptating chains in a tube, while BSW spectrum is entirely on empirical basis. However, the excellent agreement between predictions and experiments for the BSW spectrum in comparison to the two others makes it a candidate for detailed analysis and extensive use. Working with the BSW spectrum is made difficult by the fact that hypergeometric functions occur naturally in rheological material functions. We develop equations, which allow to use simple approximations and which give excess to BSW parameters by analysing dynamic moduli directly. Moreover, we highlight other properties and parameters which demonstrate the superior agreement between model predictions and experimental facts.