



Symposium 5

Thermosets and Reactive Processing



TEST REACTIONS FOR CHARACTERIZING CONCURRENT DIFFUSION AND REACTION IN MOLTEN POLYMER

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Two methods used in the domain of chemical engineering science to characterize micromixing have been adapted to polymeric viscous medium. The objective of such methods is to use chemical test reactions in order to better understand coupled mixing, diffusion and reaction fundamental processes. The first method is inspired from the use of “competitive test reactions”. The polymeric medium was maleic anhydride grafted poly(styrene-co-ethylene/butylene-co-styrene) triblock copolymer (SEBSgAM) and the reactant was a diamine soluble in SEBS. The reaction was run in a batch mixer at 190°C. When a high amine/anhydride ratio is employed the product of reaction is a mixture of amine grafted SEBS and crosslinked SEBS. Interestingly, the proportion of crosslinked polymer depends directly on the local stoichiometry ratio, that is on the local state of mixing of the reactants experienced during the reactive mixing process. It was shown that such system is sensitive to the intensity of mixing. However, due to heat dissipation, temperature control is almost impossible in sheared molten polymers and we believe that this point compromises strongly the use of this method in the domain of polymers. The second method consists in implementing a single test reaction to decouple the mixing, diffusion and reaction processes. The difficulty here is to select carefully the model reactive system given that we decided to work with reactants and products of reaction perfectly miscible in the molten polymer. We selected a monoepoxy reacting with a secondary amine in a poly(ethylene-co-vinyl acetate) (EVA) matrix and demonstrated that it is possible to study experimentally and subsequently model the diffusion/reaction, provided that laminar mechanical mixing is represented in a simplified way. The evolution of the conversion with time indicates that the reaction is diffusion controlled and the evolution of the concentration profiles of r

S05-668

Recent Developments on Electron Beam Curing of Carbon Fibre / Epoxy Composites

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The manufacturing of structural composites for aerospace applications is up to now mostly based on the use of impregnated fibres with reactive resins, which will thermally polymerise and form the crosslinked thermosetting matrix. However, epoxy systems developed to meet the requirements of the aerospace industry require a long curing cycle at high temperatures, having an important impact on the production cost of the composite parts. Therefore, the aerospace industry is seeking for a new curing method, which will enable to drastically shorten such curing cycles. This requirement clearly cannot be fully fulfilled only by improvements on standard thermally curable resins and a new technology, called Electron Beam curing, is being developed. In Electron beam curing, crosslinking reaction is not driven by thermal energy, instead, suitable initiators dissociate when irradiated with accelerated electrons, generating species that will lead to the crosslinking reaction of the epoxy resin. Moreover, the Electron Beam curing reaction is extremely fast, taking place in only a few minutes, as compared to hours in standard thermal curing. Other technical advantages of Electron Beam curing include curing at room temperature using low-cost tooling, long resin stability, ability to fabricate large integrated structures and possibility of implementing a continuous processing line. Economic evaluations from aerospace companies have shown potential cost savings of from 10 to 60 % on replacing autoclave curing by electron beam. The present work aims to evaluate the latest developments on electron beam curing focusing on the manufacturing of composites for the aerospace industry. Theoretical and practical aspects will be presented, with a deep investigation of the opportunities and challenges faced by Electron Beam curing to become an appropriate current tool for the aerospace industry.



Dynamic Vulcanisation of PP/EPDM blends: Effect of Crosslinking on Phase Inversion

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EPDM/PP-based TPVs are a particular class of TPEs, which are obtained via dynamic vulcanisation, i.e. the selectively crosslinking of the rubber while it is melt mixing with the thermoplastic phase. The crosslinking enhances the viscosity and elasticity of the rubber phase and, as a consequence, the final TPVs morphology consists of crosslinked rubber particles dispersed in a thermoplastic matrix, even if large amount of rubber are used. Although, TPVs are already commercially available from the 1970's and a large number of studies have been published, many fundamental questions, related to the effect of dynamic crosslinking on the morphology and its mechanism, are still not understood. The main objective of this work is to get new insights on the effect of crosslinking on blend phase morphology, especially on the phase inversion driven by crosslinking. Thus, blends and TPVs with different EPDM/PP weight ratios were prepared using three different molecular-weights EPDM and four different PP. EPDM/PP blends were dynamic vulcanised using the resol/SnCl₂ system, in a batch mixer. Samples were collected along the time in order to correlate the evolution of morphology with the crosslinking reaction. The EPDM gel content and the degree of swelling were used as a measure to quantify the crosslink density. Morphology was studied by TEM and SEM in back-scattering mode. The results obtained show that crosslinking of the EPDM phase was retarded in case of low Mw EPDM due to its low crosslinking efficiency. This delay enables the observation of the various stages that take place during phase inversion. A good correlation between crosslink density and morphology evolution was established. With all the data obtained was possible to plot a morphology diagram as a function of viscosity ratio and composition for blends and TPVs, which allow to get more the detail insight on the effect of crosslinking on phase inversion.

S05-205

The role of the interphase on the flow stability of Reactive Functionalized Multilayer Polymers in coextrusion process

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Coextrusion technologies are commonly used to produce multilayered composite sheets or films with a large range of applications. The contrast of rheological properties between layers can lead to interfacial instabilities during flow. Few investigations in the literature have been dedicated to their physicochemical affinity at the interface. The present study deals with the influence of this affinity on interfacial instabilities for functionalized polymers. Multilayered structures, with varying viscosity and elasticity ratios, of polyamide (PA6) and either polyethylene functionalized (PE-GMA) or pure PE were studied. It was experimentally confirmed, in this case, that the interphase of non-zero thickness (corresponding to an interdiffusion/reaction zone) should be taking into account instead of a purely geometrical interface. As a first step, the rheological behavior of the multilayered cast films was investigated in order to probe (i) the competition between the interdiffusion/interfacial reaction and (ii) the influence of various parameters related with the process. The contribution interphase effect was also studied along with the increase in the number of layers. In order to quantify the contribution of the effect of the interphase triggered between the neighboring layers, an expression was developed to take it into account and to quantify its thickness. As a second step, an experimental strategy to optimize the process was formulated by listing the different parameters in control of the stability of the reactive multilayer flows. Coextrusion of bi-, tri- and fivelayered structures was carried out. The reaction rate /compatibilization plays a major role that must be taken into account. Furthermore, it is necessary to obtain links between the classic factors that are introduced in the evaluation of the theoretical stability charts and the obtained experimental ones. Hence, based on this analysis, guide-lines for stable coextrusion of reactive polymers were provide



NANOSTRUCTURED THERMOSETS BASED ON THE SELF ASSEMBLY OF BLOCK COPOLYMERS: CONTROL OF PROCESSING AND PROPERTIES

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Nanostructured thermosets, TS may be obtained by the self-assembly of amphiphilic block copolymers, BCP in a reactive solvent and fixation of the resulting morphologies by the cross-linking reaction. In particular, BCP self-assembled into vesicles and micelles can significantly increase the fracture resistance of cured epoxies with a minimum impact on Tg and modulus. BCP used for these purposes are composed of one block that is immiscible in the TS precursors and at least another one that is initially miscible and does not phase separate during the network formation. In this way the self-assembled structure is fixed by the cross-linking reaction. Various immiscible blocks have been employed to generate stable nanostructures in epoxies cured with different hardeners. The election of the miscible block is strongly dependent on the hardener selected to perform the cure. Examples of miscible blocks are: PEO, PMMA and PCL. The search of a miscible block for a specific epoxy-hardener combination is not a trivial task due to the variety of mechanisms of network formation involving different types of hardeners. PMMA may be a convenient selection as a miscible block because it is soluble with epoxy in all proportions. However, for most hardeners it becomes phase separated during polymerization well before gelation. On the other hand, poly(N,N-dimethylacrylamide) (PDMA) is miscible both in non-polar solvents such as cyclohexane and in highly-polar solvents such as water, methanol and ethanol. Therefore, the family of random copolymers poly(MMA-co-DMA), with different proportions of both monomers, should be a useful choice as a “universal” miscible block for the synthesis of nanostructured thermosets. The fact that BCP chains can form microphase separated structures in TS precursors is also a key to control processing. The Order-Disorder Transition, ODT of the blend depends on the segregation power of the BCP and it can be used for the control of the rheology during process

S05-224

Reactions of grafted polypropylene at surfaces and interfaces during interface-reactive injection moulding

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The low polarity of the polypropylene (PP) surface often leads to problems on further processing of the surface, e.g. by painting, bonding or the formation of bimaterial composites during two-component injection moulding. A surface modification is then required to get processable surfaces. The surface modification is always done as a separate processing step. Moreover, it sometimes does not result completely in the desired effects. With the interface-reactive injection moulding, a method is coming available to overcome the need for a separate surface modification. A purposive surface modification or composite formation may be carried out during the injection moulding process. For that, an ultrathin layer of a functional polymer (a modifier layer) is applied in the mould prior to the injection of the plastic melt. Due to the high temperature of the melt surface on hitting the modifier, chemical reactions are initiated, which bound the modifier chemically to the plastic surface. In this contribution, the results with a maleic anhydride grafted PP (PPgMAN) are presented. Although simple grafting of PP with functional groups increases its reactivity in the melt, an effect on the surface properties could not be established. However, modifiers containing amino groups could be bounded chemically to the PPgMAN surface during the injection moulding of PPgMAN. Beside the saving of a separate processing step, this way of surface modification has different advantages. The results are presented. On the other hand, the production of composites of PPgMAN with polyester fails due to their incompatibility. The application of an ultrathin layer of a reactive modifier on the surface of the first component by adsorption resulted in the formation of composites with high bond strength. These methods may open routes to the cost-effective production of surface-modified PP parts and composites with PP.



In Situ Production of Polyamid 6 / Layered Silicate Nanocompounds

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Nano-scaled layered silicates are suitable for improving the mechanical properties of thermoplastic polymers. In order to achieve a significant improvement, the silicates have to be intercalated and subsequently exfoliated in the polymer. Thus, there is a large boundary surface between filler and matrix, leading to the desired reinforcing effect. However, the standard procedure of melt compounding usually requires mixing with high shear stress. This may lead to unacceptable polymer degradation. As an alternative to melt compounding, an in-situ process for the production of PA6-Nanocompounds is investigated. During the in-situ production, the layered silicates are dispersed in the monomer Caprolactam before the polymerisation, leading to an intercalation process. The polymerisation process itself takes place in a 26 mm co-rotating twin screw extruder. As an example, the production of a compound containing 2 % homogeneously dispersed nano-scaled silicates was successful. Process parameters like residence time and shear stress, as well as the type and quantity of both activator and catalyst play a significant role in establishing the process. The paper thoroughly discusses the influence of material parameters, process conditions and compound morphology on the resulting mechanical properties.

S05-273

The rod-coil block polyimide thermoplastic/ epoxy resin blend

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A series of rod-coil block polyimides have been synthesized by introducing Jeffamine D2000 into polyimide chain and completely characterized by FT-IR, NMR and TGA. These rod-coil polyimides can form different pattern by self-assembly, but also can enhance the properties of epoxy resin. The results indicated that micro & nano structure in large-scale can be obtained in the polyimide thermoplastic/epoxy resin blend. In the view of the difference in miscibility and the phase behavior for the blends of sub-chain (D2000 and polyimide) of the rod-coil block polyimide with epoxy after and before curing, the formation of micro and nano structures was judged to be via the mechanism of reaction-induced microphase separation. After developing in solvent such as chloroform, DMF and NMP to remove rod-coil polyimides, micro & nano porous of different scale can be obtained in the crosslinked epoxy film through control of the type and content of block polyimides, and the curing conditions. This is a very facile approach to prepare micro & nano- porous epoxy film, which would find wide applications such as chemical and biological separations, catalysis, photonic devices and micro-electronic materials.



INFLUENCE OF ADDITIVES ON INJECTION MOULDING Process OF WOOD/MELAMINE RESIN COMPOSITES

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Natural wood shows limited processability compared to polymeric materials. Thus, efforts on research have been made in order to extend the applicability of modern polymer converting technologies to wooden materials. The limitation in the design possibility and functionality of the wooden materials could be overcome with the use of wood plastic composites (WPC). With polymer processing techniques like extrusion or injection moulding, three dimensional structures could be produced with WPC. In last few years, a new generation of melamine resin (HIPE®ESIN from AMI) was developed which shows thermoplastic flow behaviour. Based on this special melamine resin, recipes of wood / melamine resin composites HIPE®WOOD(*) were developed. The combination of the good melt flow characteristics of HIPE®ESIN, the suitable additives and processing aid, optimised recipes as well as optimised processing technology are the main reasons for the success of HIPE®WOOD(*). These new developed WPCs show excellent processing behaviour in compounding as well as in injection moulding processes combined with very good mechanical performance and surface aesthetic (wood-like feeling). With HIPE®WOOD, WPC could be used for new applications with very high requirements in stiffness, creep resistance, scratch resistance and in particular heat deformation resistance at high service temperature. The influences of wood content and additives such as modifier, processing aids, lubricants, catalyst etc. on the compounding behaviour, flow behaviour, curing characteristics and processing behaviour by injection moulding and on the final properties of wood / melamine resin composites were investigated and discussed. (*) Awarded with the Schweighofer-Prize 2007 - European Innovation Award for Forestry, Wood Technology and Timber Products Innovation Prize Category Wood Products

S05-610

Reactive Plasticizers As Processing Aids For Thermoplastic Nanocomposites

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Some thermoplastics are difficult to process, especially when reinforced with nano-fillers, and are likely to suffer degradation particularly in extended processing operations such as rotational moulding. Traditional methods of reducing the molecular weight, adding inert plasticizers, and blending with a more processable polymer usually result in a reduction in the properties. Recently a new strategy has been developed in which the processing temperature is lowered by adding a small amount of a crosslinkable monomer. This monomer acts as a reactive plasticizer during processing but it can be subsequently polymerised into a thermoset phase in the thermoplastic matrix, possibly retaining the original mechanical properties of the matrix. In this work we investigate three thermoplastic/thermoset systems - PMMA/diamine-cured epoxy, PVC/diallyl phthalate (DAOP) and PC/DAOP - in the absence and presence of a montmorillonite clay. The cure kinetics of the PMMA/epoxy system was retarded by PMMA due to a dilution effect and SEM and DMTA showed phase separation varying from dispersed PMMA to a co-continuous structure to dispersed epoxy phase. The clay was intercalated but not fully exfoliated and preferred to reside in the epoxy phase. With the PVC/DAOP system, the cure kinetics of DAOP were accelerated due to a gel effect caused by grafting of PVC into the network. The processing temperature of PVC was significantly reduced by the DAOP and allowed clay to be well dispersed in the PVC. For PC/DAOP blends, the cure rate was lowered with addition of PC due to a dilution effect. DAOP formed miscible blends with PC and as an effective plasticizer. However, the molecular mobility provided to the PC chains by DAOP causes crystallisation of the PC and this places limits on the potential reduction in the processing temperature of the blend. Blends of PC with DAOP and clay filler also showed good processability.



Twin-Screw Reactive Extrusion to Prepare High-Performance Flame Retardant Polymer Composites

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Halogen-free flame retardants applied in polymers have attracted more and more attentions due to their less release of harmful smoke and gases during fire. In this paper, a novel technique, reactive extrusion, was used to synthesize environmental-friendly melamine based flame retardants for polypropylene (PP) and polyamide 6 (PA6), respectively, in a twin-screw extruder, which proves to be a good reactor. Firstly, intumescent flame retardants (IFRs) and their master batches for PP were successfully synthesized by reaction of melamine phosphate (MP) and a type of polyol (PL), together with PP carrier, in a twin-screw extruder. The effect of PP carrier resin and char former/blowing agent ratio in FR system on the flame retardancy and the water resistance of IFR/PP blend was then systematically investigated. The experimental results show that both PP carrier and char former/blowing agent ratio have a great influence on flame retardancy and water resistance of the flame retarded PP materials. The reasonable increase of PP carrier content or char former/blowing agent ratio would contribute to remarkable improvement of both the flame retardancy and the water resistance. This improvement was found to be well correlated with the improved FR dispersion, the improved compatibility and the decreased polarity of IFRs by in-situ encapsulation. Secondly, nitrogen-based melamine cyanurate (MCA) nanoparticles for PA6 flame retardation were in-situ produced and simultaneously blended with PA6 in extrusion process. SEM and TEM observations show that the in-situ formed MCA particles, with aspect ratio of about 7.5, radial size in the range of 70~300 nm (mostly 70~90nm) and crystallite size of less than 22 nm, are well dispersed in PA6 matrix at nanoscale. The flame retardancy and the mechanical properties of the obtained FR PA6 material are greatly improved by the in-situ formed MCA nanoparticles.

S05-756

POLYURETHANE REACTIVE PROCESSING : AN APPLICATION ON REACTIVE ROTATIONAL MOULDING

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Over last years, reactive polymer processing has encountered growing interest. Despite all the advantages, full understanding and control of such forming processes require complex studies based on the coupling of several dependant parameters. Among them, kinetics is obviously one of the most relevant because of its influence on viscosity, temperature, wet ability and as a basic consequence on the part quality. Rheological properties are also essential features, directly connected to the flow condition and finally to the forming ability. In the case of thermosets, especially in polyurethane, the chemorheology is one of the most complete ways to tackle and control material transformations. The aim of this work is to contribute to a better understanding of polyurethane reactive rotational moulding. First results based on thermoset polyurethane are presented and discussed. A first approach consists in determining chemical reactive mechanism by FTIR analysis. Then thermal analyses are used to characterize the exothermic effect and the non-isothermal nature of the transformation. Finally, plate-plate multiwave rheological characterisations are exploited to assess flow abilities of studied material. To correlate these ex-situ results with the real behaviour of the material during its processing, in-situ measurements have to be set up. In-situ thermal measures are readily available in wireless mode to fit with the biaxially rotated moulds. These are linked to thermal analyses. Besides, dielectrometric or ultrasonic monitoring devices could also be used to give valuable rheological and chemical information. First results of the process development and material study are detailed. Polyurethane behaviour is characterized by ex-situ experimental analyses correlated to process cycle studies. As a conclusion, non-isothermal, conversion-dependant diagrams are built to combine all the chemical, kinetic and rheological results. These results finally offer an overview of the process.



Structure and properties of poly(lactic acid) (PLA) based blends reactively compatibilized through free radical reactions

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Poly(lactic acid) (PLA) is particularly interesting for agricultural and packaging applications thanks to the twofold environmental advantage of being prepared from renewable resources and being biodegradable. Anyway the high stiffness and brittleness of this polymeric material does not allow the replacement of commodities polymers, such as polyolefins, in large scale applications. The blending with poly(butylene adipate-co-terephthalate) (PBAT) could result a promising strategy to achieve a toughened multiphase material, by taking also into account the effect of composition onto phase distribution. In particular blends containing from 20 to 25% by weight of PBAT showed an increase of about 600% of elongation at break with respect to pure PLA. Moreover, material ductility could be further improved by adopting a strategy of reactive compatibilization, i.e. inducing the formation of comb-like PLA-PBAT copolymers during the melt blending. Different routes were developed to achieve this result by exploiting the reactivity of ester groups (transesterification) or terminal groups (use of bifunctional reactive molecules). Nevertheless, since the structure of the two polymers was similar, during this work a not selective strategy was adopted consisting in the use of the peroxide 2,5-dimethyl-2,5-di(tert-butylperoxy)hexane. The phase morphology development and the final properties (torque, fluidity in the melt, tensile behaviour, thermal and dynamical-mechanical features) of the blends were studied as a function of the peroxide concentration. The elongation at break was improved up to a maximum value thanks to this approach and a corresponding minimum was observed in the value of the dispersed phase diameter. A structural characterization of the macromolecules formed during the reactive process was attempted by using size exclusion chromatography both onto blends and pure polymers melt mixed in the presence of the peroxide.

S05-1071

Preparation and Characterization of Silane Grafted Polyolefin Elastomers

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Polyolefin elastomers (POE) are copolymers of ethylene and alpha-olefins obtained by metallocene catalyst technology. The grafting of functional silane groups on different POE was studied with the aim to improve mechanical and thermal properties of the copolymers by silane crosslinking reaction after final shaping of POE products. The grafting reaction was carried out at elevated temperatures in an internal mixer. 2,5-bis(tert-butylperoxy)-2,5-dimethylhexane (DBPH) and triethoxy(vinyl)silane (VTEOS) were used as grafting system. The POE used were commercial samples with different content of butene or octene as comonomer. The competition between silane grafting reaction and peroxide induced crosslinking during grafting process was studied as function of the POE comonomer content, the radical initiator and silane concentration. The silane grafting degree was determined using Fourier Transformation Infrared Spectroscopy (FT-IR). Gel content measurements were applied to determine the degree of peroxide induced crosslinking during the grafting reaction as well as the silane caused final crosslinking degree. The gel fraction from peroxides induced crosslinking depends on silane/peroxide ratio and on type of POE used. Increasing silane/peroxide ration results in decreasing peroxide crosslinking. A model of the silane crosslinking process was developed. Mechanical and thermo-mechanical properties were examined by standard mechanical tests, dynamic mechanical analysis (DMA) and temperature scanning stress relaxation measurement (TSSR).



BIODEGRADABLE MATERIALS BY REACTIVE EXTRUSION

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During the last decades, the use of polymeric materials has grown progressively and now, these materials are one of the most attractive categories of materials. This success is mainly related to their low cost, good properties, aesthetic qualities and resistance to physical ageing and biological attacks. However, the degrading resistance of synthetic polymers, especially in such applications where they are used for a short period of time before becoming waste, the growing environmental awareness and the new environmental regulations are forcing the industries to seek for more ecologically friendly materials for their products. Most biodegradable polymers have good properties comparable to many petroleum-based plastics and readily biodegradable, having the potentiality to compete with commodity plastics. However, their relative poor physical properties, such as high brittleness, moisture sensitivity, low heat distortion temperature, difficult their processability, restricting their use in a wide-range of applications. The long-term properties of renewable materials are also very important especially if the products are not single use applications. Therefore new approaches to develop usable biodegradable materials are a subject of increasing research interest. The objective of this work is to prepare biodegradable polymeric materials based on blends and copolymers of a synthetic and a biodegradable polymer. Thus, blends and copolymers of ethylene vinyl acetate, polylactic acid and poly (ϵ -caprolactone) were prepared in a batch mixer. Characterization of the copolymer formation was performed by several analytical techniques, such as, NMR, SEM and rheology. O₂ and CO₂ measurements were carried out to monitor the biodegradability of the several materials. The results obtained show that the degradability of the copolymers was higher than the properties of the respective blends.

S05-1309

HYBRID-NANOCOMPOSITE MATERIALS: EFFECTS OF NATURE OF EPOXY RESIN AND SILOXANE COMPONENT

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This work describes the study of the relationship between viscoelastic properties, chemical composition of the epoxy matrix and typology of the nanodimensioned silica domains in new hybrids and nanocomposites obtained through two different techniques: 1) Simultaneous formation of the epoxy-network and siloxane domains via sol-gel reactions (in-situ hybrids), and 2) Direct addition and dispersion of preformed nanodimensioned silica particles in the resin (nanocomposites). All the systems underwent a two steps cure: 18 hours curing at room temperature followed by two hours of post-cure at 150 °C. The effects of the chemical composition of the epoxy resin and the chemical constitution and content of the siloxane component on the thermal and viscoelastic behaviour of the obtained materials have been widely analysed. Unexpectedly the introduction of both preformed silica and the siloxane component via sol-gel reactions, caused a decreasing of the glass transition temperature (T_g) of the epoxy matrix of the nanocomposite and hybrid material. But the TGA performed on these systems have shown an increasing of the decomposition temperature relative to their thermal oxidation. The obtained nanocomposites showed higher T_g values compared to the hybrids at the same silica content obtained via the sol-gel method. In the latter case, however, DMA spectra showed a pronounced reduction of the loss factor at the glass transition temperature. SAXS diffraction tests indicated the presence of compact domains for the nanocomposites and a fractal structure for the in-situ hybrid systems.



New method for post-processing crosslinking reaction for Polyolefins based materials

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Day by day, the use of polyolefins, particularly polyethylene, is increased in the packaging and in automobile industries. However, its applications are restricted due to its poor mechanical properties at high temperature due to its low melting point. Crosslinking is thus an important method that allows to extend the range of applications of these materials. Among the variety of ways that have been developed for crosslinking of polyolefins, the most widely used methods are irradiation, peroxide or silane-water crosslinking. All these techniques are known to provide enhanced properties of polyethylene based materials together with easy processing. Nevertheless, some considerations always limit the use of these processes. A new method to process functionalized polyolefin based materials that are able to crosslink has been developed. The crosslink occurs after the melting / compounding processing stage, at moderate temperature and without the addition of external reagents. Maleic anhydride-functionalized ethylene copolymer was processed with 1,4 butanediol in the presence of para-toluene sulfonic acid as a catalyst. To prevent the reaction in the melt, it was chosen to trap the 1,4 butanediol onto "vector" particles. The extent of the crosslinking reaction during the mixing has been studied for different processing conditions and for different particles taken as vector particles and it was found that Orgasol® polyamide hollow particles are efficient to inhibit the crosslinking reaction in the mixer. The reaction then takes place at 40°C and after 100h storage, the cured samples appeared to be highly and homogeneously crosslinked with a gel content above 90%. This new method has been scaled up from a lab scale batch mixer to a semi industrial ko-kneader and its potentials evaluated in the high temperature cable application.

S05-1363

Synthesis of grafted copolymers of EVA with either poly(ϵ -caprolactone) or polybutylene terephthalate by reactive extrusion : Influence of the nature of the ring-opening polymerisation initiator on the grafting degree

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The present work deals with a new route to synthesize by reactive extrusion grafted copolymers EVA-poly(ϵ -caprolactone) or EVA-polybutylene terephthalate. The reactional mechanism is based on the polymerisation of the ϵ -caprolactone or the cBT (cyclic butylene terephthalate) in situ in the presence of molten EVA to obtain desired copolymers. The study of the chemical reactions leading to the grafting on molecular models of EVA clarified the reaction mechanisms. For example, bulk polymerisation of ϵ -caprolactone is very fast under the experimental conditions chosen whatever the initiator used. Ti(OPh)₄ synthesized by our group is a less reactive initiator than Ti(OPr)₄ but more selective regarding transfer reactions and therefore grafting, these phenomena being explained with the delocalisation of the phenolic electrons. The transposition of the results obtained on model reactions to the melt showed that grafting on EVA agreed to the mechanisms stated on model reactions with an inferior percentage. This difference was attributed to the mixing physical parameters where chemistry happens at the interface. An other transposition of the previous approach in the case of the cBT using the specificity of the Ti(OPh)₄ showed that it is possible to reach a percentage of 30 % of formed copolymer. Rheological and mechanical studies were developed and the morphology characterized by electronic transmission microscopy (TEM) show a fine nodular dispersion (<500nm) of PBT. These results clarified the role of the phenoxide groups from the Ti(OPh)₄ in the grafting efficiency.



Design and manufacturing of thermosets-based products supported by complex numerical simulations

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Epoxy resins and liquid silicone rubbers (LSRs) are widely used in products where very high electrical insulation is required and also good mechanical and thermal resistance is necessary. These properties are strongly dependent on proper manufacturing process with minimised shrinkage and without voids and cracks. Application of appropriate materials, process parameters (mold temperature, filling time, filling velocity, initial temperature of internal parts, gelation time), as well as design and geometric parameters are key factors for better quality components. In this paper, a new approach for three-dimensional modeling all molding stages, namely filling, curing and post-curing is presented. The reactive molding simulation tool is based on a commercial CFD package, however to simulate the reactive nature of the system with exothermic effect, viscosity and reaction kinetics models were successfully implemented. A novel simulation procedure for stress and shrinkage calculations, as well as simulation results are also presented in the paper. In addition a description of a modified version of the tool dedicated to simulation of injection molding process of liquid silicone rubber was presented with supporting simulation results. A number of different products, including embedded poles, instrument transformers, bushings, were simulated and final recommendations were formulated for the manufacturers resulting in setting of process parameters guaranteeing high quality products. Finally, a complex experimental verification of the simulation results is shown, indicating for a good agreement between simulation and measurements. This confirmed the suitability of the developed simulation tool for high-quality processing of thermosetting materials with low scrap rate and faster time-to-market.

S05-106

THE MODIFICATION OF POLYPROPYLENE-WOOD COMPOSITES BY REACTIVE MIXING WITH EPOXY RESIN

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Wood plastic composites (WPCs) have found technical and marketing succession in many applications[1]. Wood is a polar material with poor interactions with polypropylene. Epoxy resins may have good interaction with cellulose structure of wood flour because of their polar functional groups. Maleic anhydride grafted PP(MPP) have shown the most potentials in improving the mechanical properties of WPCs[2,3]. The reactive mixing of epoxy resin with polypropylene and wood particles was performed on co-rotating twin screw extruder. The incorporation of PP-g-MA to the composite showed 30% increase in tensile strength from 26.5 to 35 MPa for the composite with 40% wood content. The complex viscosities of composites were increased by increasing the wood and epoxy resin content. The slope of $\eta^*-\omega$, curve increase by increasing epoxy resin in the composites, particularly at low frequency regions. It is believe that there are not considerable interactions between epoxy and PP resins, and any synergistic effect of epoxy resin on rheological parameters may be attributed to wood flour-epoxy resin interactions. The evaluation by Cole-Cole plot showed that in all range of loss modulus- G'' , the composite with optimum epoxy resin content exhibited the highest G' values. The $\tan\delta$ of 30wt% wood composite without epoxy resin is nearly constant at the frequencies lower than 1 rad/sec. It was dropped down sharply at higher frequencies by crossing the reference line of $\tan\delta=1$ at a Cross Over Point about 50 rad/sec. Using epoxy resin in the composites decreased the $\tan\delta$ by a vertical shift to lower values, with small changes in narrow gap of $\tan\delta=0.5-1.2$.



Ring-opening polymerization of decamethylcyclopentasiloxane initiated by a superbases: kinetics and rheology

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The use of phosphazene bases in combination with water was proved to be efficient in order to obtain polysiloxane polymers from cyclic monomers. Only a few minutes are necessary to obtain polymer chains with a low concentration in monomer at the equilibrium (5%). For that purpose the space between a rheometer plates is the more convenient device to monitor this reaction from a chemical and a viscoelastic point of view. Then, here is proposed a chemo-rheology study that leads in the same time to the chemical kinetics equations and to the variation of the viscoelastic functions during the polymerization. In this way different catalysts are used and their efficiency compared as a function of their "basicity tank". Viscosity versus polymer concentration or conversion shows a master curve whatever the experimental conditions involved for the catalyst suitable to be used under extrusive experimental conditions. Thus only a few experiments are needed in order to develop a model that can be used to foresee the variation of the viscosity during the reaction.

S05-332

Effect of resin chemistry on the viscoelasticity of its cured product

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Thermoset resins are widely used as adhesives as packing material in electronic industry and as matrix material in fiber reinforced composites. Previous studies showed that small errors in the mixing of a two component thermoset resin system could result in relatively large changes in the final viscoelastic behavior. Therefore a detailed study in investigating the relation between the initial resin compositions and mixing ratio on the viscoelastic behavior is performed. An aromatic two functional epoxy is mixed with three aliphatic amines having functionalities 2, 3, 4 and cured. For each of these mixed cured products the viscoelastic master curve and corresponding shift factors were determined. Depending on the crosslink density the viscoelastic curves were seen to shift about 12 decades with respect to frequency(time) axis. We were able to predict the changes in viscoelastic behavior by combining the Miller Macosko theory for crosslink density with the parameterized model for the master curve.



Influence of semi-crystalline polyesters on the properties of low temperature thermosetting powder coatings

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Solvent free powder coatings are a very attractive market with strongly increasing values. Due to the new VOC-directive in Europe the use of powder coatings, the saving of energy and slim processing lines become more and more important. Urethane powder coatings based upon uretdione crosslinkers are known for their outstanding properties like weathering resistance, superior flow properties and surface finish quality. However, the high curing temperatures prevented the penetration of such powder coatings into the market for the coating of thermo-sensitive substrates until recently. A few years ago a suitable catalyst system and, recently highly flexible and glossy powder coating prototypes based on amorphous polyester resins were developed at the IPF which allow the coating of aluminium sheets at temperatures between 140°C and 150°C. For the application on wood materials a further reduction of the curing temperature was necessary. Therefore, the use of semi-crystalline polyester resins was studied in non-reactive polyester mixtures and model powder coatings as well. In addition, a better flow and, resulting from that, an improved film appearance at lower temperatures was expected with the use of certain amounts of these polyesters. The influence of semi-crystalline polyesters on the flow properties and the reactivity in melt was studied by rheological measurements, DSC and WAXS. The best polyester mixtures showed a significant reduction of melt viscosity in a narrow temperature range between 110°C and 130°C compared to the amorphous polyester. Depending on the amount of semi-crystalline polyester the melt mixtures as well showed a certain degree of crystallinity. In model powder coatings the melt viscosity minimum was shifted to lower temperatures and the curing temperature was reduced to 120-130°C. The resulting films are highly flexible, smooth and glossy.

S05-439

Melt functionalization of polypropylene in the presence of N-bromosuccinimide

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Free radical grafting of maleic anhydride onto polypropylene by reactive extrusion is a very common process for post-synthesis functionalization. However when high grafting levels are required one has to cope with dramatic degradation leading to poor mechanical properties. The presence of N-bromosuccinimide (NBS) in the reactive medium as a source of bromine radicals is here assumed to quench PP macroradicals in a reversible way to promote grafting instead of chain scission. Higher grafting levels (up to 3wt% as determined by acid-base titration) can therefore be achieved with limited degradation. Both NMR (1H and 13C) and FTIR spectroscopies have been used to ascertain the amount, the position and the structure of the grafted moieties which were shown to be isolated succinic anhydride rings grafted along the polymer backbone. No evidence of poly(maleic anhydride) or interacting anhydride moieties have been observed. Besides, bromine radicals are also responsible for iPP epimerization leading to an isotactic/atactic stereoblock polypropylene whose structure has been evidenced by 13C NMR. This partial destruction of isotacticity induces a decrease in crystallinity that eventually confers an elastomeric behavior to the grafted polypropylene. Functionalization of polyethylene and ethylene-propylene copolymers in the presence of NBS is currently under investigation. In the future, several non-brominated reagents will be tested to avoid the use of NBS.



Comparative Study of the One Step and Two Step In-situ Compatibilization of PP/PA6 Blends

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An attempt was made to study the efficiency of the one-step in-situ compatibilization of PP/PA6 blends and compare the results with that of the two-step compatibilization using a commercial PP-gr-MA. The one-step compatibilization process was performed on the PP/PA6 samples with the same blend ratio (80/20) but varying in Maleic anhydride content and peroxide concentration. All reactive blending processes were carried out in a modular co-rotating twin screw extruder. The formation of the PP-gr-PA copolymer, preferentially occurred in PP/PA interface, could be followed by characteristic peaks of carbonyl vibration of the imide group in FTIR spectrum. The SEM results showed much smaller PA particle size in the samples prepared using one-step compatibilization compared to that in samples produced by two step method with using the same level of PP-gr-MAH. This was an indication of greater interfacial enhancement and therefore, higher compatibilization efficiency achieved in one-step method. From the SEM results it was found that the increasing of initial MA concentration led to larger PA particle size which could be related to secondary reactions between excess MA and PA. The results of melt linear viscoelastic measurements showed higher storage modulus and greater complex viscosity at whole shear rate range for the sample prepared by one-step reactive method with using low level of peroxide in comparison with the simple blend and the sample compatibilized by the two step method. These results could be explained in terms of increasing the molecular weight of PA phase via reacting with MA. This was evidenced by higher storage modulus and complex viscosity along with presence of straight chain imide group absorbance peaks in the FTIR spectrum of the samples which were prepared by melt reacting of PA with MA compared to neat PA.

S05-560

Study on Morphology and Thermal Properties of Epoxy/Silane Modified Nanoclay Nanocomposites

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Epoxy-clay nanocomposites have been produced using silane modified montmorillonite. The clay was first purified using a 1-inch hydrocyclone apparatus. The laser particle size analyzer (LPSA) results and X-ray diffraction (XRD) patterns showed that the impurities and large particles (greater than 5 microns) are removed from the samples. The purified clay was modified with various amounts of (gamma)-3-aminopropyltrimethoxysilane as modifier. The results showed that interlayer spacing increases with increasing the amount of modifier and the basal distance in the organoclay was more than 2.1 nm which was larger than that of the original clay (1.24 nm). The synthesized organoclay was mixed and swollen by a mixture of epoxy resin and stoichiometric amount of curing agent at different temperature, mixing time and agitation. Finally, the compounds were cured in an oven at 90 °C for 2 hrs. The nanostructure materials were characterized using X-ray diffraction (XRD), transmission electron microscopy (TEM), thermogravimetric analysis (TGA) and differential scanning calorimeter (DSC). The XRD patterns showed that the interlayer spacing of clay in the nanocomposites increases and the 001 peak of the montmorillonite was shifted to smaller 2theta and in many cases disappeared. The XRD and TEM results demonstrated that the layers of clay in the nanocomposite samples were partially exfoliated. The curing behavior of the epoxy-clay nanocomposite system was investigated by Differential scanning calorimetry (DSC). The results showed that this type of modifier has no effect on the curing rate of the nanocomposite.



Innovative, stitched preforms for high performance fibre reinforced-plastics

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The cost-reduced manufacturing of complex textile preforms used for liquid composite moulding of high-performance fibre-reinforced polymer composites is of utmost importance for today's aerospace industry. Stitching technologies are considered to be one of the key approaches [1] for this challenging goal. However, the potential reduction of in-plane mechanical properties [2,3] induced by stitching may outweigh the cost saving and the possible improvement of out-of-plane mechanical properties [4,5]. To obtain superior overall mechanical performance, this study intends to adopt innovative thermoplastic stitching yarns to carbon fibre-reinforced epoxy composites. These low melting yarns have the potential to minimize the maximum fibre undulation, toughen the polymer matrix locally and to pre-stabilize dry preforms by thermobonding. Particularly in this study, a non-crimped fabric was stitched using a modified lock-stitch with three types of yarns, i.e., a standard polyester yarn, low melting polyamide yarns and low melting and matrix soluble "phenoxy" yarns. Taking the polyester yarn stitched laminates as a reference, both polyamide and "phenoxy" yarns reveal significant improvement in mechanical properties such as compression strength, interlaminar shear strength and fatigue life. These promising results accentuate the feasibility and benefits of adopting polyamide and "phenoxy" yarns for high performance composites. References: [1]Weimer C, Mitschang P. Aspects of stitch formation process on the quality of sewn multi-textile-preforms. *Comp Part A* 2001; 32(10): 1477-1484. [2]Beier U, Fischer F, Sandler JKW, Altstädt V, Weimer C, Buchs W. Mechanical performance of carbon fibre-reinforced composites based on stitched preforms, *Comp Part A* 2007; 38(7): 1655-1663. [3]Mouritz AP, Leong, KH, Herszberg I. A review of the effect of stitching on the in-plane mechanical properties of fibre-reinforced polymer composites. *Comp Part A* 1997; 28(12): 979-

S05-782

FORMULATION OF EPOXY-AMINE SYSTEMS FOR PREPREG PRODUCTION

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Industries producing advanced composite materials are strongly demanding in the quality their product must achieve. Composite materials used in the production of structural components must comply with requirements of good thermo-mechanical resistance, dimensional stability as well as good processability. Among the thermosetting polymers, epoxy resins play a significant role due to their excellent mechanical and chemical properties. The aim of this work has been to develop formulations of reactive epoxy systems with high performances and improved processability and durability. Epoxy precursors based on Di-Glycidyl Ether of Bisphenol A (DGEBA) have been reacted with polyfunctional aliphatic and aromatic amines. The chemical reactivity has been related to the nature of curing agent and to the thermo-mechanical properties of resulting crosslinked resin. In this paper, importance has been given to the study of the thermal properties of the final formulations with particular relevance to their glass transition temperature. Different epoxy systems were formulated and characterized by thermal and rheological analysis, and FT-IR technique.



Spontaneous Polymerization of Acrylic Acid with Aziridinyl Containing Compound

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A spontaneous polymerization of acrylic acid (AA) with aziridinyl containing compound occurred at ambient temperature without any catalyst. This polymerization process involves three subsequent reactions are proposed: 1. An exothermic acid-base neutralization reaction takes place between AA and aziridinyl containing compound; 2. That neutralization heat triggers aziridinyl ring-opening reaction and that carboxyl group (of AA) plays as a nucleophile and results in an amino-ester bond formation; 3. A final product is obtained from that amino group reacts with its acrylic double bond via the inter- or intra-molecular Michael addition reaction. A mono-aziridinyl containing compound, methyl 3-(aziridin-1-yl) propanoate (MAP) was synthesized via the Michael addition reaction of aziridine (AZ) and methyl acrylate (MA). The linear amine-ester alternative copolymer, poly(β -amino-ester), was obtained from this spontaneous polymerization while MAP reacted with AA. The aqueous phase gel permeation chromatography (GPC) illustrated the average molecular weight (M_n) and polydispersities (PDI) of the resulting polymer, in this report. To prove this spontaneous polymerization mechanism, a model reaction of trimethylacetic acid (TMAA), MAP and ethyl acrylate (EA) had been designed and each step was identified by NMR and IR.

S05-1094

Characterization of Nanocomposites produced with Thermosetting Resins and Silica Nanoparticles

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In this study we analyze the effects of the addition of silica nanoparticles (14 nm) with and without surface modification on the properties of vinyl ester and ethylene propylene diene monomer elastomer (EPDM). We found that the presence of silica nanoparticles increase the mechanical strength and shows a maximum at a critical concentration for both resins. On the other hand, the surface modification using a coupling agent affected the mechanical properties of the nanocomposites. The mechanical properties are compared with those composite composed of silica particle at macroscopic scale and commercial dielectric material. The different between micron and nanoscale fillers is the biggest increases in interfacial area in nanocomposite. In addition, analyses of the dielectrical and structural properties are presented.



2D Simulation of epoxy resin flow during Reactive Rotational Modling (RRM) by finite element and meshless (SPH) methods

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Reactive rotational moulding (RRM) [1] of epoxy/amine thermoset is controlled by the increase of the viscosity due to the crosslinking phenomenon. The RRM process involves three coupled phenomena: chemical crosslinking, thermal transfert and free surface flow. To be able to predict correctly the reactive flow behavior during the process, we need to take into account the simultaneous resolution of these three problems. At first, a chemical and kinetic characterization of the reactive system is achieved. Then a thermal and rheological analysis is carried out and the Time-Temperature-transformation (TTT) [2] diagram is built up. Auto catalytic and non catalytic mechanisms were considered to determine the conversion ratio during the process. We looked for kinetics parameters and their dependence on temperature using an inverse method to get the optimal set of parameters. In order to simulate the RRM, the flow of an epoxy/amine liquid resin inside a horizontal rotating cylinder was considered. We have used the two following numeric methods: 1. The first approach is a finite element method. The volume of fluid (VOF) method was used to track the free surface. The behavior of the fluid was considered as newtonian before gelation and a gel model [3] was used to predict the gel point. The effect of strain on viscosity was neglected. 2. The second approach is the meshless Smoothed Particle Hydrodynamics (SPH) [4] method. It is a pure lagrangien way to simulate the flow and it seems to be more suitable when we have free surface flow in a complex geometry. References 1.Crawford, R. J.; Throne, J. L., Rotational Molding Technology; Plastics Design Library, 2002. 2.Enns, J. B.; Gillham, J. K., Journal of Applied Polymer Science 28, 2567 1983. 3.Castro, J. M.; Macosko, C. W., SPE Technical Papers 26, 434 1980. 4.Monaghan, J. J., Reports on Progress in Physics 68, 1703 2005.

S05-1273

Electron beam induced modification of Polypropylene in the presence of TMPTMA

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Polypropylene and its copolymer with 8% of ethylene were modified by free radical promoted grafting of trimethylolpropane trimethacrylate (TMPTMA) at different electron beam irradiation doses. The effect of irradiation dose and monomer concentration on the extent of modification in terms of grafting efficiency and polymer chains structure variations were investigated. The modified samples were characterized respectively by FTIR to determine the structure of grafted groups and the degree of functionalization, by MFI to evaluate changes of molecular structure and by DSC and TGA to measure the final thermal properties. In addition solvent extraction with xylene was performed to highlight the presence of gel and extending of crosslinking reaction. The degree of functionalization increased with increasing the TMPTMA concentration and irradiation doses. MFI and thermal analysis results confirmed the presence of branched structure in modified polymers



The Study and Characterization of Curing Kinetics of the Polysulfide Resin by Using DSC

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One important aspect of a resin is the curing kinetics associated with the materials. Kinetics refers to the modeling the effects of temperature and time on the degree of curing. In this study mechanism and kinetics of the cure reaction of a synthetic polysulfide resin were characterized by dynamic and isothermal DSC analysis. Physical and mechanical properties of dry Film were also measured glass temperature, hardness, impact resistance and tensile of cured polysulfide resin were compared.