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Rubber-Clay Nanocomposites. The control of nanostructures to steer material properties

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Layered clays are attracting increasing interest in the rubber field, as they can improve the functional properties of an elastomeric compound at a concentration of only 3-5wt %, while being based on inexpensive natural mineral fillers. It is generally believed that, to have a high reinforcing effect, the polymer should intercalate among the layers. Fully exfoliated polymer-clay nanocomposites, notoriously difficult to attain, lead to even superior physical properties, thanks to the nanoscale polymer-clay interactions. We prepared rubber/clay nanocomposites based on diene rubbers, by compounding either isoprene or styrene-butadiene rubbers with organo-modified and pristine montmorillonite (MMT), and also by mixing the rubber with pristine MMT and the organic modifier (OM), an ammonium salt bearing organic radicals. In particular, pristine MMT was delaminated and was re-aggregated in the presence of the organic-modifier, leading to a MMT/OM intercalate structure, what we call an "OM-Intercalate". The basal spacing of the OM-Intercalate was found to depend on the nature of the ammonium salt and also on the rubber: in Natural Rubber the basal spacing was found to be nearly double with respect to the usual MMT/OM intercalate, obtained treating MMT with OM in a polar solvent or in the synthetic rubbers. These nanostructures were characterized through X-ray diffraction measurements, Differential Scanning Calorimetry and by Transmission Electron Microscopy. Their effect on physical mechanical properties of the composites was examined, analyzing in particular static and dynamic reinforcement. The effect of nanostructures on rheological shear and elongational behaviour, and on time-dependant thixotropic characteristics were also evaluated. A correlation between nanostructures and material properties is here presented and discussed.

S12-1167

A new method for characterization of the distribution of nanofiller in rubber blends

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Nanofillers in rubber compounds like carbon black (CB), silica, layered silicates, and carbon nanotubes are of interest regarding the possibility to influence their application properties in an effective manner. Basically, the degree of filler dispersion is one of the main factors influencing the final compound properties, that requires the availability of suitable methods for the qualitative characterization of the dispersion and distribution mechanisms as well as the quantitative determination of the filler dispersion degree and especially the phase specific distribution of the filler into the different phases of rubber blends. The online during the mixing process measured electrical conductance was used successfully for the investigation and time dependent description of the dispersion and distribution of CB in rubber compounds and rubber blends, respectively. Beside this, a thermo-gravimetric supported method was developed for the quantitative analysis of the CB dispersion and the evaluation of CB phase specific distribution in the phases of binary rubber blends. It was shown that the wetting behavior of the rubber components and the rubber-filler interaction are the main influencing factors concerning the distribution kinetics. The influence of the matrix properties like viscosity as well as polarity and the effect of the mixing regime on the phase specific CB allocation were systematically investigated. The methods were proved to be applicable for other fillers like silica and carbon nanotubes.



Physical and tribological properties of the modified PTFE nanopowder filled EPDM

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Polytetrafluoroethylene (PTFE), a highly crystalline polymer with melting temperature around 330°C, possesses unique properties. Chemically inert, it has high chemical and heat resistance with upper service temperature around 260°C. Since its invention it has found limited applications especially as an additive because of its high molecular weight and inert surface. However, by mid 1950's Crandell used PTFE as a reinforcing additive to improve the tear strength of silicone rubbers while by late 60's it was further used in fluoroelastomers. For tribological purposes, PTFE and its fluoropolymers have found a wide use as a solid lubricant in applications such as bushings. Although, it has unique low friction characteristics, it suffers from high wear rate because of its smooth molecular structure. For this reason, it is commonly used in conjunction with various kinds of fillers, thermoplastics and resins in order to exploit its inherent low friction characteristics and at the same time reduce its high wear rate behaviour. Recently the development of chemically coupled PTFE compounds has opened a new route in producing enhanced wear resistant materials for high performance tribological applications. In order to expand its utility in technical elastomers, a new class of modified PTFE filled SBS, NBR and EPDM compounds were produced. Modified PTFE micropowder were also incorporated in a carbon black filled NBR composition for sealing applications. However, a comprehensive investigation based solely on the friction and wear mechanism of PTFE coupled elastomers along with their physical properties in the mentioned studies has not been reported so far. Our preliminary investigations conclude that electron beam irradiated PTFE nanopowder in EPDM enhances the physical properties. However, the factors influencing the physical properties of the PTFE based EPDM might not hold true for their tribological properties.

S12-375

Microstructure Controlling Parameters in Interfacially Compatibilized EPDM rubber/Montmorillonite Nanocomposite: Rheology/Permeability Correlation

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Nanocomposites vulcanizate based on Ethylene Propylene diene monomer rubber (EPDM) / Montmorillonite, and sulfur curing system have been fabricated via melt mixing process in the presence of EPDM-g-MAH as interfacial compatibilizer. The influence of the EPDM matrix and EPDM-g-MAH mooney viscosity as well as their structural parameters upon the extent of the exfoliation and flocculation of the clay nanolayers have been evaluated by the calculation of the nanolayers aspect ratio using modified halpin-Tsai model. Computed aspect ratios exhibited more exfoliation and flocculation of the silicate nanolayers for the NC samples based on highly branched, but low molecular weight EPDM as matrix. This was consistent with the XRD and TEM micrographs. This has been also verified by dynamic melt rheological measurements within the low frequency region. Maleated EPDM has been shown to be effective in the prevention of flocculation of the nanolayers and increasing their disperse state. When unvulcanized composites with highly exfoliated microstructure were annealed at 90°C for 48 hrs, exfoliation to flocculation transition was observed, indicating that flocculated structure is more thermodynamically preferred. This was confirmed by the increase in permeability with increasing the in annealing time. The degree of tendency for the nanosilicates to flocculate in the matrix of EPDM was found to be dictated by the maleation degree and mooney viscosity of the EPDM-g-MAH.



Curing cycle optimization of a thick section rubber part

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The curing cycle optimization is a first order concern for rubber industry both to control the part quality and to reduce curing times. Thick parts curing control is very delicate due to low thermal diffusivity of these polymers. In this paper, we present a numerical method for the optimization of boundary curing temperatures that monitor a mould. The model is two-dimension axisymmetric under transient conditions. The heat and the vulcanization kinetic equations are solved on the domain. On this direct problem we build an inverse problem (conjugate gradient method and adjoint equations), which is used to estimate the optimum temperatures applied as boundary conditions in order to obtain a desired state of cure which is stabilized across the part thickness. As a first step, we describe the thermally controlled mould. We detail its thermal regulation in heating and cooling. We also describe the thermal instrumentation including an original measuring device recording temperatures directly within the moulded part while minimizing thermal disturbances during measurement. Then, an example of model validation is presented by comparing the results of a numerical simulation (Comsol software) with those obtained experimentally under the same conditions. Finally, we describe the curing optimization model and we present an example of moulding cycle optimization. We also describe the ways to overcome difficulties like sensitivity problems during the induction phase.

S12-868

Shape Memory phenomena and effect of Nanosilver on anti bacterial properties in Polyurethanes

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Nanosilver particles have antibacterial properties and by using them in other materials we can produce an antibacterial material for biological applications. Shape memory polymers (SMP) such as linear polyurethanes can return from its temporary shape to the original (permanent) shape upon heating. In this work elastomeric polyurethanes based on TDI and 1,4-butanediol (BD) were synthesized. Ether type polyols as soft segment were used to synthesize of polyurethanes in a two step process. The effect of nano silver on anti bacterial properties and mechanical properties of SMPs has been investigated. Differential scanning calorimetry (DSC), dynamic mechanical analysis (DMA), stress-strain relaxation and Fourier transform infrared spectroscopy (FTIR) have been used. Importing the nano silver particles into SMPs results in changes some properties of polyurethanes.



An Application of Non-linear Viscoelastic Model to Capillary Extrusion of Rubber Compounds

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Rubber compounds have high viscoelastic property. One of the viscoelastic behaviors during profile extrusion is the swelling of extrudate. In this study, die swells of rubber compounds at the capillary die have been investigated through experiment and computer simulation. Experiments and simulations have been performed using fluidity tester and commercial CFD code, Polyflow respectively. Die swells of rubber compounds in a capillary die were predicted using non-linear differential viscoelastic model, Phan-Thien-Tanner(PTT) model for various relaxation times and relaxation modes. The results of simulation were compared with the experiments. Pressure and velocity distribution, and circulation flows at the corner of capillary die have been investigated through computer simulation. It is concluded that the PTT model successfully represented the amount of the die swell of rubber compounds for various relaxation times at different modes.

S12-1143

Effect of recycled rubber and its concentration on the processing, properties and rheology of injection molded elastomers

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Recycling of thermoset elastomers is more challenging than recycling of thermoplastics. One potential route for recycling of thermosets is the preparation of crumb rubber by grinding. The resulting rubber powder can be used in asphalt, compounded with thermoplastics, or incorporated into recycled rubber/virgin rubber compounds. These rubber compounds offer environmental benefits, as well as reduced costs of the compound. For certain applications, the recycled rubber/virgin rubber compounds may be processed by injection molding. This work investigates the effect of recycled rubber content and particle size on the processing, rheology, and mechanical properties (tensile and dynamic mechanical) of injection molded elastomers. The effect of recycled rubber content and particle size on the injection process parameters, such as injection speed, injection pressure, and cure time is discussed.



Modification of thermoplastic polyurethane by melt mixing with carbon nanotubes

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Carbon nanotubes (CNT) were shown in the last years as attractive nanofillers for polymers in order to reach conductivity at low loadings, enhance mechanical strength and to influence the thermal conductivity, thermal expansion, wear and friction behaviour favourably. Most investigations were done on thermoplastic polymers and epoxy compositions. However, also for thermoplastic elastomers, like thermoplastic polyurethane (TPU), the addition of CNT may be a way to replace carbon black and to achieve, at the same time, a better property balance of the nanocomposites. In this study, an industrially available thermoplastic polyurethane (TPU) was melt mixed with different MWNT, supplied from Nanocyl S.A., Belgium. The MWNT were incorporated either as crude material or as purified material. For comparison, two carbon black types, namely Vulcan XC72 and Printex XE2, were tested. Melt mixing was performed using a DACA-Micro Compounders (volume 4,5 cm³) and for testing mechanical properties using a Brabender single screw extruder PL-19. Direct MWNT incorporation was compared with the premanufacturing of a masterbatch having 15 wt% MWNT. The electrical percolation as studied using resistivity measurements and dielectrical spectroscopy found between 2 and 3 wt% of purified MWNT, whereas the corresponding crude material shows percolation above 5 wt%. The masterbatch technique lead to lower resistivity values which can be related to a more homogeneous MWNT dispersion. The use of the now available industrial MWNT material Nanocyl®7000 showed the best results in resistivity; percolation occurred between 1 and 2 wt% by using masterbatch dilution. DSC and DMA investigation indicated that the MWNT act as nucleating agents but do not significantly influence the glass transition temperature of the soft segments. The excellent mechanical properties of TPU, especially the high deformability, can be preserved in the nanocomposite. Modulus and stress at a given strain are enhanced.

S12-1320

Extensional Flow Behavior of PP/EPDM Thermoplastic Vulcanizates

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Semi-hyperboloidal dies providing a Hencky strain of 2 have been used to obtain strain averaged extensional viscosity estimates of several PP-EPDM vulcanizates containing a high-temperature paraffinic oil. Such measurements are usually more reliable with a core-skin flow where the outer layer is a low viscosity melt that serves as a lubricant, because shear near the walls contributes greatly to the measured pressure drop. The core-skin arrangement was found to be unworkable with the TPVs however; this is consistent with the results of Kamerkar and Edwards (2007) Hence, a new procedure was developed in this work for analyzing flow curves obtained without external lubrication from semi-hyperboloidal dies of several different lengths with the same area ratio from inlet to outlet. The accuracy of this procedure depends critically on the accuracy of shear viscosity data in the relevant range of shear rates; hence slip flow of TPVs in shear must be accounted for.



Mechanism of Fiber Formation in Melt Spinning of Polyether ester Elastomer

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Thermoplastic polyether ester elastomers (PEET) consisting of crystalline polyester as the hard segment and amorphous polyether as the soft segment are known to exhibit high thermal resistance and mechanical durability in comparison with the conventional polyurethane elastomers. In the high-speed melt spinning of PEET, stress-induced crystallization of the hard segment occurred in the spinning process. Accordingly mechanical properties of the as-spun fibers varied significantly depending on the spinning conditions. In this research, mechanism of fiber structure development in the melt spinning process of PEET was investigated through the on-line measurement of the spinning process, and the structure and property analyses of the as-spun fibers. Numerical simulation of the spinning process was also performed to predict the elastic deformation of the spinline. With an increase in the take-up velocity, elastic recovery of the fiber after cut-off from the bobbin increased continuously and reached a value of about 45% at 5 km/min, while birefringence showed a tendency of saturation above 2 km/min. WAXD and SAXS patterns of the as-spun fibers were obtained. At 0.27 km/min, WAXD pattern showed no indication of crystalline orientation. Birefringence of the fiber was also significantly low. On the other hand, SAXS pattern showed a typical two-spot pattern with the indication of the effect of elongational flow in the spinning process. At 1 km/min, WAXD pattern showed highly oriented crystalline diffraction pattern of polytetramethylene terephthalate and SAXS pattern showed a distinct two-spot pattern. When the take-up velocity was increased to 5 km/min, WAXD pattern still showed highly oriented crystalline diffraction spots irrespective of the significant contraction after spinning, while SAXS pattern showed the distinct widening of the two-spot pattern along the azimuthal angle indicating the effect of orientation reduction after contraction.

S12-1374

Reactive Processing in Elastomers

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The term reactive processing means processes used in the elastomer technology (e.g.: mixing, compounding, extrusion, injection moulding) accompanied by the chemical reaction occurring between the components of rubber compounds, including reactions on the and in the elastomer macromolecules. The well known examples of such reactive processing are cold and hot mastication of natural and synthetic rubbers, used to tailored modification of rubber molecular weight and rubber viscosity, to the synthesis of graft-copolymers and in the manufacturing of thermoplastic vulcanisates (TPE-V). In our studies it has been found that reactive mixing of saturated and/or unsaturated ethylene-propylene elastomers (EPM, EPDM) at elevated temperature with the unsaturated monomers containing carboxyl groups (unsaturated mono- and dicarboxylic acids, alkylmonomaleamides R-NH-CO-CH=CH-CO-OH) in the presence of radical initiators leads to functionalisation of elastomer macromolecules with moieties containing carboxyl groups, e.g. to new carboxylated ethylene-propylene (diene) rubbers (XEPM, XEPDM). The extent of such functionalisation and the properties of carboxylated elastomers obtained depend on the conditions of reactive, the concentration and kind of modifying monomer incorporated and kind and amount of peroxide used as radical initiator. The new carboxylated elastomers can be cured both with the peroxide and metal oxide (MeO), or sulphur (XEPDM) or using hybrid crosslinking agents (peroxide + metal oxide) or even with sulphur + metal oxide in the case of XEDM). In that case the network contains both organic sulphide (C-Sx-C) and inorganic, ionic (R-CO-O(-)(+)Me(+)(-))O-OC-R') crosslinks. The XEPM and XEPDM and their cured products obtained are characterised by enhanced stress-strain properties and higher adhesion to chemical fibres (PA, PET) comparing to EPM and EPDM.



Molecular Weight Reduction of Natural Rubber by Using Supercritical Carbon dioxide

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In the view point of natural resource with aspects related to sustainable hydrocarbon feedstock, Natural Rubber (NR) is important elastomeric material. However, NR always contains ultra high molecular weight up to 106 which causes some difficulty and energy consuming in the processing line. Therefore, a developing of molecular weight reduction process for NR allows us to utilize its as an alternative hydrocarbon feedstock for bio-elastomeric materials. To breakdown the molecular structure of NR is typically carried out both from mechanical shear force and from chemical peptization. After breakdown process, much attention has been paid to effective controlling of its molecular weight. Thus, this present utilizes the advantage of supercritical carbon dioxide (sc-CO₂) as a plasticizer for reducing of NR molecular weight. By taking the advantage of its gas-like diffusivity and liquid-like density in the supercritical stage while sc-CO₂ dissolving into NR solution revealed the minimization of chemical peptizing agent (used Pentrachlorothiophenol as low as 0.5 phr) with a considerable molecular weight controlling. The NR molecular weight measurement was performed by using a Gel Permeation Chromatography (GPC) and viscosity measurement with Mark-Houwink-Sakurada equation. Experimental result showed that molecular weight of NR is reduced about 63.4% compared with the ordinary NR. Moreover, the visual swelling behavior of NR solution at temperature ranging from 303 to 333 K and pressure ranging from 0.1 to 15 MPa were investigated by using a high-pressure view cell. Its swelling can be predicted theoretically on the basis of the Sanchez-Lacombe equation of state. The solubility, diffusivity of CO₂ into NR solution and degree of swelling were used to describe the effective molecular weight controlling.

S12-1387

CARBON NANOTUBE NETWORK IN ELASTOMERS

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The high and reversible deformability of elastomers is an important factor in industrial use. In the last years filler with nanoscale dimensions, especially carbon nanotubes, become the subject of extensive research. Especially the high aspect ratio of this nanotube expects high tech materials. High entanglement nature of carbon nano tubes limits its proper dispersion in rubber matrix. In this work we investigate a novel approach for achieving a proper dispersion of carbon nanotubes through predispersion technique and followed by shear mixing. Different amount of CDV-grown multi-walled carbon nanotube (MWCNT) and -OH modified MWCNT have been employed in this study. As matrix material a 50:50 blend of solution styrene butadiene rubber (SSBR) and butadiene rubber (BR) was used. The highly-dispersed carbon nanotube network was established by different studies like dynamic mechanical thermal analysis, tensile testing, TEM studies and electrical percolation behaviour by conductivity measurements. Finally the good degree of filler networking was revealed by PAYNE - effect measurements at very low loading of MWCNT content.



synergistic effect of carbon black and nanoclay on mechanical properties of NR

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We use carbon black in rubber industries as filler. Fillers increase mechanical properties of rubber such as modulus and tensile strength. We can use some filler such as clays and so on. Mechanical properties of rubbers depend on rigidity, aspect ratio of fillers and interaction of filler and rubbers. Increasing aspect ratio and rigidity of fillers lead to increase mechanical properties of rubber composites. Aspect ratio of nanofillers is high that in small amount of nanofillers interesting results could be obtained. In this paper we study on synergistic effect of carbon black and nanoclay on mechanical properties of natural rubber. Used rubber is NR, N550 carbon black, maleic EPDM as compatiblzer and octadecyl amine modified montmorillonite . Our tests were done at loading of 5,10,15,25 Phr carbon black with fixed amount of 7 Phr nanoclay satisfactory result at synergistic effect was found 20Phr carbon black.

S12-539

SYNTHESIS AND CHARACTERISTIC NEW ETHER-ESTERS BLOCK-RANDOM COPOLYMERS

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The investigations of the possibility obtaining new block-random copolymers (terpolymers) in a two-step melt polycondensation method. The block-random copolyetheresters with rigid segments of poly(ethylene 2,6-naphthalenedicarboxylate) (PEN), poly(ethylene terephthalate)(PET) and flexible segments of poly(tetramethylene oxide) were prepared by melt polycondensation of dimethyl 2,6- naphthalenedicarboxylate, dimethyl terephthalate, ethylene glycol, and poly(tetramethylene ether)glycol (PTMEG) with molecular weight of 1000 g/mol. Thermal and mechanical properties of novel random copolymers (terpolymers) were examined by differential scanning calorimetry (DSC), dynamic mechanical thermal analysis (DMTA), thermogravimetric analysis (TGA), X-ray diffraction and other standard physical methods. DSC disclosed that this systems have a crystallization and melting behaviour typical of random copolymers (two Tg temperatures- one in the low and the other in the high temperature range). DMTA confirmed the hetero-phase structure of block-random copolymers with associated elastoplastic properties. The extensive relative elongation at break, the high elasticity, and the low hardness of the block-random copolymers containing 50-60 wt.% of flexible segments are characteristic for elastomers. In synthesised polymers the structure and morphology of phase separations is responsible for specific barrier properties. The description of occurred structure allowed to classify these materials to the group of functional materials. It is revealed that the most of synthesised materials are polyester thermoplastic elastomers.



Electron Beam Vulcanisation of Rubber (NBR, HNBR, HXNBR) at Elevated Irradiation Temperatures

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Electron beam (EB) curing of rubber is an emerging technology, which has the potential to provide significant advantages for rapid manufacturing of a variety of components for aerospace, automotive and consumer applications. Traditional thermal curing methods like sulphur or peroxid crosslinking state in long cure times, involve high energy consumption, volatile toxic by-products and create residual stresses in the materials, whereas EB curing is a fast non-thermal process which utilizes highly energetic electrons at controlled doses to crosslink polymeric materials. EB modification results in a formation of a three-dimensional network structure by recombination of macro radicals generated. Currently EB modification mostly will be done at special external radiation service providers. Because of economic aspects there are interests to save the time-consuming transport and the temporary storage. Our basic idea is a direct coupling between profile extrusion and EB crosslinking for an integration to one processing line. In this case advantages can be expected because of high temperatures of the rubber mixtures at leaving the profile extruder which results in better mobility of rubber molecules, increased diffusion rate of radiolysis products, production of a homogeneous network etc. At least it would give higher crosslinking density and improvements in mechanical properties. In this paper the influence of different rubber sample temperatures during electron irradiation on crosslinking density and selected material properties of NBR, HNBR and HXNBR with and without polyfunctional monomers and carbon black will be presented.

S12-580

Structure and viscoelasticity of plasticized EPDM networks

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The aim of these researches was to study the structure and relaxation of crosslinked and plasticized EPDM samples. Thus, the insoluble fraction, the swelling ratio as well as the elastic and viscous moduli were initially determined. The modelling of these networks has first been realised by coupling several rheological and molecular models in order to exhaustively determine the inner structure of such swollen networks. Furthermore, by adjusting the quantity of curing agent within the formulation, we managed to highlight the fact that the density of chemical crosslinks, as well as the molar mass of the elastically active polymer chains, were directly proportional to the quantity of curing agent. Its reactivity was also proven to stay constant even in presence of a large quantity of plasticizer. These calculations also led to the precise determination of the density of physically trapped entanglements between two chemical bridges. Additionally, these networks sustained compression set experiments and showed very interesting relaxation and strain recovery profiles. The evolution of the relaxation modulus allowed us to correlate the length of the dangling chain ends to the relaxation behaviour of such networks. Finally, by adjusting the experimental relaxation curves, we were able to determine the intrinsic structural parameters and to accurately predict the strain recovery profiles of such networks.



SBR Nanocomposites based on a Synergized Hybrid of Nanoclay and Carbon Black: Microstructure/Properties Relationship

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SBR nanocomposites based on nanoclay and a hybrid of nanoclay and carbon black and maleic anhydride grafted EPDM (EPDM-g-MAH) has been fabricated via melt mixing process. Effect of the carbon black on the degree of the clay nanolayers dispersion state as well as the final composite microstructure has been studied. Results have revealed that the carbon black particles can stabilize the SBR/Clay microstructure as the aggregation and flocculation of the silicate layers are prevented by the black particles. This has been shown to be the main mechanism for the synergistic characteristic of the clay/black hybrid in reinforcing the vulcanized SBR network. This has also been verified by less hysteresis under dynamic stress fields exhibited by the clay/black reinforced SBR vulcanizates, indicating less viscous motion by the SBR segments in their interface with both nano-platelets and black particles. The microstructure has been examined by XRD, SEM and melt linear viscoelastic measurements. The samples composed of 5 wt% of nanoclay and 15 wt% of black showed tensile reinforcement equivalent to the sample reinforced only by 45 wt% of black.

S12-670

STUDY OF POLYMERIC BLENDS WITH STRUCTURED ELASTOMER

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Nowadays, polymeric blends is one of the major subjects in polymer industry. The purpose of alloying or blending one polymer or more with another is to gain synergistic improvement in properties at both the micro and macro levels. The polymeric materials that contain structured elastomer and plastic materials are an important class of materials extensively studied in recent years. Mixing of two or more different polymers together makes it possible to achieve various property combinations of the final material – usually in a more cost-effective way than in the case of synthesis of new polymers. Most polymer pairs are immiscible. As a consequence, polymer blends are not formed spontaneously. At service temperatures, immiscible polymer blends have frozen non-equilibrium phase structure which depends on the process of their preparation. Melt mixing is the most wide spread method of polymer blend preparation in practice. Products from blends of plastics and plastics with crosslinked elastomers are prepared by the blends processing in molten state with the methods typical of thermoplastics. The phase structure formed in flowing molten polymer blends depends on their composition, viscosity and elastic properties of the components, interfacial tension and thermomechanical history. Because the phase structure is a function of as many factors which effects frequently cannot be separated, formulation of general rules for prediction of the phase structure is very difficult. The purpose of this paper is to present an experimental investigation of the morphology of several polymeric blends, with content of structured elastomer and plastic materials employing techniques with nanometric – level resolution – such as Scanning Electron Microscopy (SEM) and Differential Scanning Calorimeter analysis (DSC) FINANCIAL SUPPORT TO THIS WORK FROM ROMANIAN MINISTRY OF RESEARCH AND EDUCATION, NATIONAL AUTHORITY MATNANTECH WITHIN PROGRAM CEEX 88/2006, IS GRATEFULLY ACKNOWLEDGET.



Starch as a Renewable Filler for Rubber Compounds

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Starch is a reasonably cheap, renewable and environmentally friendly resource. With a view to developing a new type of rubber composite based on starch, the objective of the study was to assess the factors affecting the reinforcing effect of starch and determine how reinforcement could be maximised. In general, the study shows relatively poor reinforcement of natural rubber by starch, resulting in compounds of low stiffness and strength compared to compounds filled to a similar volume fraction with carbon black. The poor reinforcement is due to a weak interaction between polar starch and non-polar rubber and due to the large particle size of starch. However, the addition of polybutadiene maleic anhydride (PBMAH) and resorcinol formaldehyde (RF) coupling agents significantly improved the rubber to filler adhesion. If coupling agents were not used, improved reinforcement could also be obtained by using a polar matrix rubber, such as NBR and ENR, which interact strongly with the starch via hydrogen bonding. As the major drawback of using starch as filler was due to its large particle size, experiments were carried out to reduce the particle size. Water was used as a plasticiser to depress the melting temperature of starch and enable to be broken down to smaller particles during mixing of an ENR compound in a conventional rubber mixer. After removal of the water, increased stiffness properties were observed. Further improvements in the compound properties were observed by incorporating pregeletanised starch with a small amount of silica. The enhancement in the stiffness and the abrasion properties of the compound were believed to be due to an increase in the rubber filler interfacial area and a more homogenous starch dispersion in the rubber matrix.

S12-871

Microstructure –adhesion properties correlation in thermoplastic polyurethane elastomers based on blends of two type polyols

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



Nanocomposites based on functionalized single-wall carbon nanotubes and multiblock polyester elastomers

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The unique structures of the carbon nanotubes (CNTs) are responsible for extraordinary, mechanical, thermal and electrical properties. The nanotube as a whole is very flexible because of the great length. These properties, coupled with the lightness of CNTs, make them potentially attractive reinforcing material for polymers. Specific influence of CNTs on the mechanical properties can be expected if the nanoheterophase structured polyester block copolymers are used as matrix. Polymer nanocomposites based on poly(trimethylene terephthalate)-block-poly(tetramethylene oxide) (PTT-b-PTMO) copolymer and COOH- functionalized single well carbon nanotubes (SWNT) have been prepared and investigated. The nanocomposites were prepared "in situ" by introducing the fillers into the reaction mixture and the synthesis of copolymer by polycondensation in the molten state. Before introducing to reaction mixture the CNTs were dispersed in solution by ultrasonication. The thermal and mechanical properties of the composite were characterized by differential scanning calorimetry, dynamic mechanical thermal analysis, thermogravimetric analysis and tensile testing. The microstructure of the composite was examined by scanning electron microscopy and atomic force microscopy.

S12-934

Peculiarity of electric properties of epoxy/silicone rubber composites filled with carbon black

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Conducting polymer composites (CPC) still represent an ongoing topic of scientific and commercial interest. Since the utility of CPCs is well established, a new generation of efficient CPCs, possessing a low percolation threshold concentration and high conductivity, continues to be sought. More lately, the two main strategies of improving the conductivity at given filler concentrations have been followed: the double percolated networks induced by immiscible blends, and multi-filler in a single polymer matrix. The novelty of this study consists in use of thermosetting interpenetrating network with a purpose to improve electrical and mechanical properties of CPC. Three types of epoxy/silicone rubber composites filled with carbon black differing in the content of silicone rubber were prepared. Electric properties of such multi-component composites were compared with electrical properties of single polymer composites filled with carbon black. The conductivity enhancement about 2 – 3 orders of magnitude was found in composites containing only 25 % of silicone rubber in the filler concentration range from 15 – 25 wt.% of carbon black comparing to single epoxy with the same amount of filler. Electron microscopy showed a matrix structure of such CPCs in which the continuous phase is formed by epoxy resin filled with carbon black and silicone phase is arranged as separate inclusions. The presence of silicone "drops" in a composite reduces free volume space and increases volume fraction of conducting component in the epoxy matrix, thus reduces the percolation threshold for dc conductivity. Since the addition of silicon rubber is commonly used to improve mechanical properties of brittle epoxy resin, the physical and mechanical properties of composites are measured as well, to validate the influence of silicone rubber and carbon black addition on epoxy resin mechanical properties.



Chloroprene rubber devulcanization by using microwave physical process

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The chloroprene rubber is used to make several artefacts, such as diving and gymnastics outfits, cables coating, special pneumatic automobile tires, and in the shoe industry, among others. In spite of its benefits, a great problem nowadays is to recycle these used or with their lifetime expired galvanized articles, aiming to preserve the environment. The devulcanization of these products may be carried out by biological, chemical and physical processes. The main target of this work was to study the chloroprene recycling/re-use (DuPont - Neoprene®), by the physical microwave process. For this purpose, a basic formulation was done with this kind of rubber, to be used in the automobile industry. The samples irradiations were performed in microwave generator equipment, developed at IPEN, which operates with a frequency of 2,450MHz and power of 1,000W to 3,000W. The analyses of the samples irradiated with microwave and with those not irradiated were done by means of hardness, density, permanent deformation and compression (DPC), traction, stretching and reometry assays. The results showed that the chloroprene rubber irradiated with microwave presented a trend to vulcanize again and may substitute some unused rubber parts in formulations, without causing considerable losses in the physical and chemical properties.