P-01 STRUCTURAL CHARACTERISTICS OF RUBBER AND ADHESION PROPERTIES OF TEXTILE CORDS TO RUBBER

IHSSAN AMIR, IVAN HUDEC, and JÁN ŠIROKÝ

Slovak Technical University in Bratislava, Faculty of Chemical and Food Technology, Department of Polymer Materials, Radlinského 9, 812 37 Bratislava, Slovakia ihssan.amir@stuba.sk

Polyester cord play an important role in the modern tyre industry as a reinforcing materials because of their extraordinary mechanical and physical properties. Many problems concerning to the adhesion between polyester cords an tyre rubber come from the relatively low surface energy of polyethyleneterephtalate (PET) and also its chemical inertness. The standard method for improvement of adhesion between the reinforcing polyester cords and rubber matrix is established on surface modification of cords with solution or emulsion consisting of resorcinol-formaldehyde resin and vinyl pyridine latex^{1,2}.

The aim of this work is to present some results obtained by the studying of the influence of temperature and time of vulcanization on adhesion of polyester high modulus low shrinkage cord yarn (HMLS – Slovkord 1440 Dtex 1x2, twists 380/380 produced by SH Senica, Slovakia) to rubber. The rubber compounds contained natural rubber, SBR and polybutadiene rubber was used for fabric coating. The static adhesion strength to rubber and adhesion strength after dynamic stress (the sample was exposed to a cyclic flexural stress with frequency = 7.5 Hz for 12 h in a chamber at 80 ± 1.5 °C) to rubber was studied by means of Henley test method according to STN 6201464. The crosslink density of rubber matrix was determined from the results of their swelling in xylene at laboratory temperature according by ASTM D6814-02.

The study was based on two-factor five-levels experiment. The first factor was temperature of vulcanization (x_1) and the second factor was time vulcanization (x_2) . The experimental results were treated by the complete regression analyses, using the general regression equation in the form:

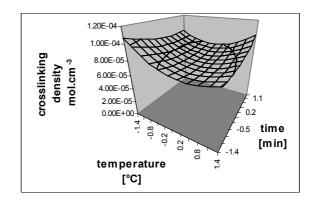
 $Y = b_0 + b_1x_1 + b_2x_2 + b_{12}x_1x_2 + b_{11}x_1^2 + b_{22}x_2^2$ where Y – evaluated parameter, b_0 , b_1 , b_2 , b_{11} , b_{12} , b_{22} – regression coefficients, x_1 , x_2 – independent variables on the coded levels.

The variability of the individual dependent parameters due to the experimental error of their estimation as well as their variation due to the inaccuracy of the used regression model was specified by means of a variance analysis. The adequacy of the regression equations was evaluated by applying F-test, on the significance level α =0.05.

Table I
The influence of time and temperature of vulcanization on
the adhesion properties of polyester cord to rubber and
crosslinking density

| Temperature | Time of | Static | Dynamic |
|---------------|---------------|----------|----------|
| of | vulcanization | adhesion | adhesion |
| vulcanization | | strength | strength |
| 157,0 | 14,1 | 170,8 | 177,5 |
| 192,0 | 14,0 | 139,8 | 132,3 |
| 157,0 | 33,9 | 172,8 | 161,5 |
| 192,0 | 33,9 | 130,5 | 127,5 |
| 150,0 | 24,0 | 143,0 | 112,8 |
| 200,0 | 24,0 | 124,8 | 120,7 |
| 175,0 | 10,0 | 161,2 | 140,0 |
| 175,0 | 38,0 | 108,8 | 104,3 |
| 175,0 | 24,0 | 101,0 | 80,8 |
| 175,0 | 24,0 | 112,5 | 101,5 |
| 175,0 | 24,0 | 128,5 | 126,3 |
| 175,0 | 24,0 | 125,5 | 111,3 |
| 175,0 | 24,0 | 137,3 | 131,5 |

The results of the influence of time and temperature of vulcanization on the adhesion properties of polyester cord to rubber are summarized in table I and for crosslinking density of rubber matrix is illustrated in Fig. 1.



From comparison of regression coefficients of adhesion properties with its critical values is evident, that temperature and time of vulcanization statistically not influenced on adhesion properties of polyester cord to rubber.

From results of crosslinking density is evident, that both mentioned factors influence the crosslinked density, what is able to be connected with changing of the number and character of cross bond.

Following receives results we can state, that temperature and time vulcanization statistically meaningly exclude on statically a dynamic adhesion toward cord with RFL modification. Though on crosslinked density was he determined statistically prominent influence.

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P-02 CONTINUOUS SILANIZATION REACTION IN CO-ROTATING TWIN SCREW EXTRUDER

YASEMIN ATSIZ^{a,b}*, J. W. G. MANI^b, and R. H. SCHUSTER^b

^a University of Hannover, ^b Deutsches Institut für Kautschuktechnologie e.V., Eupener str. 33, D-30519, Hanover, Germany yaseminatsiz@hotmail.com

The mixing of a silica based rubber compound with help of a conventional discontinuous mixing process is performed with several mixing stages. Especially in silica based tires, these stages are necessary to complete the silanization reaction. Inorganic silica and organic rubber are highly incompatible materials which makes the mixing difficult. The silica surface is therefore regularly modified by means of silane to achieve compatibilization of the silica to the rubber where the silane is bonded to the surface of the silica. The reactions takes place between the silyl groups of the silane and silanol groups of the silica filler. This chemical bonding process between silica and silane is called silanization reaction¹. This work focuses on experimental investigations on surface modification of silica with silane in E-SBR in a co-rotating twin screw extruder.

The temperature in the zones of the co-rotating twin screw extruder were studied for different temperatures but this work is discussed only for a constant zone temperature of 150 $^{\circ}\text{C}$.

The completion of silanization reaction is indirectly measurable by analyzing filler-filler interaction. This filler-filler interaction is estimated by G_{\min} values obtained from rubber process analyzer (RPA). The G_{\min} decreases to lower values for the experiments carried out at 150 °C. The uniformity of heating in all zones of twin screw extruder for 150 °C influences the increase of the silanization rate. High mixing temperature improves the silanization rate due to the temperature dependence of the reaction and a reduced sterical hindrance of the silyl propyl group of the silane by increased thermal mobility².

The reactive extrusion in a twin screw extruder requires additionally optimum process parameters to assure required silanization reaction. The compound characteristics show that the filler-filler interaction reaches lower values in comparison to compound which indicates optimum silanization reaction. The filler dispersion and filler-

filler interaction corresponds to the characteristics of the reference compound mixed in the internal mixer.

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P-03 ATMOSHERIC-PRESSURE PLASMA TREATMENT OF TEXTILE MATERIALS FOR INDUSTRIAL USES

<u>LUDMILA CERNAKOVA^a*</u>, MICHAL JASSO^a, RENATA SZABOVA^a, IVAN HUDEC^a, and MIRKO CERNAK^b

^aInstitute of Polymer Material, Slovak University of Technology, Radlinského 9, 812 37 Bratislava, Slovakia, ^bDepartment of Physical Electronic, Masaryk University, Kotlářska 2, Brno, Czech Republic ludmila.cernakova@stuba.sk

When looking for an application in automotive industry, plasma surface engineering technologies are in competition with a multitude of conventional processes, which have proven their performance, quality and process stability for decades. The use of plasma based surface treatment depend on the elimination of different obstacles that actually prevent the wider use, like cost reduction and the difficulty to get the necessary capacity. Even though it is supposed that in a few years plasma-based coatings will become a standard coating procedure, even for large serial productions in automotive¹. Plasma-based processes are environmentaly friendly, and can often eliminate organic-solvent based adhesives and paints and replaced them by water-based equivalents.

Since recently the plasma technology is being introduced in textile industry as well. Fields of application are functionalizing and design of surface properties of textile fibers². Principal applications of textile materials in automobile sector are interior fabrics used in kick panel, package shelf, seat fabric, truck liners, load decks, cabin air filters etc.

To meet the requirements for cost-effective in-line surface treatments of polypropylene products and other polymeric materials a novel surface discharge type the Diffuse Coplanar Surface Barrier Discharge (DCSBD) plasma source has been developed at the Institute of Physics, Comenius University³. In this plasma source a thin layer of macroscopically uniform high-density plasma is generated at atmospheric pressure without any contact with electrodes, which protects the electrodes erosion and ensure long life reliable operation. DCSBD plasma sources

have been used success-fully on PP nonwoven fabrics to enhance the reactivity of their surfaces⁴.

The aim of our work was to study the hydrohilization of polypropylene (211 g cm⁻²) and polyester textile materials (105 g cm⁻²) using DCSBD plasma source with one side or both sides electrode. Plasma treatments using one side electrode were carried out in the air or nitrogen atmosphere step by step from right side and back side of textile various times up to 10 seconds. When the both side electrode was used, the textile material was activated in one step from right side and back side of the textile.

It is widely known that the plasma treatment process results in a physical and/or chemical modification of the first few molecular layers of the surface, which can improve the wettability of the inert polymer surfaces. We used the absorptivity of water drop into textile samples to indicate the hydrophilicity of samples before and after plasma activation. Absorptivity was determined by taking a series of sessile drop images by CCD camera in order to determine not only the initial contact angle, but also the change of the drop profile in the time due to wetting of polymer surface⁵.

It was found that plasma treatment vas very effective, as only 1 second activation led to significant shortening of absorption time of water in comparison with untrated samples, for polypropylene textile from 35.8 ± 2.3 s for untreated sample, to 4.9 ± 0.6 s for polypropylene treated in air or 4.0 ± 0.6 s treated in nitrogen atmosphere. The longer time of plasma activation in air up to 10 s didn't changed the absorption time significantly, On the other hand, in nitrogen atmosphere the absorptivity was 1.5 ± 0.1 s after 5 s of activation.

The best results in studying the hydrophilization of polyester textile material were obtained in nitrogen atmosphere using the both side electrode. The absorption time changed from 6.2±0.6 s for untreated sample to 0.44±0.1 s after 3 s of activation.

The chemical changes on plasma modifier textile surfaces were verified by diffuse reflectant infrared spectroscopy.

The very short time of plasma activation using DCSBD plasma source, before subsequent operation like painting or coating of textile material, make it suitable for in-line processes.

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P-04 NEW BIOMODIFIED FLEXIBLE POLYURETHANE FOAMS: COMPARATIVE AND ECOTOXICOLOGICAL STUDY

JAN DAVID*, LUCY VOJTOVÁ, JIŘÍ KISLINGER, JIŘÍ KUČERÍK, JARMILA VRÁNOVÁ, HELENA ZLÁMALOVÁ-GARGOŠOVÁ, MILADA VÁVROVÁ, and JOSEF JANČÁŘ

Faculty of Chemistry, Brno University of Technology, Purkynova 118, 612 00 Brno, Czech Republic xcdavid@fch.vutbr.cz

Flexible polyurethane (PU) foams are expanded polymers made by addition polymerization of multi-functional alcohols (polyols) and difunctional isocyanates. Flexible PU foams play the key role in automotive industry¹.

Since the recycling of used PU foams is complicated and expensive due to their thermosetting character², both from environmental and economic reasons this work was focused on the use of cellulose and starch derivatives or wheat protein easy available in Europe for the synthesis of biodegradable flexible PU foams. The common industrial recipe for PU foam synthesis was modified by using sodium salt of carboxymethyl cellulose (CMC-Na), acetylated starch (AS), cellulose acetate (CA), 2-hydroxyethyl cellulose (2-HEC) and wheat protein-gluten (WPG) as the bio-polyols.

The substitution of bio-polyol for commercial polyether polyolPEP was successful up to 30 wt.% of CMC-Na, 20 wt.% of AS, 10 wt.% of CA, 10 wt.% of 2-HEC and 5 wt.% of WPG.

By means of Fourier Transform Infra Red Spectroscopy (FTIR) and Thermogravimetrical Analysis (TGA) the chemical incorporation of bio-polyols into the PU foam structure and the influence of bio-polyols on the thermal stability of the foam were proved.

The interest in biological testing is growing rapidly and toxicity testing is now gradually incorporated in environmental legislation in many countries. Therefore, both the alternative ecotoxicity testing, which is quick, cheap and sensitive³ via the screening toxkit Thamnotoxkit FTM (with *Thamnocephalus platyurus* freshwater fairy shrimps) and the standardized long-term test of the root growth inhibition of white mustard (*Sinapis alba*) were used for the ecotoxicity evaluation of water leaches of modified PU foams.

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P-05 NANOADDITIVES TO PREVENT UV RADIATION IN PP FIBRES

MÁRIA DULÍKOVÁ^a*, ANNA UJHELYIOVÁ^a, ONDREJ BREJKA^b, ANTON MARCINČIN^a, and JOZEF RYBA^a

^a Slovak University of Technology in Bratislava, Faculty of Chemical and Food Technology, Institute of Polymer Materials, Department of Fibres and Textile Chemistry, Radlinského 9, 812 37 Bratislava, ^b Research Institute for Man-Made Fibres, Join-Stock Company, Štúrova 2, 059 21 Svit, Slovakia maria.dulikova@stuba.sk

Ultraviolet radiation (with wavelength between 200 and 400 nm) in sunlight is responsible for accelerated aging of different materials and also causes health problems like sunburn, skin-aging or cancer. Skin can be protected from UV radiation by proper clothing. Because fabric is composed of fibres that can absorb, reflect or scatter radiant energy, it has the ability to absorb or block most of the incident radiant energy and prevent it from reaching the skin. However, barrier properties of textile material depend on several parameters: chemical structure of the fibre, fabric construction, particularly porosity, thickness and weight, contents of UV-absorbers, fluorescent whitening agents and other finishing chemicals that can be added to the textile materials¹. One of the effective nanoadditive is TiO₂ which acts as UV absorber. Nanoadditive is incorporated into the fibres during the process of their preparation, the effect to UV-protection is permanent. It is the main advantage using such nanoadditive that cannot be removed by washing and can present better coloration.

A suitable quantitative method for evaluating the protection ability of modified fibres is spectrophotometry where UPF factor is determined. Transmittance of polypropylene fibres modified by nanoTiO₂ was measured by spectrophotometer Libra S12, thereafter UPF, UVA and UVB factor were calculated². The method for the measurement of textile materials has been modified on fibres because only UPF of textile materials and clothes is reported in references.

In this paper there were used the different types of nanoTiO₂ and different dispersants on the modification of PP fibres and UPF of the PP fibres was evaluated. An increase of UPF of modified PP fibres in comparison with unmodified PP fibres has been observed as well as with

increase of nanoTiO2 concentration.

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P-06 APPLICATION OF LIGNIN IN RUBBER BLENDS

JOZEF FERANC^a*, ZUZANA KRAMÁROVÁ^a, PAVOL ALEXY^a, MIROSLAV ĎURAČKA^b, IVAN HUDEC^a, PETR ŠURI^c, ANTON KARVAŠ^c, and MARTINA HAJŠOVÁ^a

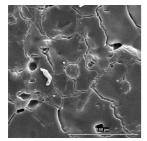
^a Department of Plastics and Rubber, Institute of Polymer Materials, Faculty of Chemical and Food Technology, Slovak University of Technology, Radlinského 9, 812 37 Bratislava, ^b VUCHT a.s., Nobelova 34, 836 03 Bratislava, ^c Matador a.s., Rubber Research Institute, T. Vansovej 1054, 020 01 Puchov, Slovakia jozef.feranc@stuba.sk

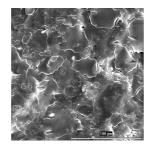
Lignin is a natural amorphous polymer, which, together with cellulose and hemicellulose, is one of the main components of wood. Cellulose fibers mainly consist of cellulose microfibrils bounded together by amorphous lignin matrix. The make-up of the wood reveals the potential of lignin to act as a compatilizer between hydrophilic natural fiber reinforcement and a hydrophobic matrix polymer¹. The biosphere contains 3·10¹¹ tons of lignin with an annual increase of about 2·10¹⁰ tons². The polymer structure of lignin is considered to be a three-dimensional network composed of phenylpropane units³. Lignin structure is dependent on wood species and processing conditions⁴.

Papers concerning the use of lignin as a stabilizer for plastics and rubbers acting as an antioxidant or modifier of the mechanical properties have been published^{5,6}. Autors⁷ observed stabilization effect of lignin in natural rubber. The obtained results show that tested lignin acts as an antioxidant for natural rubber filled with carbon black during thermal aging. The optimum concentration was found to be about 2–5 wt.% (4–8 phr) similarly as was observed in composites.

In this work influence of three types of industrial lignin was tested in model rubber blends based on natural rubber. The tested lignins contained from 5 to 10 % of natrium, calcium or magnesium. Processability of lignins, their compatibility with rubber matrix as well as influence of lignins on mechanical and dynamic-mechanical properties of vulcanisates was tested.

a





b

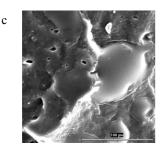


Fig. 1. SEM of natural rubber vulcanisates filled with 30 phr of lignin containing Ca (a), Mg (b) and Na (c)

Dosage of lignins varied from 0 to 40 phr in natural rubber blends. Decreasing of scorch time as well as optimum of vulcanisation was observed with increasing of lignin concentration. Addition of lignin causes decreasing of network density in model vulcanisates. Chemical reaction between lignin and vulcanisation system can be assumed based on various chemical structure of it. Also reaction of lignin with rubber chain or catalytic action of lignin can be possible.

Addition of lignin containing magnesium or calcium causes improvement of mechanical properties of NR vulcanisates. Significant increasing of tensile strength as well as elongation at break was observed above the 20 phr concentration of lignins in the blend. The good compatibility of these two types of lignins with rubber matrix was confirmed based on SEM measurements. Lignin polymer was very good dispersed in rubber matrix into small domains with very good compatibility on interphase. In case on lignin containing Na, the compatibility was not such good and also large domains with low cohesion was identified (Fig. 1). This can be responsible for lower values of mechanical properties of prepared Na-lignin/NR vulcanisates.

Changes of dynamical – mechanical properties were also observed by Ca and Mg lignin addition. Increasing of lignin content causes decreasing of maximum value of tg δ simultaneously with increasing of tg δ at 0 °C. Lignins are potentially utilizable as component for rubber blends. They are able to modify mechanical, dynamical-mechanical properties and cure characteristics as well.

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P-07 INFLUENCE OF FILLER-STABILIZER INTERACTION ON PHOTO-OXIDATION AND STABILIZATION OF iPP AND sPP/BOEHMITE NANOCOMPOSITES

AGNESA FIEDLEROVÁ^a, ŠTEFAN CHMELA^{a*}, and EBERHARD BORSIG^{a,b}

^a Polymer Institute, Slovak Academy of Sciences, Dúbravská cesta 9, 842 36 Bratislava, ^b Department of Fibre and Textile Chemistry, Faculty of Chemical and Food Technology, Slovak University of Technology, Radlinského 9, 812 37 Bratislava, Slovakia upolfied@savba.sk; upolchme@savba.sk; upolebor@savba.sk

In the past decade polymer nanocomposites have received attention in fundamental research as well as in industry exploitation. One reason is that individual polymers, their mixtures or classical composites can not fulfill demands made upon modern engineering materials. Engineering plastics are often used in outdoor applications. Performance during application is a key feature of any such type of plastics. PP is quite sensitive to deteriorate under the action of light and heat. For the most application especially at outdoor it is necessary to use stabilizing system. PP nanocomposites were found to be more degradable than pure PP under UV irradiation^{1–4}.

Following the new trend in preparation of polypropylene nanocomposites with enhanced properties for industrial utilization iPP and sPP nanocomposites containing Disperal OS2 (Boehmite) nanofiller were prepared. The amount of nanofiller in samples was 1, 5 and 10 wt.%. The photo-oxidation of pure iPP, sPP and their nanocomposites in the absence and in the presence of light stabilizers of HAS type (Hindered Amine Stabilizer) – Chimasorb 944 as well as in our laboratory synthesized combined HAS/phenol – TMP was tested.

The course of photo-degradation was followed by FTIR spectroscopy. During the photo-oxidation of polypropylene different carbonyl products (ketones, acids,

Chimasorb 944

TMP

esters, etc.) absorbing in the region of 1600–1850 cm⁻¹ and different compounds containing hydroxyl group (hydroperoxides, alcohols) absorbing in the region of 3200-3600 cm⁻¹ were formed. The course of photodegradation was represented as an influence of carbonyl absorption against the irradiation time. The shape of carbonyl envelope of pure iPP and sPP was similar as in the case of iPP and sPP nanocomposites. It evidenced the formation of the same products of photo-oxidation in the case of pure iPP and sPP as well as in their nanocomposites. Differences were found in induction periods of photooxidation: these were much shorter in all nanocomposites in comparison with the induction period of pure iPP and sPP. There is a clear prodegradation effect of filler for both types of polypropylene used. The extent of this effect depends on the amount of filler and on the type of polypropylene used. In the case of sPP samples, the prodegradation effect is proportional to the amount of filler in the whole concentration range of filler content used. In the case of iPP, there is a pro-degradation plateau at 5 wt.% content of filler and higher concentration of filler (10 wt.%) does not increase the rate and the course of photo-oxidation. Two long term stabilizers of HAS family were tested - commercial oligomeric stabilizer Chimasorb 944 (CHIM) and synthesized combined HAS/phenol (TMP). Stabilizing efficiency depends on the filler content. CHIM is able to stabilize just the nanocomposites with the lowest content (1 wt%) of filler. There is no stabilizing effect of this HAS in the case of higher amount of nanofiller (5 and 10 wt%) in both types of polypropylene. By contrast, the combined HAS/phenol - TMP revealed some stabilizing efficiency over the whole range of filler content. The possible reasons for this difference are discussed. Interaction of filler with some HAS stabilizers were studied in cyclohexane as a model liquid for polypropylene by

UV-spectroscopy. Interaction resulted in fixing of additive on filler. Much stronger interaction has been obtained for oligomeric CHIM in comparison with low molecular HAS.

Acknowledgement. This work was supported by the Project VEGA 2/5108/25, Slovakia.

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P-08 INFLUENCE OF PRODUCTION PROCESS TO MECHANICAL PROPERTIES OF TYRE TEXTILE REINFORCEMENT MATERIALS

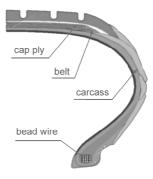
PETER GAŽO* and VIERA ŠURIOVA

Rubber Research Institute, Matador a.s., T. Vansovej 1054, 020 01 Púchov, Slovakia peter.gazo@matador.sk

Reinforcing materials used in the tyre construction play an important role especially in the form of composites in combination with rubber compounds. Various construction requirements are imposed on reinforcing materials depending on their use:

Bead wire – is a lengthened steel wire with several high strength threadings. It makes it possible to mount and demount the tyre to/from the rim and the carcass plies are wrapped around the bead wires.

Carcass – is the most important structural element of the tyre. According to the construction requirements for



Scheme 1. Distribution of reinforcement materials in a passenger car radial tyre

a given tyre, one, two or more overlapping plies are used.

Belt – usually constructed from overlapping steel cords. As far as passenger car radial tyres are concerned (high-speed categories) a textile cord ply, laid in the direction of the tyre axis, is used in addition to the steel breakers. This ply is known as a cap ply.

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P-09 CHARACTERIZATION OF THE FATIGUE BEHAVIOR OF SHORT GLASS FIBER REINFORCED POLYMERS

<u>CHRISTOPH GUSTER^{a,b}*</u>, GERALD PINTER^c, ZOLTAN MAJOR^c, WILFRIED EICHLSEDER^b, and REINHOLD W. LANG^{a,c}

^a Polymer Competence Center Leoben GmbH, Parkstrasse 11, 8700 Leoben, ^b Chair of Mechanical Engineering, University of Leoben, Franz-Josef-Straβe 18, 8700 Leoben, ^c Institute of Material Science and Testing of Plastics, University of Leoben, Franz-Josef-Straβe 18, 8700 Leoben, Austria

Christoph.Guster@mu-leoben.at

The increasing interest in engineering plastics for cyclically loaded structural components in automobiles necessitates proper fatigue design methods for these materials. One possibility which is already used for components made of metals is the fatigue life calculation with local stresses and local S/N-curves. One aim of a big research project in our group is the generation of a comprehensive database which is necessary for the applicability of fatigue life calculation with local S/N curves for fiber reinforced composites. First of all the effect of fiber orientation and concentration as well as stress ratio on the fatigue behavior of two materials was investigated.

Because of the importance of lightweight constructions and the reduction of production time and costs, nowadays other materials more and more substitute components, which are made so far of metals. The usage of short-fiber-reinforced plastics instead of metals seems self-evident in many cases because of their high specific strength and the favorable manufacturing processes.

The available mechanical properties of this material group from datasheets are mostly measured under monotonic loads like tensile strength, yield strength and fracture elongation. But these material data are not sufficient for the dimensioning of parts having regard to geometry, loading conditions and material behavior. One method which is already used for dimensioning dynamically loaded components made of metals, is the fatigue life calculation with local S/N-curves. These local S/N-curves, determined by the material, are essentially influenced by component specific effects, such as fiber orientation, type of loading, size, stress temperature, production process and many more.

The first step to determine dynamical material data is taken by un-notched specimens. Every real component has notches and these notches cause stress peaks in the component. But not only notches influence the fatigue strength of component structures. Hence other effects such as different cyclic loading (tension, compression, bending, etc.), fiber orientation, stress ratio temperature and frequency have to be analysed. Furthermore the fatigue strength of a component could differ from the fatigue strength of the test-specimens. Therefore one of the main problems in this regard is to transfer the material parameters determined on test specimens correctly to complex component structures.

For the finite element analyses of components made of fiber reinforced polymers, the knowledge of fiber orientation and distribution is an essential part, because the local material behavior depends on these parameters. Information about the fiber orientation in a simple testing specimen can be gathered by checking the morphology. Therefore it is necessary to take out samples at different specimen positions for analyzing with microscopic methods^{1,2}. For complex components and during product development, the orientation of the reinforcing fibers should be characterized by molding simulation. By knowledge of the local fiber orientation it should be possible to calculate the resulting local material behavior which is also an input parameter for the finite element analyses.

For tests documented in this poster two different short-fiber-reinforced and mineral-reinforced polymers were selected. Types of matrix as well as percentage of fibers and mineral fillers of both materials were different. One material has a thermoplastic partial aromatic polyamide matrix with 40 % glass-fibers and 25 % mineral fillers (PA 6T/6I-GF40+MX25) and was obtained from EMS-Grivory. The other material has a thermosetting matrix based on phenol-formaldehyde plastic with 30 % glass-fibers and also 30 % mineral fillers (PF-GF30+MX30) and was obtained from Vyncolit. The glass fibers of both materials have a nearly cylindrical cross section with a diameter of 10 to 15 μ m and a length of 100 to 150 μ m.

For characterizing the material behavior, the flat specimens as shown in figure 1 were used. The test specimens were fabricated different for each material. Depending on fabrication type they had different morphology, which was also analyzed. Therefore molding simulations as well as microscopic methods were used. The so called standardized specimens of both materials were made by injection molding. The short-specimens were milled out of injection molded thermoplastic plates and compression

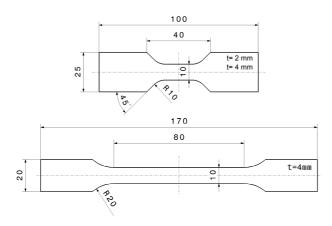


Fig. 1. Top: short specimen, Bottom: standardized specimen

molded thermosetting plates. The reinforced thermoplastic plates had a dimension of $100 \times 100 \text{ mm}^2$ and two different thicknesses of 2 and 4 mm. To estimate the influence of fiber orientation on the fatigue behavior, the PA 6T/6I-GF40+MX25 specimens were milled out in flowing direction (longitudinal) and also transversal.

Experimental procedure

Constant amplitude fatigue tests were made for generation the S/N-curves or Wöhler-diagrams. These tests are used for analyzing fatigue strength of a material under sinusoidal loading with constant stress amplitudes. To avoid hysteretical heating, resulting of too large testing frequency, tests at different frequencies (5, 10 and 30 Hz) were made, where the heating in middle position of the specimens was detected during the whole cyclic test. Due to these tests, the testing frequency for all other tests was fixed by 10 Hz.

All tests documented in this article were made with the standardized and short specimens shown in figure 1. They were performed stress controlled with a servohydraulic test rig (MTS, USA) at room temperature and standard conditions.

To generate S/N-curves the nominal stress amplitudes S_a and the number of cycles N have to be plotted in double logarithmic way. At each stress level there were tested at least 3 specimens, so the slope k could calculated by using the principle of the Gaussian distribution^{3,4}.

Since project start there were generated a lot of S/N-curves for characterizing different influences on fatigue behavior. Within this paper only some representative Wöhler-diagrams for the influence of fiber orientation are shown

Figure 2 shows the influence of fiber orientation on fatigue behavior of the PA 6T/6I-GF40+MX25 material. All specimens were tested under tension/tension (R=0,1). The standardized specimens reach the highest nominal

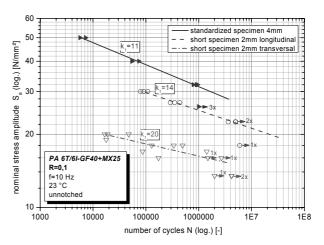


Fig. 2. Influence of fiber orientation on fatigue behavior of PA 6T/6I-GF40+MX25

stress amplitudes with very small statistical scatter of measuring points followed by short specimens with thickness 2 mm. The slopes k of the 4 mm standardized specimen and the 2 mm longitudinal short specimen are nearly the same. The S/N curve of the 2 mm transversal short specimen runs more flat. These effects result out of the different fiber orientations influenced by different manufacturing processes. As described above, the standardized specimen is injection molded without any cutting machining like milling. On the other hand, the short specimens are milled out of plates. The arrangement of fibers in the two geometries is quite different because of very complex flowing conditions^{5,6} and other parameters which are summarized in⁷. The average fiber orientation of the whole specimen cross section was determined by molding simulation. The calculated middle fiber orientation for the standardized specimen was about 94 %. This means that 94 % of the reinforcing fibers are oriented in longitudinal specimen direction. But in the 2 mm short specimen only 75 % of fibers are oriented longitudinal. So the difference of reachable nominal stress amplitudes in S/N-curves can be explained.

Acknowledgement. The research work of this paper was performed at the Polymer Competence Center Leoben GmbH (PCCL, Austria) within the framework of the Kplus-program of the Austrian Ministry of Traffic, Innovation and Technology with contributions by Institute of Material Science and Testing of Plastics (IWPK) and Department Product Engineering, Chair of Mechanical Engineering (AMB) both University of Leoben and BMW-Group, Engineering Center Steyr (MAGNA Powertrain ECS) and EMS-Grivory. The PCCL is funded by the Austrian Government and the State of Styria and Upper Austria.

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P-10 SOME ASPECTS OF TYRE ADHESION EVALUATION

JOZEF HAVAJÍK*, MIROSLAV ONDÁŠ, and MARTIN RYPÁK

Rubber Research Institute, Matador, a.s., T. Vansovej 1054, 020 01 Púchov, Slovakia jozef.havajik@matador.sk

Adhesion between tyre and road is one of the most important parameters of the tyres, mainly from the safety point of view. Task of this poster is the understanding of the some conventional car tests and some sophisticated outdoor + indoor tests for tyre adhesion evaluation.

For this area of the tyre development were applied:

- car handling and braking test procedures in MATADOR, a.s.,
- customer indoor and outdoor tests performed by TNO Automotive Netherlad and by IABG mbH Germany for tyre forces and moments measurements,
- car manoeuver simulations developed by University of Žilina – Faculty of mechanical engineering.

In this poster are presented and compared basic adhesive properties of tyres on dry surfaces, mathematical methods and criterions for their evaluation, for example:

- subjective + objective test methods and their advantages and disadvantages,
- braking, circle handling tests with statistical ANOVA evaluation,
- signal filtering from force and moments measurements generated by tyre, evaluation based on the MAGIC FORMULA,
- adhesion criterions: tyre frictions, stiffness,
- handling simulation as a tool for the tyre adhesion evaluation.

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P-11 THE PHOTOLYSIS OF DYES CONTAINING BENZOTHIOXANTHENE CHROMOPHORE LINKED WITH HINDERED AMINE IN POLYMER MATRICES

MARTIN DANKO*, <u>PAVOL HRDLOVIČ</u>, and ŠTEFAN CHMELA

Polymer Institute, Slovak Academy of Sciences, Dúbravská cesta 9, 842 36 Bratislava, Slovakia upoldan@savba.sk

A novel dyes based on benzothioxantheneimide chromophore covalently linked with sterically hindered amine (HAS) were prepared and their light stability was tested in polymer matrices. The following dyes namely: 2-(2,2,6,6--tetramethyl-4-piperidyl)-thioxantheno[2,1,9-dej]isoquinoline-1,3-dione (BTXINH) and N-alkoxy derivative 2-(1-(1'--phenylethoxy)-2,2,6,6-tetramethyl-4-piperidyl)-thioxantheno[2,1,9-dej]isoquinoline-1,3-dione (BTXINOR) have been prepared. For comparison the parent dye without HAS structural unit benzothioxanthene-3,4-dicarboxylic anhydride (BTXA) and the N-alkyl derivative 2-(1--dodecyl)-thioxantheno[2,1,9-dej]isoquinoline-1,3-dione (BTXID) and the stable nitroxyl radical as 2-(1-oxo--2,2,6,6-tetramethyl-4-piperidyl)-thioxantheno[2,1,9-dej] isoquinoline-1,3-dione (BTXINO) have been tested as well. The structures of imidic dyes are shown on scheme below.

Spectral properties of these dyes in solution and polymer matrices of polystyrene (PS) poly(methyl methacrylate) (PMMA) and poly(vinyl chloride) (PVC) have been measured¹. The light stability of these dyes and model compounds were examined in thin polymer films (50 µm) in a merry go round set up equipped with 250 W mercury arc with luminophore. The course of photolysis was monitored by UV absorption at the longest wavelength band around 450 nm. The zero order kinetics was applied. The rate of photolysis was determined as slope of the dependence of log I/I₀ on time. The photolysis rate was in the range 10^{-4} to 10^{-3} hr⁻¹. The rate of decomposition was the lowest for parent amine BTXINH in all polymer matrices. The photolysis rate of all other dyes under study was higher. The distinct stabilization effect of HAS structural unit on the decomposition rate was not observed. The light

stability of the dyes was more influenced by the polymer matrix. The photolysis proceeds more rapid in the PS and PVC matrices as compared with PMMA.

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P-12 DESIGN OF HYBRID SILICA MATRICES WITH CONTROLLED PORE SIZE AND LONG-TERM PORE SIZE STABILITY

TOMÁŠ NEDELČEV^a, <u>JAROSLAVA JAŇOVKOVÁ^a</u>, DUŠAN CHORVÁT J.R.^b, IGOR KRUPA^a*, and IGOR LACÍK^a

^a Polymer Institute SAV, Dúbravská cesta 9, 842 36 Bratislava, ^b International Laser Center, Ilkovičova 3, 812 19 Bratislava, Slovakia upolkrup@savba.sk

Sol-gel chemistry is based on the hydrolysis and polycondensation of molecular precursors such as metal alkoxides, consisting of silicon, titanium, zirconium or other metallic elements in their structure¹. The mild characteristics offered by the sol-gel process allow to introduce organic molecules inside an inorganic network. Inorganic and organic components can then be mixed at the nanometric scale, in virtually any ratio, leading to the so-called hybrid organic-inorganic nanocomposites. These hybrids are extremely versatile in their composition, processing, and optical and mechanical properties².

The aim of this work is focused on the preparation of hybrid silicagel monoliths and films with controlled porosity and pore stability based on the various organofunctional silanes. An influence of catalysts, silane/solvent ratio, post-processing conditions on the quality of organic/inorganic hybrid films will be investigated in the first step. Homogeneity, brittleness, transparency, porosity, diffusion properties as well as mechanical properties were tested. Organosilanes, involving aminosilane and epoxysilane, were used for a modification of hybrid films, to ensure both appropriate flexibility and strength of the films.

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P-13 INTRODUCING HERACRON® (KOLON *p*-ARAMID) TIRE CORD

OK HWA JEON, JAE WOONG LEE, IL JEONG*, and CHANG BAE LEE

KOLON Industries, Inc., Kolon Central Research Park, 212, Gongdan-Dong, Gumi-City, Gyungsangbuk-Do, Korea jeonteng@kolon.com

Automotive tires are the composite materials composed of fibers, steel and rubber. The reinforced materials for tires require unique properties including anti-fatigue, tensile strength and resilience. Therefore, the adequate materials for tire cords are selected by the application of the tires. In general, rayon, nylon, polyester, steel and aramid have employed as cord materials for tires.

Aramid is an aromatic polyamide fiber which contains amide group (-CONH-) obtained through the polymerization of terephthalic acid and *p*-phenylenediamine. Due to the outstanding features of *p*-aramid fibers such as tenacity (~26 g/d), modulus (~1000 g/d) and elongation at break (~2.5%), they are contributing to high-performance tires as cord materials. Recently, aramid tire cords are commercialized for light-truck capply which is the cover part of steel belt within tires and airplane tires. We introduce KOLON's *p*-aramid fiber, HERACRON® and its application for tire cords.

P-14 PORE STRUCTURE OF PYROLYTIC CARBON BLACK

<u>ZUZANA KOREŇOVÁ</u>, JUMA HAYDARY, JOZEF MARKOŠ, and ĽUDOVÍT JELEMENSKÝ*

Department of Chemical and Biochemical Engineering, Faculty of Chemical and Food Technology, Slovak University of Technology, Radlinského 9, 812 37 Bratislava, Slovakia ludovit.jelemensky@stuba.sk

The pyrolysis of rubber from the sidewall (sample I) and tread (sample II) of a passenger car tire was carried out in a nitrogen flow at a temperatures range from 500 °C to 800 °C. Two characteristic stages were observed in the DTG curves. The first stage corresponded to the decomposition of processing oil, plastifier, and additives, whereas the rubber polymer was decomposed in the second stage. Several properties of the carbon black formed by the pyrolysis such as ash content, specific surface area, and pore

size distribution were determined. A change of the internal structure of the rubber particle in the meso- and macroregions of the pore size was observed. Properties of the pyrolytic carbon black produced from the tire sample I were similar to those of the commercial carbon black N 330, meanwhile the carbon black obtained by pyrolysis of the rubber sample II showed the specific surface area comparable with that of the commercial carbon black N 220. Furthermore, an increase of the specific surface area of pyrolytic carbon blacks with the pyrolysis final temperature was observed.

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P-15 POSSIBILITIES OF BIS-MALEIMIDES' APPLICATION IN ADHESION SYSTEMS OF REINFORCED VULCANIZATES

K. KOSÁR*, P. LEHOCKÝ, J. BALKO, and ZS. VÉGH

VUCHT a.s., Nobelova 34, 836 03 Bratislava, Slovakia kkosar@vucht.sk, plehocky@vucht.sk, jbalko@sa.vucht.sk, zvegh@vucht.sk

The poster deals with the results of tests gained by using bis-maleimid in adhesion systems to improve adhesion of vulcanizate to reinforcing brass-plated steel cord. The components of classical adhesion system (cobalt containing substance, sources of resorcinol- formaldehyde resin, silica) are subsequently replaced by bis-maleimid in a skim rubber compound. The obtained results of adhesion measurements and the other properties of vulcanizates show the possibilities and advantages of using bismaleimid in adhesion promoting systems.

The results also demonstrate that the presence of bismaleimide in rubber compound significantly reduces the undesirable reverse reactions during over-cure. It slightly increases the network density of the vulcanizates (higher modulus and hardness – and it enables to decrease the sulphur dosage and in this way to gain vulcanizates with improved heat stability).

P-16 SYNTHESIS OF NAPHTHALENE UNIT CONTAINING POLY(2-OXAZOLINES)

JURAJ KRONEK*, JOZEF LUSTOŇ, and ANGELA KLEINOVÁ

Polymer Institute, Slovak Academy of Sciences, Dúbravská cesta 9, 842 36 Bratislava, Slovakia upolkron@savba.sk

2-Oxazolines provide thermally initiated addition reactions with a wide range of reagents, for example with carboxylic acids, phenols, thiols and amines¹⁻³. This property provides a basis for the construction of AB_x monomers containing a 2-oxazoline unit and another functional group^{4,5}. It is an ideal way for the preparation of polymers with designed properties by the incorporation of special structural unit into monomer containing more polymerizable groups.

Properties of aromatic poly(ether amide)s can be changed by the substitution of benzene ring in main chain. In our work, benzene ring was substituted by naphathalene moiety. Polymers containing naphthalene unit were prepared by two methods: by the polymerisation of bis(2-oxazolines) with dihydroxynaphthalenes or by homopolyaddition of compounds representing AB type monomer containing phenol group, oxazoline ring and naphthalene unit. (6-Hydroxy-2-naphthyl)-2-oxazoline, monomer of AB type, was prepared from 6-hydroxy-2-naphthoic acid by multi-step synthesis consisting of esterification, amidation and cyclization steps. For AA+BB polymerisations, 1,4-phenylenebis(2-oxazoline) or 1,3-phenylenebis(2-oxazoline) and various dihydroxynaphthalenes were used. Polyadditions were in both cases thermally initiated and were done in melt or in solutions of high boiling solvents. Structure of the obtained poly(ether-amides) was confirmed by NMR and FTIR spectroscopy.

The described polymer represent novel naphthalene unit containing poly(ether amide) for applications in material science. Study of their thermal and photochemical properties showed a strong influence of the structure of monomers on the properties of polymers.

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P-17 PREPARATION OF ITACONIC ANHYDRIDE GRAFTED ISOTACTIC POLYPROPYLENE VIA REACTIVE EXTRUSION

FRANTISEK KUCERA*

Faculty of Chemistry, Brno University of Technology, Purkynova 118, 612 00 Brno, Czech Republic kucera-f@fch.vutbr.cz

Chemical modifications of bulk polymers provide new polymeric materials without demand of new monomers for polymerization. Reaction of polypropylene (PP) with maleic anhydride is currently the best known modification process^{1,2}, which increases adhesion of grafted PP to metals, glass fibres and to other fillers, increases miscibility with polar polymers such as nylon, polyethyleneterephthalate etc. Modification reactions of isotactic polypropylene (PP) using itaconic anhydride leads to new coupling agents for composites preparation³ is closely linked with its better adhesion, dyeability and miscibility. Otherwise, a utilization of itaconic acid^{4,5} brings two obvious advantages. First of them is fact, that itaconic anhydride can be prepared on basis of renewable resources and second is its less toxicity compare to maleic anhydride. In this work, itaconic anhydride is monomer used for grafting onto backbone of isotactic PP. Grafting reaction by reactive extrusion were used for grafting of itaconic anhydride by the reaction in a melt state of polymer and in presence of free radical initiator.

$$R* + CH_{2} - CH_{2$$

Scheme 1. Grafting of itaconic anhydride onto PP, β -scission of PP, homopolymerization of IAH

Reactive extrusions were carried out in mixer 50 ml and in twin screw extruder type DSE 25 (both Brabender, Germany), Melt Flow Index (MFI) was measured using MFI tester CEAST6542/000 (CEAST S.p.A., Italy). FT-IR Spectra were taken on FT-IR spectrometer Nicollet Impact 400 D (Thermometric, USA). Peak of C=O groups occurred at 1771 cm⁻¹ was used to indicate amount of grafted itaconic anhydride.

The main results of this work represent experimental data of $M_{\rm w}$ (MFI) and α in dependence on both $c_{\rm L101}$ and $c_{\rm IAH}$. These data are suitable for setting conditions for production of itaconated PP.

The PP powder H4m in reaction system PP/Luperox 101/IAH as grafting agent was stabilized using K10P. Obtained yields of grafting reaction with IAH depending on peroxide concentration are presented in Fig. 1. Efficiency of grafting (α) depends on the peroxide concentration, with increasing concentration of initiator, part of IAH grafted onto PP chain increase in reason of increasing concentration of macroradicals.

Mw, observed using MFI of PP, depends strongly on

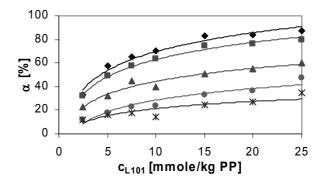


Fig. 1. Dependence of efficiency of grafting α on Luperox 101 concentration; Concentration of IAH ranging from 0,11 mole % to 0,75 mole %. $C_{\text{K10P}} = 0,42$ mmole/kg PP

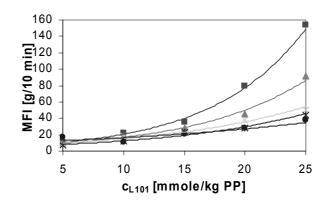


Fig. 2. Dependence of MFI on Luperox 101 concentration; C_{K10P} =0,15 mmole/kg of PP, concentration of itaconic acid, was from 0,5 mole % to 3 mole %

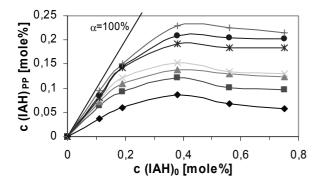


Fig. 3. Dependence of concentration of IAH grafted onto PP versus initial concentration of IAH; C_{L101} was 2,5; 5,0; 7,5; 10,0; 15,0; 20,0; 25,0 mmole/kg PP. C_{K10P} =0,42 mmole/kg of PP

concentration of added stabilizer. Three stabilization types were used for tests of their effectivity, BHT, Kingnox 10P and Kingnox 76. Kingnox 10P was found to be the most effective stabilizer and concentration 0,42 mmole/kg PP was established for grafting reactions with IAH. It was ascertained that commercial PP granules GB003 are unsuitable for grafting reactions for reason of their high stabilization. Initiator of grafting reactions, Luperox 101, influenced the $M_{\rm w}$, observed by MFI, the most of all used additives. By increasing concentration of peroxide, βscission occurs and causes decrease of $M_{\rm w}$ of modified PP. Efficiency of grafting reactions increases correspondingly with increasing concentration of peroxide. High yields of grafting are connected with great decrease of $M_{\rm w}$. MFI reaches in samples of high yields up to 100 times higher values than raw PP and $M_{\rm w}$ decrease form initial value 346 kg/mole to $M_{\rm w}$ of modified PP about 100 kg/mole. Also last variable, concentration of grafting agent, affects $M_{\rm w}$ of grafted PP. With addition of even small amount of itaconic anhydride (0,11 mole%), the MFI shows substantially lower values than PP samples extruded without grafting agent.

Results of grafting reactions with IAH were summarized as dependence of $c(IAH)_{PP}$ on $c(IAH)_0$ in Fig. 3. Concentration of grafted IAH increases with increasing initial concentration of IAH. Highest efficiency of IAH grafting is around $c(IAH)_0$ =0,4 mole %. And afterwards concentration of grafted agent decreases or stays the same. Adding higher amount of IAH than 0,4 mole % seems to be inefficient, because majority of this amount won't be possible to graft onto PP chain. Lower amount of IAH grafted on PP above initial concentrations higher than $c(IAH)_0$ =0,4 mole %, are probably caused by the chemical structure of IAH radical.

In conclusion, stabilizer Kingnox 10P was selected as the most effective stabilization for grafting reactions on PP chain. Luperox 101 was chosen for initiation of the free radical grafting reaction on PP chain. Relationship between initial concentration of Luperox 101 and starting concentration of itaconic anhydride to yield of grafting

reaction and molar mass were elucidated.

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P-18 POLYMERIC COMPOSITES BASED ON FILLERS FROM RENEWABLE RESOURCES

FRANTISEK KUCERA^{a*}, JAN VANEREK^b, and JAROMIR SVOBODA^b

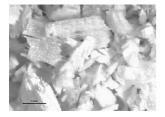
^a Faculty of Chemistry, Brno University of Technology, Purkynova 118, 612 00 Brno, ^b Faculty of Civil Engineering, Brno University of Technology, Veveri 95, 602 00 Brno, Czech Republic

kucera-f@fch.vutbr.cz, vanerek.j@fce.vutbr.cz

Nowadays according to the requirements of the environmental policy the production trends to using the waste or renewable materials. Such an aim was the reason why the new composites materials (such as wood-plastic composite) have been developed. The new strategy of the authors was focused for using the renewable native materials as fillers to the polymeric matrix.

The polypropylene and polyethylene were chosen as a polymeric matrix; both were obtained from the Chemopetrol Litvínov. The wooden spruce and oak strands, technical hemp and jute fibers were chosen as fillers for the experimental tests. All these fillers were sorted to the lengths of 0,5 till 2,0 mm. Additional the jute fiber were sorted for the lengths of 20 mm for other experimental testing. All these raw materials consist of cellulose, hemicelluloses, lignin and other accessory materials, whose content depends on each specimen. Content of cellulose is significant aspect for the sorption characteristic of these materials, because the water is bounded to the OH– groups of cellulose. The exact chemical contents of all these materials are made by chemical analyses ways.

The coupling-agents as the adhesion promoter in wood fiber-filled composites were purposely added for improving the adhesion between the polar wooden particles and non-polar polymeric matrix. These additives MA PP (Licomont AR 504) and MA PE (Licocene 4351) were obtained from the Clariant Company.



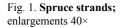




Fig. 2. **Oak strands**; enlargements $40 \times$

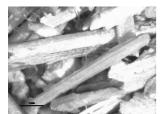


Fig. 3. **Hemp strands**; enlargements $40 \times$



Fig. 4. **Jute fibers**; enlargements 40×

The compounding of the components proceeded in the Brabender mixer at temperature corresponding the melting temperature of matrix. Each mixture was premixed before putting them into the mixing zone. Minimum of the filling was determined at 20 % volumetric (corresponds c. 30 % weight ratio), maximum was determined at 60 % volumetric (corresponds c. 70 % weight ratio). The moisture of incoming fillers achieved approximately the value MC 2 %. After melting and compounding the mixtures was the final composite pressed into the open form with the thickness 2 mm.

The main purpose was to achieve the maximum of filling the polymeric matrix; on the other side taking into the account the thickness of the fillers. We tested also the influence of fillers to reinforcement of the matrix. An important characteristic, which is crucial for using them as reinforcement, is the aspect ratio. We expect the best results from the mixture with jute fibers, which fulfill the aspect ratio value above 50 till 100.

The main properties, which are going to be tested, are

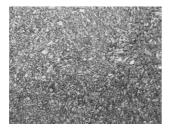


Fig. 5. **Hemp-polyethylene composite**; weight ratio: 70 % Hemp, 28,8 % PE, 1,2 % PP MA)

the mechanical behavior of all the samples, before all the tensile strengths and impact resistance. Very important point of view is the microscopic determination of the volumetric contents of fillers in the composites, its geometric shape and fillers orientation including the possibility of existed pores and the fillers' dispersity.

As a suitable method appears the double screw extrusion process extruding the composites profile.

The significant role of the final composites is based on the additives, which improved before all the fire resistance, biological resistance and UV stability. After optimalization of the mixture in the laboratory condition authors will check up the suitable processing method.

After all the parameters evaluation is the main aim to find an acceptable utilization e.g. in building industry, where the achieved characteristics of composites fulfill the required demands.

Acknowledgement. This experiment arises from the financial support of VVZ MSM 0021630511,, Progressive Building Materials with Utilization of Secondary Raw Materials and their Impact on Structures Durability" and GA ČR 103/05/P270 ,, Proposal of New Fiber Composite Material with Utilization of Wood fiber and Polymer matrix".

P-19 STUDY OF ADHESIVE PROPERTIES OF SELECT POLYMERS MODIFIED BY PLASMA

<u>ŠTEFAN KURUC*,</u> IGOR NOVÁK, MARIAN ŠTEVIAR, and IVAN CHODÁK

Polymer Institute, Slovak Academy of Sciences, Dúbravská cesta 9, 842 36 Bratislava, Slovakia upolkurs@savba.sk

The polyamide 6 (PA 6) foils were modified by dielectric surface barrier discharge (DSBD) plasma $^{1-6}$. A process of plasma modification was done due to improving adhesion between PA 6 and more polar polymers. The plasma treatment was made in oxygen, or nitrogen atmosphere. All experiments were performed by atmospheric pressure (P=1 bar). Increasing of adhesion was confirmed with two physical methods, i.e. peel testing, and measurement of the surface free energy by Surface Energy Evaluation (SEE) system.

The chemical modification of surface properties was indicated by FTIR spectroscopy. ATR-FTIR spectroscopy was helpful to show us creating of new source hydrophilicity on surface containing polar functional groups like NH₂-and –CO-NH₂.

This contribution shows the time behaviour of surface energy of polymer during ageing, average peel strengths dependencies on the time of modification with cold plasma in both atmospheres (N₂ and/or O₂). As a result is significant increase of the surface energy and its polar component of PA 6 modified by DSBD plasma in oxygen or ni-

trogen plasma at atmospheric pressure were confirmed. This increase significant even of for short times of modification of polymer by plasma, and was further increased for longer times of modification. The peel force of adhesive joints polyacrylate – PA 6 modified by DSBD plasma depends on the type of the plasma used.

Acknowledgement. Projects APVV 99-035004 and VEGA 2/7103/2.

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P-20

IMIDIZED METHACRYLIC RESINS AS POLYMER ADDITIVES WITH IMPROVED HEAT RESISTANCE

<u>DIETER LATH^{a*}</u>, LUCIANO CANOVA^b, ELENA LATHOVÁ^a, IVICA JANIGOVÁ^a, RODERICK FERGUSON^c, and JOHN M. G. COWIE^c

^a Polymer Institute, Slovak Academy of Sciences, 84246 Bratislava, Slovakia, ^b Polimeri Europa, Istituto G. Donegani, 28100 Novara, Italy, ^c Heriot-Watt University, School of Engineering and Physical Sciences, Chemistry, Edinburgh EH14 4AS, Scotland upollath@savba.sk

Imidized methacrylic resins were prepared by modifying the methacrylic units of the polymer by reaction with different amines 1,2 and glutarimidic cycles along the polymer chains were formed. These cycles in imidized polymers allow achiewing of $T_{\rm g}$ values up to 215 °C and the materials can be used for improving other polymers that may form miscible blends with them.

In our contribution we examine the phase behaviour of two imidized poly (methyl methacrylate)s differing in substituent volume (*N*-methyl and *N*-phenyl derivatives) with statistical styrene/acrylonitrile copolymers and poly (vinyl chloride). By computer curve-fitting segmental interaction parameters were evaluated as a function of temperature and they provide an useful quantitative guide for the description of the interactions in these blends and for the prediction of the miscibility with other polymers.

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P-2

POLYMER MISCIBILIZERS – FORGOTTEN COMPATIBILIZERS OF IMMISCIBLE POLYMER BLENDS

<u>DIETER LATH^{a*}</u>, RODERICK FERGUSON^b, JOHN M. G. COWIE^b, and VALERIA ARRIGHI^b

^a Polymer Institute, Slovak Academy of Sciences, 842 36 Bratislava, Slovakia, ^b Heriot-Watt University, School of Engineering and Physical Sciences, Chemistry, Edinburgh EH14 4AS, Scotland upollath@savba.sk

Polymer miscibilizer is a polymer additive that can promote miscibility between two other polymers that are otherwise immiscible. The simple Flory-Huggins model is used to calculate the miscible regions based on the criterion of negative curvature of the Gibbs free energy surface (the spinodal condition).

Binary statistical acrylonitrile copolymers (with styrene and methyl methacrylate) and statistical styrene/methyl methacrylate copolymers were used to test this concept of a polymer miscibilizer. The results obtained illustrate the fact that a significant miscibility enhancement occurs when the compositions of the miscible pair are inside their miscibility windows and there is practically no miscibility enhancement when these compositions are outside their miscibility windows. In ternary blends with the appropriate copolymer compositions the miscibility in the system can be easily changed by altering the component ratios.

P-22

CHARACTERIZATION OF THE DEFORMATION AND FAILURE BEHAVIOR OF SILICONE ELASTOMERS FOR AIRBAG APPLICATIONS

A. SCHWARZ^a, <u>Z. MAJOR*^b</u>, E. CANIBANO^c, M. GONZALES^c, and R. W. LANGA^{a,b}

^a Institute of Materials Science and Testing of Plastics, University of Leoben, Leoben, ^b Polymer Competence Center Leoben GmbH, Leoben, Austria, ^c CIDAUT Valladolid, Parque Techologico de Boecillo, Spain major@unileoben.ac.at

Novel high performance silicone elastomers are frequently used in safety relevant applications in the automotive industry, in which they are exposed to high rate me-

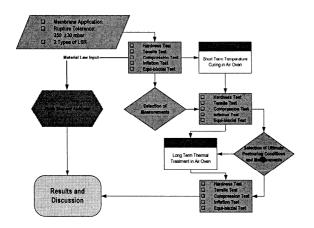


Fig. 1. Project flow chart for the characterization and comparison of the suitability of two LSR types for the usage as a membrane application in automotive

chanical loading. For airbag applications these materials must reveal both high degree of elasticity and high rupture strain under biaxial loading conditions.

The overall objectives of this paper are:

- to develop and implement a proper test methodology to characterize the deformation and failure behavior of silicone elastomers.
- to characterize the mechanical behaviour of two silicon elastomer types selected both in unaged (uncured and cured) and in aged (post-cured) conditions,
- to derive material laws for further finite element simulations.

Part of the vast range of silicone elastomers is formed by the class of liquid silicone rubbers (LSR) which stand out due to their stable main chain bonds (*i*) an inherent high heat and oxygen resistance and (*ii*) high application temperature range from -50 °C to 300 °C. In the experimental part of the paper, two different apparently similar filled liquid silicon elastomers grades for membrane applications were investigated. While the first grade, Elastosil LR 3004/50, is currently in the production for many airbags and provided by Wacker Chemie GmbH (Münich, D), the second type, Silbione LSR 4350 was supplied by Rhodia SA (Boulogne-Billancourt, F) for the investigations.

The basic material characterization test series using uncured materials included the determination of the Shore A hardness values, the characterization of the uniaxial tensile, compression and the biaxial deformation and rupture behaviour¹. Using an adapted set-up, a friction-free stress-strain diagram was evaluated for the compression behaviour². A one-camera experimental set-up in combination with bubble inflation tests was used to analyse equibiaxial deformation data. Furthermore, based on the mechanical tests parameters for hyperelastic material laws were determined using a fitting procedure in a finite ele-

ment code³.

For both materials a short-term postcuring at high temperatures was assessed with the aim of stabilizing their mechanical properties. The effects of an additional thermal curing at 90 °C over a time period of 3000 hours were also investigated. The results of the mechanical characterization both in cured and in the additional thermal post-cured state showed a significant difference between the materials selected.

The experimental works and results described in this paper are a part of a larger research project. The general structure of the project work is shown in Fig. 1.

Acknowledgement. The research work for this paper was performed at the Polymer Competence Center Leoben GmbH (PCCL, A) within the framework of the K_{plus}-programs of the Austrian Ministry of Traffic, Innovation and Technology with the contributions of the University of Leoben as scientific partner and the CIDAUT as company partner. The PCCL is founded be the Austrian Government and the State Governments of Styria and Upper Austria.

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P-23 PROPERTIES OF MELT-MIXED COMPOSITES CONTAINING CARBON NANOTUBES AND VARIOUS TYPES OF POLYPROPYLENE MATRICES

MATEJ MIČUŠÍK^a*, MÁRIA OMASTOVÁ^a, IGOR KRUPA^a, EMMANUEL LOGAKIS^b, CHRISTOS PANDIS^b, POLYCARPOS PISSIS^b, PETRA PÖTSCHKE^c, and JÜRGEN PIONTECK^c

^a Polymer Institute, Slovak Academy of Sciences, Dúbravská cesta 9, 842 36 Bratislava, Slovakia, ^b Department of Physics, National Technical University, Zografou Campus, 157 80 Athens, Greece, ^c Leibniz Institute of Polymer Research Dresden, Hohe Str. 6, 01069 Dresden, Germany

upolmmic@savba.sk

The extraordinary electrical, mechanical and thermal properties make from carbon nanotubes (CNT) a very promising material in many applications. Also thermoplastic composites research is trying to exploit the exceptional

properties of CNT for preparation of new materials¹. However, when CNT are used as the nanofiller in thermoplastic matrices, problems appear with dispersion and agglomeration of CNT and compatibility with the polymeric matrix during the processing. One way to solve these problems is the surface modification of CNT with functional groups² or coating with conductive polymers³.

In this work the dilution of a commercial polypropylene masterbatch containing 20 wt.% CNT (Hyperion, USA) by various types of polypropylene (PP) matrices was used for preparation of nanocomposites. Maleinated PP (PP-MA) as well as unmodified PP matrices with different melt flow indexes (MFI = 2, 8, 12 g/10 min) were used. Since CNT act as nucleating agent, their presence influenced the crystalline morphology of the polymer and consequently the physical and mechanical properties of prepared composites. These properties are also influenced by the polymer/CNT interfaces, which render the dispersion of the filler in polymer matrix. Therefore crystallization kinetics, thermal, rheological, and mechanical properties of the composites as functions of PP-type and CNT content were studied. Phenomena of charge transport in composites below and above percolation threshold are also reported.

PP-MA matrices show enhanced interaction with CNT, what is reflected as the strongest increase of the Young's modulus with increasing CNT content. The lowest conductivity percolation threshold of around 2 wt.% CNT was found when using PP-MA with MFI=2. We observed a shift in crystallization and melting to higher temperatures by increasing the amount of CNT. The increase of crystallization rate was more pronounced by PP-MA matrix with MFI=8. The quality of crystals was the best in the nanocomposites prepared with PP-MA MFI=2. In samples with unmodified PP matrices the effect of CNT on the melting behaviour is less pronounced.

Acknowledgement. The research was supported by German-Slovak bilateral project "Electrical conductive nanocom-posites" (D/05/15215) and by project of the Scientific Grant Agency of the Ministry of Education of Slovakia and the Slovak Academy of Sciences (VEGA 2/7103/27).

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P-24 EFFECT OF PROCESSING METHOD ON THE MORPHOLOGY AND PHYSICAL PROPERTIES OF PCL NANOCOMPOSITES

<u>DANIELA MOŠKOVÁ</u>^a*, IVICA JANIGOVÁ^a, BÉLA PUKÁNSZKY^b, and IVAN CHODÁK^a

^a Polymer Institute, Slovak Academy of Sciences, Dúbravská cesta 9, 842 36 Bratislava, Slovakia, ^b Laboratory of Plastics and Rubber Technology, Budapest University of Technology and Economics, H-1521 Budapest, P.O.Box 17, Hungary daniela.moskova@savba.sk

Nanocomposites based on polycaprolactone (PCL) and native or organically modified layered silicates (Cloisite with different organophilization) were prepared by melt mixing in either mixing chamber or co-rotating twin screw extruder to compare the influence of mixing mode and rate on the structure of composites. The structure and properties of the composites were characterized by SEM, TEM, wide-angle X-ray diffraction and rheological measurements which provide additional information about structure.

The experiments revealed that various fillers differ in their effect on properties while structure is strongly affected by the homogenization method. The X-ray diffraction peak of the silicate is shifted towards smaller 20 angles indicating the intercalation of the polymer chains inside the silicate galleries. These results show that larger degree of intercalation and/or exfoliation of PCL/ organically modified Cloisite C20A is achieved by extrusion. TEM images for the PCL/C20A clearly reveal that nanoclay sheets are homogeneously dispersed in the PCL matrix. TEM images for the PCL/CNa (sodium montmorillonite without organic modification) show several large domains and clay aggregates in the micrometer range. Exfoliated nanoclay sheets for the PCL/CNa are observed only in composites prepared via extrusion. In order to estimate the differencies in composite structure in quantitative terms, SEM analysis was performed.

More detailed information on the structure and interactions of the composites was obtained by the investigation of the Payne effect, i.e. the decrease of the storage modulus G' with increasing strain amplitude¹.

Viscoelastic properties of nanocomposites appeared to be more solid-like and especially in the terminal region the data were interpreted in terms of rheological percolation threshold. Structural changes were analyzed as a function of silicate content by constructing modified Cole-Cole plots² and by the evaluation of the frequency dependence of complex modulus.

Acknowledgement. APVV, grant No. 51-050505.

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P-25 PHOTOCHEMICAL CURING OF ALIPHATIC URETHANE ACRYLATE COATINGS

VIERA JANČOVIČOVÁ* and <u>IVETA</u> <u>MRLLÁKOVÁ</u>

Faculty of Chemical and Food Technology STU Bratislava, Radlinského 9, 812 37 Bratislava, Slovakia viera.jancovicova@stuba.sk

One of the most effective methods of fast creating spatial crosslinked polymer is based on a multifunctional monomer or oligomer exposure by UV light by the presence of a photoinitiator^{1,2}. Urethane acrylate oligomers are desired ingredients in free radically cured formulations and they provide chemical, heat and water resistance and adhesion. The chemical nature and structure of these oligomers determines the physical properties obtained upon curing or polymerisation.

Photochemical curing of coatings prepared from urethane acrylate Craynor 925 (Sartomer, France) with various content of initiator 2-hydroxy-2-methyl-1-phenylpropane-1-one (Ciba Speciality Chemicals, Switzerland) was investigated by FTIR spectroscopy. The conversion degrees (X) and the reaction rates (Rp) were calculated from double bond band decrease at 810 cm⁻¹. The samples were cured at various light intensities in the range from 7 to 23 mW cm⁻². The mixture composition was optimised. The maximal values of X and Rp were reached at the initiator concentration of 3wt.%.

The influence of external conditions (irradiation intensity, layer thickness, air oxygen presence) on the curing process and the quality of the cured film was observed. The highest conversion degree and curing rate were achieved at irradiation intensity of 23 mW cm $^{-2}$, layer thickness of 10 μm in the absence of oxygen. The gloss change 3 of layers during curing and final gloss of cured layers were also influenced by curing conditions. The gloss increased with irradiation time. It was obvious that the value of final gloss was primarily increased via using layer with higher thickness (30 μm); the influence of irradiation intensity is lesser.

The low stability of inks towards environment influence presents problem. The solution can be their protection towards sun light with varnishes. The total colour difference ΔE of inks after their irradiation with total light dose of 20 MW m $^{-2}$ was calculated. The urethane acrylate coatings (layer thickness $10{-}30~\mu m$) increased the ink stability in about 30 %.

Acknowledgement. We thank the Slovak Grant Agency for the financial support (Project VEGA 1/2454/05 and VEGA 1/2455/05).

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P-26 MECHANICAL PROPERTIES OF ELASTOMER / LAYERED SILICATE COMPOSITES

ZUZANA NÓGELLOVÁ**, IVAN CHODÁK*, and ZUZANA KRAMÁROVÁ*

^a Polymer Institute, Slovak Academy of Sciences, Dúbravská cesta 9, 842 36 Bratislava, ^b Department of Plastics and Rubber, Faculty of Chemical and Food Technology, Radlinského 9, 812 37 Bratislava, Slovakia upolnoge@savba.sk

Composites with two different elastomeric matrices, namely natural rubber (SMR) and styrene-butadiene copolymer (SBR) were filled with various layered silicates, either native or modified. Besides commercial organically modified montmorillites, namely Cloisite 10A, Cloisite 15A and Cloisite 20A, natrified Cloisite Na and bentonite from Slovak provenience were used. Mechanical properties of the composites were investigated.

It was found that particle size of bentonite plays certain role; the mechanical properties of composites filled with filler milled to particle size below 15 or 45 microns did not differ significantly, while the presence of particles above 45 microns with dimensions up to 250 microns resulted in lower both tensile strength and elongation at break.

Surprisingly to certain extent, the mixing of various filler in two elastomeric matrices revealed different behaviour. While in SBR rubber the three fillers, namely Cloisite 10A, 15A and natrified bentonite BL15 almost did not differ regarding tensile strength and elongation at break and also the both values remained almost the same in the concentration range of the filler from zero up to 10 wt.%, SMR matrix was much more sensitive to the concentration as well as quality of the filler. With increasing filler concentration, tensile strength and deformation at break increased significantly with rising amount of Cloisite 10A and medium effect was observed for composites filled with Cloisite 15A, no changes were found for BJ15.

The behaviour in SBR rubber is surprising since organomodified Cloisites should form a kind of nanostructures via at least partial intercalation if not exfoliation, while this behaviour is not expected for unmodified bentonite BJ15. The differences were quite pronounced for SMR matrix; besides chemical effects, higher viscosity of SMR, resulting in higher shear stress during mixing might be a reason for the observed behaviour.

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P-27 INVESTIGATION OF AGEING OF POLYETHYLENE TEREPHTHALATE MODIFIED BY COLD PLASMA

IGOR NOVÁK^a*, IVAN CHODÁK^a, MOHAMED M. CHEHIMI^b, IVICA JANIGOVÁ^a, and MILENA ŠPÍRKOVÁ^c

^a Polymer Institute, Slovak Academy of Sciences, Dúbravská cesta 9, 842 36 Bratislava, Slovakia, ^b Interfaces, Traitements, Organisation et Dynamique des Systemes, Universite Paris 7- Denis Diderot, 1 rue de la Brosse, 750 05 Paris, France, ^c Institute of Macromolecular Chemistry, Academy of Sciences of the Czech Republic, Heyrovského nám. 2, 162 06 Praha 6, Czech Republic upolnovi@savba.sk

The use of cold plasmas in the treatment of polymeric materials^{1,2} is a dry process of modification which can tailor polymers in order to modify their surface energy and adhesion to other materials. The most important feature of the plasma technique is that the surface properties of polymer can be modified without changing their intrinsic bulk properties. It is well known that plasma modification of polymers leads to changes in surface and adhesive properties. Depending on the gases used, different functional groups are formed in a thin surface layer of the polymer.

The surface and adhesive properties of polyethylene terephthalate (PET)³⁻⁷ modified by surface barrier discharge (SBD) plasma at atmospheric pressure and/or radio-frequency discharge (RFD) plasma at reduced pressure (*P*=45 Pa) have been studied. The influence of low-molecular weight-oxidized material (LMWOM) on surface and adhesive characteristics of PET, which is a generally accepted effect in the case of electric discharge plasma modification of polymers⁸, has been also investigated. It has been concluded that surface energy and its polar component of PET modified by SBD and/or RFD plasma significantly increased in comparison with unmodified polymer. The peel strength of the adhesive joints PET modified by SBD plasma – polyacrylate in N₂ and/or O₂ increased with time of the activation by plasma.

The values of the surface energy of PET modified by SBD plasma significantly diminished due to ageing. The

samples of PET modified by plasma have been washed with methylalcohol. It was observed that ageing of washed sample was less intensive in comparison with unwashed sample of the polymer. The values of surface energy for washed and unwashed PET foils modified by SBD plasma were after 30 days of ageing almost identical.

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P-28 ECOLOGISATION OF RUBBER COMPOUND FOR PASSENGER CAR TYRES

<u>DARINA ONDRUŠOVÁ^a*</u>, MARIANA PAJTÁŠOVÁ^a, MILAN OLŠOVSKÝ^a, ANTON KARVAŠ^b, and EUGEN JÓNA^b

^a Faculty of Industrial Technologies, TnU AD, I. Krasku
 491/30, 020 01 Púchov, ^b Researche Center, Matador, a.s.,
 T. Vansovej, 1054/45, 020 32 Púchov, Slovakia
 ondrusova@fpt.tnuni.sk

One of the main priorities in rubber industry is ecologisation of rubber compounds in according with high quality of products. Many accelerators, that are important component in all sulphur curing systems, must be considered as critical from toxicological aspects. Accelerators, containing secondary amine fragments may to form dangerous cancerogenic Nitrosamines according to the reaction¹:

$$\begin{array}{c} R \\ N-H + N_2O_3 \end{array}$$
 $\stackrel{R}{\longleftarrow}$ $\begin{array}{c} N-N=O + HNO_2 \\ R \end{array}$

The creation of Nitrosamine-free vulcanization systems is one of the importent environmental problems in the car tyres production. Present work deals with formation of Nitrosamine-free vulcanization system of rubber compond for passenger car tyres by the method of substitution of commercially used sulphenamide accelerator (Vulkacit

DZ) with some new accelerators on the base of Dithiophosphates, that do not form dangerous Nitrosoamines. Advantages of dithiophosphate accelerators are wellknown².

The new Nitrosamine-free vulcanization systems were prepared with the addition of three new dithiophosphate accelerators (Rhenocure SDT, Rhenocure ZDT and Rhenocure TP)³. In the function of plasticizer was used low-aromatic oil (RAE). Vulcanization characteristics and physical properties of new prepared systems were compared with the properties of commercial rubber compound for passenger car tyres.

The results of measurements suggest on synergistic effect of combination Zn-dithiophosphate (Rhenocure ZDT, Rhenocure SDT) with Vulkacit DZ⁴.

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P-29

STUDY OF THE ELECTRICAL PROPERTIES OF RUBBER/CARBON BLACK COMPOSITES DURING UNIAXIAL DEFORMATION AND RELAXATION

<u>SILVIA PODHRADSKÁ</u>*, MÁRIA OMASTOVÁ, and IVAN CHODÁK

Polymer Institute, Slovak Academy of Sciences, Dúbravská cesta 9, 842 36 Bratislava, Slovakia upolpodh@savba.sk

During the past years growing interest has been devoted to the study of the electrical properties of flexible conducting composites during mechanical deformation. Two types of deformations can be used, pressure or longitudinal deformation. The effect of pressure during moulding on the electrical resistivity of elastomers was published by Thompson et al. ^{1,2}. They observed a decrease of several orders of magnitude in electrical resistivity of Neoprene GRT/carbon black composite when applying pressure.

Suggested mechanism explaining the effect is the formation of covalent bonds between carbon black particles that are pushed into closer proximity due to high pressure in the mould. Similar trends were observed for other rubbers composites containing EPDM, acrylonitrile, and NBR as a matrices².

In our work the influence of longitudinal deformation on the changes of electrical properties of conducting composites was investigated. Two composites, ethylenepropylene rubber (EPDM Keltan 4703, DSM, The Netherlands) or styrene butadiene rubber (SBR, SKS 30, KAU-ČUK a.s. - Unipetrol group, Czech Republic) filled with 35 wt.%. carbon black (Vulcan XC-72R, Cabot Corp., USA) were prepared by melt mixing. Testing specimens were prepared by compression moulding at 145 °C for 30 min followed by fast cooling at ambient conditions. Two Cu wires were attached as contacts on the both ends of each specimen. Conductivity of EPDM/CB composite was 2·10⁻³ S cm⁻¹, while for SBR/CB composite one order of magnitude higher conductivity, $6.10^{-2} \,\mathrm{S \, cm^{-1}}$ was found. Changes of electrical current were measured in dependence on mechanical deformation consisting of three consecutive steps. The first one is longitudinal deformation of the sample to 50 %, 100 % or 200 % of the original length. The second step is relaxation of mechanical stress in the extended state of composite during 30 min. The last step is recovery of the conducting system after quick release of the mechanical stress.

Longitudinal deformation of the EPDM/CB sample resulted in a decrease of conductivity due to induced disintegration of conducting links between the conductive filler particles. During the initial elongation of SBR/CB composite, a decrease of current is observed followed by an increase after few seconds. This phenomenon can be explained by orientation of SBR chains during longitudinal deformation.

We have found that different behaviours of composites with EPDM and SBR matrices depend on structures of rubber matrix and on interactions between matrix and conducting filler. During relaxation in elongation state an increase of the current was observed which was explained by partial reconstruction of conducting paths in composites. After releasing the mechanical stress, rapid decrease of current was measured, but conducting paths recovered partially during 20–40 min of relaxation.

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P-30 THE FUNCTIONALIZATION OF FIBRE MATERIALS SURFACES FOCUSED ON ELECTRICAL PROPERTIES

$\frac{SILVIA\ PODOBEKOV\acute{A}^a,\ ANNA\ MUR\acute{A}ROV\acute{A}^{a*}\,,}{ANDREJ\ RUSN\acute{A}K^a,\ VLADIMÍR\ \check{D}URMAN^b,}$ and JOZEF RYBA a

^a Slovak University of Technology, Faculty of Chemical and Food Technology, Radlinského 9, 812 37 Bratislava,
 ^b Slovak University of Technology, Faculty of Electrical Engineering and Information Technology, Ilkovičova 3, 812 39 Bratislava, Slovakia anna.murarova@stuba.sk

One of the requirements for fibre materials designed for automobiles, an area sensitive for electrostatic discharges and field, are their adequate electrical properties. The electric resistance for classic synthetic fibres is 10^{12} – $10^{14}\,\Omega$ m. In order to increase the fibre materials security in automobiles the fibre materials are being functionalized focusing on electric properties. There are different modifying proceedings how to increase electrical properties on the level of polymers, fibre materials surfaces or by implementing carbon and metallic fibres to textiles^{1,2}.

The pigments based on aluminium and carbon – graphite and Printex L-6 are used in our paper for blocking electrostatic charge creation on surfaces of polyethyle terephthalate (PET) and polypropylene (PP) fibre materials.

The measured values of volume and surface resistivity were used to evaluate their dependence from type of pigment, way of pigment fixation and pigment concentration. The effect of fibres' surface functionality was evaluated based on electrostatic surface potential measurement.

Based on the achieved results, the Printex L-6 pigment is the most effective pigment of all among the evaluated ensemble. The Printex L-6 (5%) pigment causes decrease of fibres' surface resistibility from $10^{14}~\Omega$ to $10^7~\Omega$ and decrease of volume resistivity from $10^{12}~\Omega$ m to $10^5~\Omega$ m. The creation of surface electrostatic potential on pigmented surfaces of fibre materials is inhibited.

The pigmentation of surfaces of the PET and PP textile materials with pigments based on carbon classifies their electric properties to the category of semi-conductors.

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P-31 MECHANICAL PROPERTIES OF MODIFIED PA 6 FIBRES BY NANO-ADDITIVES

<u>JOZEF RYBA*</u>, MICHAL KRIŠTOFIČ, IVETA VASSOVÁ, SILVIA PODOBEKOVÁ, and MÁRIA DULÍKOVÁ

Department of Fibres and Textile Chemistry, Institute of Polymer Materials, Faculty of Chemical and Food Technology, Slovak University of Technology, Radlinského 9, 812 37 Bratislava, Slovakia jozef.ryba@stuba.sk

The main task of this work was to prepare modified polyamide 6 (PA 6) fibres by commercial nano-additives and to study the influence of nano-additives to mechanical properties of fibres.

Composite consisting of a polymer and layered silicate (modified or not) frequently exhibit improved mechanical and material properties when compared to those of polymers containing a small amount (≤ 5 wt.%) of layered silicate¹.

The fiber structure formation was affected by the takeup velocity, the conditioning after spinning. Only a few investigations of the melt or solution spinning of polyamide nanocomposite are available².

PA 6 fibres were modified with 0.25, 0.50, 1.00, 1.50 and 5.00 wt.% of Cloisite 15A and Cloisite 30B.

The main influence to the end-use properties has the content of nano-additives in modified PA 6 fibres.

The mixtures consisting of PA 6 and nano-additives was melted on twin-screw co-rotating extruder (LabTech Scientific) and chips of modified PA 6 were prepared.

The spinning of blends was performed on the laboratory model equipment with and without the lubricant. Drawing of prepared fibres was performed on laboratory drawing unit. For valuation of mechanical properties were made three drawing ratios (λ = 3, 4, 5).

Properties of modified PA 6 fibres like fineness, tensile strength, modulus and elongation at break (Instron 3343) were determined.

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P-32 CROSS-LINKED ELASTOMERIC COMPOSITES WITH MAGNETIC PROPERTIES

RENÁTA SZABOVÁ*, JÁN KRUŽELÁK, DENISA BELLUŠOVÁ, GABRIELA KYSELÁ, and IVAN HUDEC

Department of Polymer Materials, Faculty of Chemical and Food Technology, Slovak Technical University in Bratislava, Radlinského 9, 812 37 Bratislava, Slovakia renata.szabova@stuba.sk

The cured elastomeric composites with magnetic and non-magnetic fillers have characteristic elastic and magnetic properties, too. They are interesting commercial materials thanks to their wide application in clamps, refrigerator door latches, intelligent tires, bearing sleeves, etc. Compared to the ceramic magnets, the elastomeric magnetic composites offer a greater degree of design flexibility and improved processibility. Ferrites are one of the best magnetic fillers for the preparing of the elastomeric magnetic composites. They are inexpensive, stable and have wide range of technological applications (1–3).

The aim of this work is to present some results obtained by the studying of the physical-mechanical and magnetic properties of cured composites on the basis of unsaturated elastomers (natural rubber, butadiene and butadiene-styrene rubbers) filled with the combination of carbon black (N-330 and N 550 type) and strontium hexagonal ferrite SrFe₁₂O₁₉, type FD 8/24 (coercive force 155 kA m⁻¹, remanent magnetization Br 235 mT, average particle size ranges 1-30 µm). The composites were compounded in laboratory mixer FARREL BR 1600 and cured in a hydraulic press at 150 °C and 20 MPa. The room temperature magnetic measurements of prepared composites were carried out using TVM-1 magnetometer at a vibration frequency 80 Hz and sensitivity 10-11 Wb. Their tensile properties (modulus, tensile strength, elongation, hardness) before and after thermo-oxidative ageing (Geer's method) were measured according to the corresponding ISO-norms. The crosslink density was determined from the results of their swelling in xylene, using Flory-Rehner equations modified by Krause for the filled cross-linked composites.

The study was based on two-factor five-level planning experiment. As independent variables weight ratio of strontium ferrite (F) to carbon black (C) $x_1 = F/C$ and total content of strontium ferrite and carbon black $x_2 = F+C$ have been chosen. The experimental results (physical-mechanical properties and remanent magnetization Br of prepared composites) were treated by the complete regression analyses, using the general regression equation (*I*) in the form:

$$Y = b_0 + b_1x_1 + b_2x_2 + b_{11}x_{12} + b_{12}x_1x_2 + b_{22}x_{22}$$
 (1)
where Y – evaluated parameter, b_0 , b_1 , b_2 , b_{11} , b_{12} , b_{22} – regression coefficients, x_1 , x_2 – independent variables on

the coded levels.

The variability of the individual dependent parameters due to the experimental error of their estimation as well as their variation due to the inaccuracy of the used regression model was specified by means of a variance analysis. The adequacy of the regression equations was evaluated by applying an F-test on the significance level $\alpha=0.05$.

The statistical treatment of the experimental results showed that the chosen factors - the weight ratio of ferrite and carbon black F/C and the total content of both fillers F+C in rubber compounds - affected the appreciated physical-mechanical properties of the prepared crosslinked composites and their remanent magnetization, too. The modulus $(M_{200},\ M_{300},\ M_{500})$ and tensile strengths are non-linearly decreasing with the increasing of F/C, hardness and elongation are changed slightly with this factor. The total content of fillers in rubber compounds has an influence on tensile strengths of cross-linked composites, predominantly. Remanent magnetization B_r of prepared composites is non-linearly increased mainly in the area of higher total content of both fillers F+C and weight ratio of magnetic and nonmagnetic fillers F/C, too. Because the B_r values are relatively high, it can be predicted that in this way prepared elastomeric magnetic composites have appropriate magnetic properties usable in suitable application.

The residual values of modulus after thermooxidative ageing are higher than the modulus of the original probes. The highest values of modulus and also the tensile strengths have composites with low content of ferrites. The extension of the ageing is connected with the deterioration in these properties. The extension of ageing time is also connected with the slightly increasing of hardness and decreasing of elongations, simultaneously.

In the network of the prepared cross-linked composites were determined predominantly polysulfidic and monosulfidic cross-links at the low values of F/C and polysulfidic and disulfidic cross-links at higher values of F/C, respectively. The ageing results in the decreasing of polysufidic cross-links and increasing of disulfidic cross-links, too.

The obtained results showed that composite materials with magnetic properties can be prepared by the compounding of unsaturated elastomer systems and ferrites and their following sulphur cross-linking at the appropriate conditions. The physical-mechanical properties, their changes during the thermo-oxidative ageing and remanent magnetization B_r are dependent on the ferrite content in the elastomer compounds.

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P-33 BALL AND SOCKET JOINTS WITH PLASTICS INSERTS FOR PASSENGER VEHICLES

MAREK SZOSTAK* and WOJCIECH ROLIRAD

Poznan University of Technology Institute of Materials Science, Piotrowo street 3, 61-138 Poznan, Poland Marek.Szostak@put.poznan.pl

In the work the trade-off studies of ball and socket joints with POM and PA 6.6 inserts for BMW series 3 has been shown. The joints has been tested on the special equipment, where the elongation, tensile and impact strength has been investigated. The static measurements have been made with working load 30–50 kN and drawing speeds 1, 10, 20 mm min⁻¹. The dynamic tests applied the forces in the range between 30–55 kN. The real forces present in the ball and socket joint has been determined during the car trial run on the racing track in Nuerburgring and Hendlingkurs in Germany. The measured amplitude of the forces was 40 kN (from –24 kN to +16 kN).

The results of static and dynamic measurements of ball and socket joints with POM and PA 6.6 inserts are presented appropriately in tables I and II.

Looking at the results of the measurements we can see that the POM inserts have much higher stiffness to compare with PA 6.6. The POM parts loose quickly mechanical strength when the load exceed 40 kN, but high temperature not cause the clearance in ball and socket joints what was observed for PA 6.6 inserts above 70 °C. For POM inserts the cracking of sleeve was also observed for the load higher than 55 kN but it take place when the speed of the impact hammer is 7,11 m s⁻¹ and have the energy of 850 J, which represent extreme values. Due to such properties of ball and socket joints every year more and more car producers take the decision to use the joints with POM inserts. Such a solution has been also used for BMW passenger cars series 3.

Table I
Results of the static tests of ball and socket joints

| Load | POM Insert | | PA 6.6 Insert | |
|------|------------|-------|---------------|-------|
| [kN] | δ [MPa] | ε[mm] | δ [MPa] | ε[mm] |
| 30 | 65,5 | 0,070 | 34,4 | 0,088 |
| 40 | 40,3 | 0,097 | 26,7 | 0,112 |
| 50 | 20,6 | 0,144 | 22,0 | 0,146 |

Table II
Results of the dynamic tests of ball and socket joints

| Load | POM Insert | | PA 6.6 Insert | |
|------|------------|-------|---------------|-------|
| [kN] | δ [MPa] | ε[mm] | δ [MPa] | ε[mm] |
| 30 | 75,1 | 0,068 | 63,2 | 0,064 |
| 40 | 50,3 | 0,081 | 51,1 | 0,079 |
| 50 | 24.0 | 0.130 | 32.0 | 0.112 |

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SURFACE MODIFICATION OF POLYETHYLENE IN DIELECTRIC SURFACE BARRIER DISCHARGE

MARIAN ŠTEVIAR^a*, IGOR NOVÁK^a, ŠTEFAN KURUC^a, IVAN CHODÁK^a, JAROSLAV MOSNÁČEK^a, IVICA JANIGOVÁ^a, MOHAMED M. CHEHIMI^b, and MILENA ŠPÍRKOVÁ^c

^a Polymer Institute, Slovak Academy of Sciences, Dúbravská cesta 9, 842 36 Bratislava, Slovakia, ^b Interfaces, Traitements, Organisation et Dynamique des Systemes, Universite Paris 7- Denis Diderot, 1 rue de la Brosse, 750 05 Paris, France, ^c Institute of Macromolecular Chemistry, Academy of Sciences of the Czech Republic, 162 06 Praha 6, Czech Republic upolstev@savba.sk

The low values of surface energy of low-density polyethylene (LDPE) can be significantly increased by using various methods of surface modification. The higher surface energy of LDPE is necessary for bonding or printing. The most advanced method of LDPE surface modification is based on modification by barrier discharge plasma $^{1-3}$. The surface of LDPE was pre-treated at various times by dielectric surface barrier discharge (DSBD) plasma in $\rm O_2$ and/or $\rm N_2$ at atmospheric pressure. The changes in surface properties of LDPE modified by plasma $^{4-6}$ were analyzed using contact angle measurements, as well as Scanning Electron Microscopy (SEM) measurements.

The contact angles of polar testing liquids on the surface of LDPE modified by DSBD plasma in O_2 with time of activation decreased. The contact angles of polar liquids (e.g. water, ethylene glycol, formamide) decrease significantly even for short time (5 s) of activation of LDPE by DSBD plasma due to an increase of the surface polarity.

The changes in surface topography of LDPE modified by DSBD in O_2 were evident (increase of the roughness), in the case of modification of LDPE by DSBD in N_2 no meaningful changes were observed.

Surface properties LDPE modified by DSBD plasma were substantially higher regarding to unmodified polymer due to higher polarity of the polymeric surface. SEM microphotos show the roughening of the LDPE surface modified by DSBD mainly in O₂ atmosphere as a consequence of the DSBD plasma modification.

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P-35

THE EFFECT OF METAL COATED CARBON BLACK FILLING ON THE PHYSICAL AND MAGNETIC BEHAVIOUR OF NATURAL AND SYNTHETIC RUBBERS

E. ÜRÖGIOVA^a*, J. A. PIEST^a, G. HEINRICH^a, N. PROBST^b, E. GRIVEI^b, A. PRONIN^c, and J. WOSNITZA^c

^a Leibnitz Institute for Polymer Research, Hohe Straße 6, D-01069 Dresden, Germany, ^b Erachem Comilog SA, Avenue Louise, 534, B-1050 Brussels, Belgium, ^c High Magnetic Field Laboratory Dresden, Bautzner Landstraße 128, D-01328 Dresden, Germany ueroegiova@ipfdd.de

The interest in metal coated carbon black filled rubber compounds has grown over the last years as a consequence of their improved mechanical and electro-magnetic properties with respect to other types of filled, and of unfilled rubber compounds. This poster illustrates the investigation of the influence of metal coated carbon black particles (CB) (nickel, iron coated CB) on the magnetic, the mechanical, and the reinforcing effect in different rubber composites, i.e. CB filled natural and synthetic rubber composites, and metal coated CB filled composites. The incorporation of magnetic fillers in the rubber matrix imparts magnetic properties. Besides, it is expected to changes other physical properties of the compound.

Because the macroscopic and mechanical properties of filled composites depend strongly on the polymer matrix, magnetic fillers, and interfacial interaction between the components, knowledge of the optical parameters (complex dielectric constant and complex magnetic susceptibility) knowledge of the latter is necessary to relate the mechanical properties to the compound's microscopic structure. The electro-magnetic properties are investigated as a function of applied magnetic induction, applied irradiation frequency and of applied temperature.

P-36 MECHANICAL STRENGTHENING OF PLASTIC FOILS BY THIN GLASS-LIKE LAYERS

MILAN MIKULA*, <u>ALEXANDRA VALASEKOVA</u>, MIROSLAV VAŠÍČEK, and KAROL VAŠKO

Institute of Polymer Materials, Faculty of Chemical and Food Technology STU Bratislava, 812 37 Bratislava, Slovakia

milan.mikula@stuba.sk

Very thin inorganic layers (e.g. SiO_x called glass like) were extensively studied in last years in combination with plastic foils as excellent barrier layers against permeation of gases and moisture^{1,2}. However, application of inorganic layers changes also mechanical properties of a substrate foil. Particularly, disruptive barrier of the system enhanced, so the breakthrough or cut resistance is higher, similarly to the strengthening effect of glass fibre fabric in foils, laminates or composites that is very well known. Because of the tendency to develop relief cracking, the layers must be thin (~ 50 nm) and overcoated by protective and fixation polymeric layer, e.g. by crosslinked heteropolysiloxanes^{3,4}.

Nanocomposite laminates of SiO_x/poly(ethylene terephthalate) (PET) with different thickness of oxide layer deposited by vacuum evaporation and different covering layers were characterized by SEM microscopy, surface energy, water adsorption, FTIR spectroscopy including IR photoacoustic spectra and other techniques. Mechanical properties were tested by tear strength and by special disruptive test using newly designed puncture tester⁵ that gives the puncture depth of a metal spike penetrating through the foil.

It was found that inorganic oxide layer (much thinner than substrate foil) causes little changes in tear stress characteristics, while the breakthrough parameters are changed considerably with the presence of oxide layer.

The very interesting IR photoacoustic spectra correlate better with the presence of oxide nanolayers than standard absorption spectra measured by reflection ATR techniques.

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