In May 2005, the first International Conference on Polymeric Materials in Automotive, PMA 2005, was organized in Bratislava as a reflection of steeply rising importance of automotive industry in Slovakia, derived from the presence of dominant investors in Slovakia, namely Volkswagen, PSA, and recently Kia Hyundai including a number of other companies – suppliers of plastics and rubber parts being a significant part of them – building up their new facilities in the country. The conference attracted almost 200 participants from 21 countries and was considered as successful by all attendees. The appreciated feature consisted in a fact that, although targeted to polymeric materials used in automotive industry, the scope of the conference was kept highly scientific. Thus, new ideas have been presented, many of these being far away from industrial application, still contributing significantly to a progress in the area.

Slovakia has recently experienced a significant flow of direct investment from abroad. This tendency seems to be continuing as a result of well educated and highly skilled labor force and ideal central location serving as a gateway to Eastern Europe.

Reflecting this development, for the second time Slovakia will host the participants of the International Conference on Polymeric Materials in Automotive, PMA 2007. Similar to the PMA 2005, the conference is targeted on various aspects related to plastics and rubber in the automotive industry, with the aim to exchange the innovative approaches towards new polymer products increasingly having a decisive influence on the design and appearance of new generation of automobiles. Developing goals such as aesthetic appeal and comfort, safety and lightweight construction, as well as quality and cost are affected directly by the material concept and the corresponding processing and product technology.

International scientific conference on rubber, Slovak Rubber Conference, is organized every year by the Rubber Research Institute of Matador Púchov. In 2007 this traditional event will be a part of the second International Conference on Polymeric Materials in Automotive.

Prof. Ivan Chodák, DSc.
Chairman of the Program Committee

IL-01
AUTOMOTIVE APPLICATIONS OF THERMOPLASTIC ELASTOMERS

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Thermoplastic elastomers (TPEs) are rubbery materials with fabrication characteristics of conventional thermoplastics and many performance properties of thermoset (vulcanized) rubber. TPEs can be processed by the same methods such as injection molding, extrusion, blow molding, rotational molding as most thermoplastic materials, including polyethylene, polypropylene, and polyvinyl chloride. On the other hand, their basic properties are very similar to those of conventional rubber materials, such as natural rubber, SBR, EPDM, NBR, polychloroprene. Thermoplastic elastomers offer a variety of practical advantages over vulcanized rubber, such as simple processing with fewer steps, shorter fabrication times, and the possibility of recycling of production and post-consumer scrap. These and other advantages are the main reasons why the applications of TPEs in the automotive industry have been growing at constantly increasing rate during the past two decades. This contribution will discuss properties of the thermoplastic elastomers that are widely used in automobiles and their specific applications.

IL-02
MULTI-FUNCTIONAL NANO-MATERIALS FOR ADVANCED AUTOMOTIVE APPLICATIONS

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A b s t r a c t

Specific types of multi-functional nano-materials provide viable technology platforms for new-generation opto-electronic devices suitable for fabrication of passive or active control systems equipped with functional features such as: photo-chromic effects on window panes, decorative or functional patterns including active colour and texture, „roll-up" displays, large-area electroluminescent lighting panels, and others. These functional devices are of increasing interest of designers in the automotive, aerospace, construction and other industries.

This paper discusses selected next-generation intelligent materials for special-effects and devices focussing on transparent polymers and coatings with in-built UV and IR absorption-reflection functionality and electro-conductivity for the passive or active control of interior temperature and/or climate and special decorative effects in automotive applications.

E m e r g i n g   m u l t i - f u n c t i o n a l   o p t o -
e l e c t r o n i c   a n d   e l e c t r o - c h r o m i c
m a t e r i a l s   a n d   s y s t e m s

A range of optical, electrical and other properties of functional coatings or inks can be controlled by surface-tailoring specific types of nano-materials and functional molecules which can be compounded into nano-thin functional coatings. Depending on the end-application and production scale, the individual sub-components of „intelligent devices" can be fabricated using commodity printing processes such as roll coating, screen-printing or ink-jet printing. Through co-lamination, these can be subsequently assembled into thin, pliable envelope which, in turn, can be easily integrated with desired surfaces of the automotive interior or exterior.

The key scientific and technological challenges faced bu functional materials and coatings stem from the requirement to control the key functional properties of thin films fabricated with the use of the dedicated nano-materials, e.g.: (*i*) high optical clarity and transparency, (*ii*) controllable charge character and charge density, (*iii*) high conductivity, (*iv*) controlled opto-electronic and/or opto-chromic properties, and (*v*) compatibility with the coating's carrier polymer; (*vi*) good adhesion between supporting polymeric substrate (thin film) and the functional coating.

The desired clarity and optical transparency of functional coatings in the visible band of the electromagnetic radiation spectrum are achieved by matching refractive index of functional particles with that of the coating's matrix, and ascertaining that the size of additives is significantly less than half-wavelength of the visible light. An average size of nano-particles should be less than 200 nm, and preferably within the range of 5 to 30 nm.

Indium tin oxide (ITO) is one of most interesting materials for multi-functional devices utilising opto-electronic and other effects. In the form of a thin continuous films ITO exhibits optical transparency at the level of 80 to 95 %, high electronic conductivity, and the ability to absorb infrared radiation. Due to the above properties, thin ITO films are particularly suitable for fabrication of: (*i*) transparent electrodes for thin-film electro-luminescent displays and electro-chromic devices; (*ii*) transparent conductive coatings for radiation detectors; (*iii*) solar cells and energy storage devices; (*iv*) opto-electro-chromic coatings for effective management of solar radiation through targeting absorption of UV and I-R radiation.
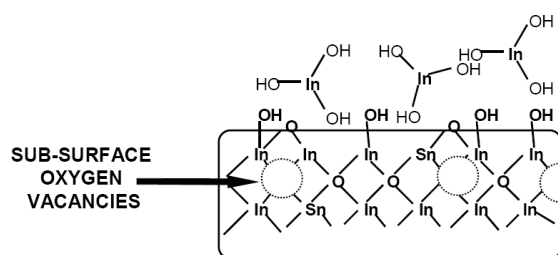
Fig. 1. **Schematics of the ITO surface and sub-surface structure illustrating the following:** (a) the termination of the bixebyte lattice with both, bridging and non-bridging oxygen atoms (oxygen vacancies), and (b) hydroxylated indium, In (OH)$_3$, providing suitable sites for the attachment (chemisorption) of organic molecules such as dispersants and organic dopants

Flexible opto-electronic devices based on indium oxide

Pure indium oxide (In$_2$O$_3$) is a wide-gap n-semiconductor whose relatively high conductivity is attributed to the presence of doubly charged oxygen vacancies (V_o^{**}) which provide conduit for the charge transfer. Doping indium oxide, eg by Sb, Sn of F significantly increases its conductivity. During incorporation of the dopant, eg. tin, the atoms enter ITO lattice (eg. as Sn^{4+} ions) substituting In^{3+} ions in the cation sites, and act as *n*-type donors. As the Sn contents increases, the unit cell is enlarged and the host lattice becomes disturbed. The addition of tin atoms increases carrier concentration, and hence conductivity, but reduces charge mobility due to the lattice distortion.

The following challenges need to be overcome in the fabrication of effective transparent electro-conductive ITO coatings for opto-electronic applications: (*i*) minimisation of the size of dispersant molecules to reduce percolation threshold arising from the separation of individual ITO nano-particles, (*ii*) substitution of non-conductive
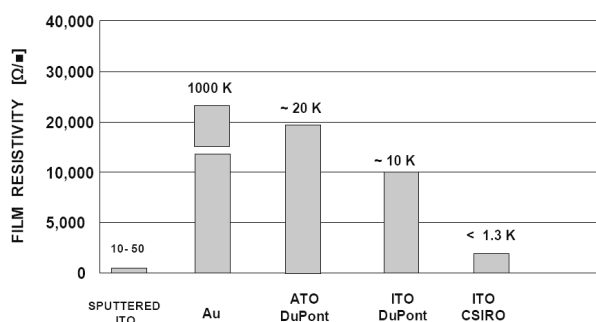

Fig. 2. **Comparative data on conductivity of printable nano-oxide films on a flexible transparent PET substrate** (30 μm): commercially available ITO coatings, ATO coating and and a new generation CSIRO coating with ITO nano-particles doped by self-assembled electro-conductive organic molecules

dispersant molecules by molecules containing charge-conducting moieties, (*iii*) grafting electro-conductive molecules onto non-bridging oxygen atoms within oxygen vacancies to prevent gradual deactivation of the conductive lattice. Functionalisation of ITO surface with self-assembled molecules equipped with charge-conducting moieties leads to significant improvement of the ITO film conductivity, as illustrated in Fig. 2. It also provides a significant reduction of the rate of deterioration of conductivity of ITO films exposed to ambient air, as illustrated in Fig. 3.

Spectrally selective nanomaterials

The new generation UV- and IR absorbing and reflective nanomaterials can offer an effective management of energy embodied in solar radiation spectrum which is transmitted through windows and inadvertently converted by automotive body panels into radiant heat transmitted to the interior through the body panels. The key constituents of the overall energy embedded in solar radiation are as follows:

– UV radiation band (200–400 nm):   5%
– visible radiation band (400–700 nm):   43%
– near-IR radiation band (700–2500 nm):   52%

The typical IR radiation reflectance of a painted automotive panels depends on the pigment's colour and varies within the range of 0.7 for white and 0.04 for black colour. Consequently, the dark metal panels exposed to solar radiation can attain the surface temperatures as high as 72–75 °C after as short a time as 15–20 minutes. The absorbed heat is subsequently transmitted to the cockpit interior.

An effective blocking of energy embedded in the IR region of solar radiation spectrum is offered by VO$_2$. In an unmodified state it exhibits transition from semi-conducting to metallic state at 57 °C, which is further lowered to 29 °C when doped with tungsten at the level of 1.9 %. Consequently, above their respective phase transition temperature, coatings containing nano-sized VO$_2$ are able to retain high optical transparency whilst performing as effective IR radiation reflectors.
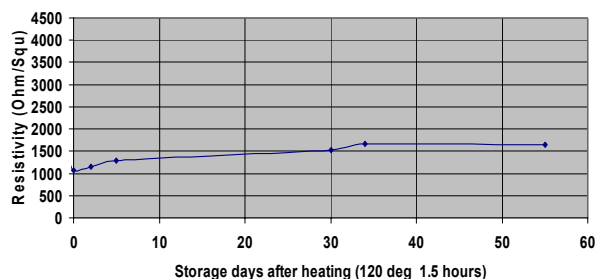

Fig. 3. **Stabilisation of long-term conductivity of thin ITO film doped by self-assembled organic electro-conductive molecules**
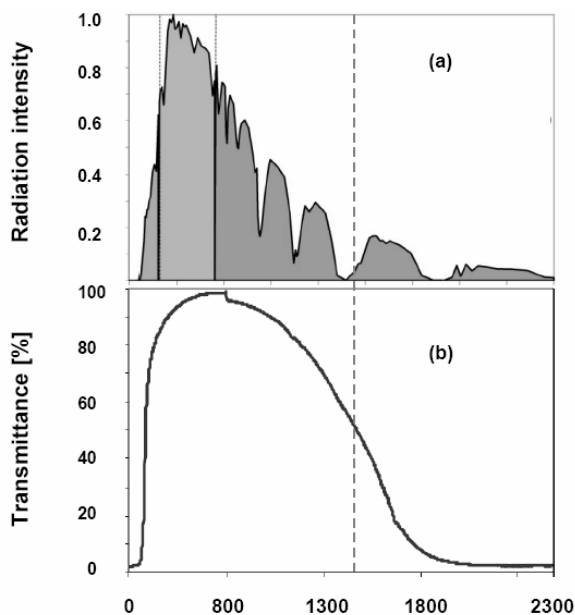
Fig. 4. **(a) Full spetrum of solar radiation, and (b) UV-Vis-NIR spectrum on a nano-structured ITO coating**

ITO-based coatings can offer additional management of transmitted residual tails of IR energy due to absorption of significant amount of IR radiation in the wavelength band of 1100−2500 nm, as illustrated by UV-Vis-NIR spectrum of an ITO coating in Fig. 4b. It can bee seen from this figure that approximately the following quantity of IR radiation is absorbed by an ITO film:

−   12. 5%   wavelength above 950 nm,
−   25 %   wavelength above 1100 nm,
−   50 %   wavelength above 1450 nm.

IL-03
MATERIALS SCIENCE AND ENGINEERING IN TYRE DEVELOPMENT FOR OPTIMISING TYRE PERFORMANCE

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We report about some recent progress in materials science and engineering in passenger car tyre development for optimising tyre performance.

The presentation is divided into two main parts.

After a short introduction we present an overview about topical main features of the product tyre and about
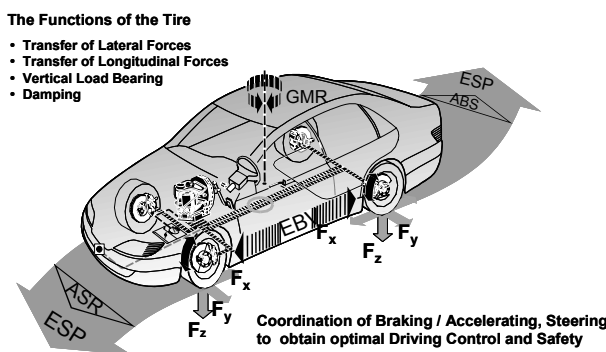
tyre functions (see Fig. 1).

The tyre is not a stand alone product. It is part of the system constituted by street and automobile. Thus, research efforts will lead in the future to a more integrated approach. Therefore, it is necessary to combine different R&D areas as chemistry, mechanics, simulation, sensorics, electronics, controlling and brake technology to come to a new interactive braking and driving system (Fig. 2). Beside tyre design, construction and materials we emphasize tyre functions as part of the whole car system and show how these functions influence comfort, driving dynamics and safety of cars to a great extend. Several tyre performance criteria and requirements will be discussed like comfort, steering behaviour, driving stability, wet and dry grip, endurance and economy.

In the second part we focus on development tools especially in material science and tyre mechanics to optimise tyre performance. We demonstrate how recent developments in tyre materials science are used to improve development criteria for tyre traction, rolling resistance, abrasion, handling, etc. Several examples will show how new concepts and tools of rubber and tyre mechanics can be incorporated into tyre simulation − especially Finite
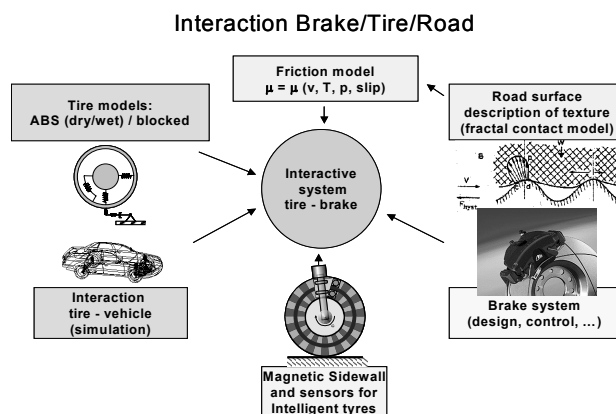

Fig. 1. **Functions of a tyre**

Fig. 2. **Tyre as part of an interactive system**

Element Analysis (FEA) − to accelerate and improve tyre engineering.

In the case of tyre tread materials development we mention several recent research activities dealing with reinforcement in elastomers where the main attention is to gain insight into the relationship between disordered filler structure on different length scales and specific mechanisms contributing to reinforcement. Improved understanding of reinforcing mechanisms and physical behaviour of rubbers find applications in materials engineering and materials development of high performance tyre treads. For example, using the technology of precipitated silica with a reinforcing agent (e.g., the polysulfidic organosilane TESPD), together with special solution polymerized statistically styrene-butadiene copolymers (S-SBR) as hydrocarbon polymer matrix, the *green tyre tread* could be developed. In effect, when compared to carbon black technology, significant tyre performance improvement can be observed. The silica-technology improves fuel economy (rolling resistance) and overall braking performance over conventional tyres, especially, in case of anti-braking system (ABS) supported wet skid behaviour.

In the case of tyre modelling we show how numerical simulation methods are nowadays a usual tool for modern tyre design and tire development. With the finite element method (FEM) at hand, the design engineer is capable to investigate the structure virtually without building a prototype construction. Parametric studies are carried out and influence factors determined in order to obtain a better product and a shorter time to market. Moreover, quantities like stresses and strains within the structure, which cannot be measured by experi-ments, are determined with the FEM. A lot of re-search has been carried out in order to provide reliable material models. Nonlinear elasticity as well as inelastic features have to be taken into account. State of the art general purpose FE codes provide adequate libraries for material models. The gap between experimental characterization and simulation has to be closed by a syste-matic identification process in order to determine the material para-me-ters of the models. Some basic procedures are provided by the commercial pro-grams but usually own methods have to be used.

A final conclusion and outlook presents some current developments as „intelligent" tyres.

IL-04
WHAT SWELLING OF COMPLEX ELASTOMERS TELLS US ABOUT COMPOSITION, STRUCTURE AND REINFORCEMENT

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Introduction

Thermoplastic polymers comprised of two chemically linked, immiscible components with very different physical properties, such as occurs in polyurethanes, derive beneficial properties from the separation of the components into nanoscale domains. Here, we consider the segmented poly(ester urethane), Estane™, an example of an important class of industrial polymers, used as an adhesive and binder. Estane™ consists of crystalline (hard) and rubbery (soft) segments that phase separate into hard and soft segment-rich nano-domains, resulting in an extended, cross-linked network. Estane™ is distinct from other polyurethanes in having relatively low hard segment, 23 percent by weight.

Swelling experiments are common in polymer physics to determine the properties of polymer networks including those of polyurethanes[1–7]. In combination with small-angle scattering, swelling experiments have been used to determine the polymer network structure and chain statistics[3–5]. Small-angle neutron scattering (SANS) measurements on polymers swollen with mixtures of protonated and deuterated solvents can provide additional information on the polymer domain structure and composition when analyzed with contrast variation techniques.

The objective of this work is to use swelling with solvents that are mixtures of protonated and deuterated forms of either benzene, toluene or one of the xylene isomers as a contrast variation technique with SANS as a means of determining the size, shape solvent distribution and composition of the hard and soft segment-rich domains in Estane™. Thus, we expand on earlier attempts to study domain morphology and composition with SANS measurements of polyurethanes with deuterated soft segment[8] and x-ray[9,10] measurements on higher hard segment content polyurethanes. This approach is necessary in the study of commercial polyurethanes, as deuterated model compounds that might otherwise be used in this type of study are not necessarily completely equivalent to the actual product. Further, the results, when compared with those obtained with samples swollen with solvent consisting of mixtures of deuterated and protonated plasticizers, provide insight into the mechanism of plasticization in these polymers.

Results

We used two models to describe the SANS data as a function of contrast. Both model the Estane™ as a fluid of spherical, discontinuous hard segment-rich domains in a soft segment-rich matrix. These models are the so-called fluid model, used by others to describe the structure of other low hard segment-rich polyurethanes[10] and Pedersen's micelle model[11]. Each model incorporates a length scale associated with a solvent-excluding core of the discontinuous, hard segment-rich domain that has significant neutron scattering contrast relative to the matrix, and a larger length scale that defines the closest center-to-

center approach of the discontinuous domains. The micelle model includes a third length scale associated with a corona that surrounds the discontinuous domain core. We find that the micelle model completely describes the data. The fluid model requires the *ad hoc* addition of an additional length scale. The models, which are in good agreement with each other, show that only 0.05 volume fraction of the hard segments are incorporated into the discontinuous domains and that these domains, which have a radius of about 5 nm, have a number density of order 10^{17} cm^{-3}, giving a volume fraction of 0.05. The results show that in Estane™ there is considerable mixing of the hard and soft segments and that in particular there is a significant amount of soft segment in the hard segment-rich, discontinuous domains.

Swelling experiments with plasticizer suggest that the plasticizer preferentially swells the matrix plus corona domains, and that it removes hard segments from the core domains into the corona plus matrix domains, reducing the density of cores by about a factor of two, suggesting that the dissolution of crystalline domains is at least one mechanism for polymer plasticization.

Discussion

The Koberstein-Stein model for segregation of hard segments into the hard and soft domains specifies that the hard segments will phase separate into a corresponding domain when at least critical number, N_c, of hard segment monomers are chemically linked in tandem. Otherwise, the hard segments will be dissolved in the soft segment phase[9] Koberstein and collaborators have variously estimated N_c to be 3–4 (ref.[7]) or 5 to 6 (ref.[9]) in MDI-BDO-based polyetherurethanes. Our results for this MDI-BDO based polyesterurethane are in accord with the lower end of these estimates.

It has been noted repeatedly in the literature that neither the classical theory of rubber elasticity nor the various extensions of this theory to networks can explain the shear modulus observed ($G \approx 2.2$ MPa) for Estane™. The notion that the crystalline domains act solely as network cross-links requires an unphysically large functionality for the cross-links by at least two orders of magnitude. One is struck, however, by the observation that when small spheroid fillers are used, onto which polymers have been grafted, that the reinforcement achieved at 0.05 volume fraction of these modified fillers is similar to that obtained with 0.2 volume fraction unmodified filler. This suggests that the properties of Estane™ are best understood in terms of a filled system highly coupled to the embedding matrix by rubbery polymer connected to the crystalline, discontinuous domains.

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IL-05
SCIENCE FOR SUSTAINABILITY OF NATURAL RUBBER

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Abstract

Natural rubber (NR) is standing alone among the materials and indispensable for our society. However, it is predicted that the demand of NR will be much larger than the supply in near future. Now, we should pay attention for sustainability of NR. In order to appeal the importance of NR, scientific study on NR is also useful. In this lecture, the smartness of strain-induced crystallization of crosslinked NR, the preparation of new green NR nanocomposite, and the chemical recycling of NR vulcanizates using supercritical carbon dioxide are presented.

Introduction

Natural rubber (NR) is a unique biomass *i.e.* it is only one polymeric hydrocarbon among many biopolymers, its source is almost always *Hevea brasiliensis*, and it is one of the most important industrial materials among many polymeric ones. NR is indispensable for pneumatic tires, especially the tires for heavy-duty uses *e.g.* tires for aircrafts and heavy trucks, and for rubber bearings in a seismic isolation system. Also, thin NR films manufactured from

Hevea brasiliensis

NR latex *e.g.* surgical gloves, condoms, and rubber tubes in biomedical and health care fields are very important materials. AIDS might be more rampant without condoms. NR is a plant, and CO_2 is absorbed through its photosynthesis. Thus, NR works to diminish the green house effect on the earth. These points of NR are very valuable for our society.

The demand of NR has been gradually increasing, and surpassing the supply which is increasing but by a slower rate than the demand. In the end of previous century, it was predicted that the demand of NR will be 1.4 times larger than the supply in 2020[1]. Recently, the demand of NR after 30 years is predicted to be *ca.* 15 million tons (twice of present demand)[2]. Latest abrupt increase of the price of NR suggests the acceleration of the unbalance between the demand and supply of NR.

The NR plantations in Malaysia, which had been the biggest producer of NR for many years, are now decreasing by the governmental development policy in order to accelerate its economic growth by its industrialization. This trend will spread to the other developing countries which are now producing NR. Therefore, some means have to be figured out for the dramatic increase of NR production in 20 years. How to increase the NR supply will be very important issue in next 10 years. We should consider the sustainability of NR for our safe and comfortable lives. Rise of price of NR may be the most effective motivation to maintain and expand the NR plantations. From the view point of science and technology, on the other hand, fundamental study on NR is also expected to progress the sustainability of NR. Importance of NR should be emphasized all over the world. In this conference, three topics from our studies on NR are reviewed in order to appeal the importance

of NR through „Science for Sustainability of Natural Rubber" not only for academic side but also for industrial side.

Strain-induced crystallization of crosslinked natural rubber

One reason for excellent mechanical properties of NR has been assumed due to its strain-induced crystallization ability. In order to appear the characteristics of NR, sulfur-cured NR vulcanizate was prepared and its strain-induced crystallization behavior was compared with that of sulfur-cured synthetic isoprene rubber vulcanizate[3,4]. Synthetic isoprene rubber (IR) is mainly composed of *cis*-1,4-poly (isoprene) unit, but its stereoregularity is lower than that of NR. Additionally, non-rubber components such as proteins and lipids are not included in IR and they are considered to influence the mechanical properties of NR. By using a synchrotron radiation system, NR was found to be crystallizable by smaller strain and smaller stress than IR, when the samples with similar network-chain density were compared. The crystallization of NR was increased gradually, whereas that of IR tended to be increased rapidly. The attainment of higher stress values of NR samples was also recognized. These characteristics of NR may be factors of its excellent mechanical properties and toughness.

On the other hand, peroxide-crosslinked NR is nowadays utilized more and more owing to their high transparency, lower compression set and improved heat resistance. Therefore, it becomes important for practical applications to reveal characteristics of strain-induced crystallization for peroxide-crosslinked NR in situ during deformation. Recently, we reported the characteristics of strain-induced crystallization of peroxide-crosslinked NR (ref.[5]). The elongation ratio at the onset of strain-induced crystallization was found to become smaller with the increase of network-chain density for peroxide-crosslinked NR, differently with the results of sulfur-cured NR, where the elongation ratio at the onset of strain-induced crystallization was independent on network-chain density. The results of peroxide-crosslinked NR agreed with the prediction by Flory[6,7] and were consistent with the classical theory of rubber elasticity[8]. Therefore, the network structure of peroxide-crosslinked NR was suggested to be more homogeneous comparing with that of sulfur-cured NR.

Preparation of green nanocomposite natural rubber

Reinforcement of rubber is one of the most important processes in rubber technology[9]. It results in a higher stress and improvement of various mechanical properties such as tear, tensile strength and wear. However, there are also disadvantages such as increases in hysteresis and compression set. It is well known that the carbon black is the most effective reinforcing filler for rubber composites, although it always makes rubber products black colored. As an alternative, silica is the other important filler in rubber industry. A problem of silica, however, is a poor dispersion in rubbery matrix due to the strong interaction between silica particles. Recently, we found an effective catalysis for highly *in situ* silica filling[10]. *n*-Hexylamine gave the generation of 71phr of *in situ* silica in the uncured NR matrix. A novel *in situ* silica filled NR vulcanizate of high *in situ* silica content (NR-71Si) showed unique characteristics. For, examples, the hysteresis loss and permanent set of NR-71Si were significantly smaller than those of con-

ventional sample (NR-71VN). The *in situ* silica filled „green" nanocomposites will be useful as eco-materials[11].

Devulcanization of natural rubber vulcanizates using supercritical carbon dioxide

Nowadays, a lot of rubber products are produced and utilized in our society. The world total amount of consumed rubber in 2004, for an example, was ca. 20.2 million tons and *ca.* 41 % of the amount were supplied from NR (ref.[12]). The demand of NR is more and more increasing for the various productions. Accordingly, a lot of used NR products are also generated and its treatment becomes a big problem. Thus, rubber industry is confronting the subject how to handle the used rubber products[13]. Since many commercial rubber products are produced as composites with inorganic fillers of nanometer size using a sulfur-cure system for crosslinking in general, the devulcanization process may be the most favorable method for the handling. Especially, a recycling process to obtain the rubber molecule of same molecular weight with that before the vulcanization is desirable. Namely, a selective devulcanization reaction on the crosslinking points is necessary in order to keep the quality of the virgin rubber molecule. In our study, environmental-friendly chemical recycling process in supercritical carbon dioxide (scCO$_2$) was established for sulfur-cured tire rubbers[13–17], where diphenyl disulfide (DD) was found to be useful as a devulcanizing reagent for rubber vulcanizates. The presence of fillers such as carbon black and silica was also found not to prevent the devulcanization reaction under scCO$_2$. Not only NR but also synthetic rubber vilcanizates were recycled by this chemical process.

Conclusion

NR is an excellent and indispensable material for many industrial and household applications. Lack of NR brings about a lot of problems in our society. Since NR is one of the plants, we should keep good fields for NR productions. Destroy of the NR plantations for economic growth may be wrong. Economic growth of the countries which are now producing NR can be attained by continuous production of NR. The countries with high performance rubber industries should appeal the importance of NR through „Science for Sustainability of NR" not only for industrial side but also for academic side. Good balance between the production and consumption surely works as a role for the construction of sustainability society on the earth.

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IL-06
CRYOGENIC TYRE RECYCLING,
AND ENGINEERING APPLICATIONS
FOR THE RECYCLED RUBBER

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Short presentation of RECIPNEU, Cryogenic Process description, Product specifications of cryogenic rubber powders / granulates, Main engineering applications / World Markets: Rubber Infill for artificial grass football fields, and Asphalt Rubber for road paving („*in-situ* wet process", up to 25 % rubber content in the bituminous binder).

IL-07
MONOMODAL AND BIMODAL POLYPROPYLENE (PP)/ETHYLENE-PROPYLENE COPOLYMER (EPC) REACTOR BLENDS FOR HIGH IMPACT STRENGTH APPLICATIONS

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A b s t r a c t

Beside the generation of polypropylene (PP) / ethylene-propylene copolymers (EPC) as heterophasic ethylene-propylene copolymers (reactor blends) characterized by a monomodal EPC rubber phase also bimodal reactor blends are able to be produced. The morphology of such blends determines the mechanical performance of the material in an essential way. EPC composition, compatibility between the phases, microrheological behavior and crystallization behavior determine the morphology formation during synthesis and following melt processing. Quantification of morphology by image analysis on the basis of electron microscopy as well as AFM delivered extensive information to establish morphology-property relationships. A controlled formation of the phase morphology enables an optimal mechanical performance of reactor blends for high impact strength applications.

I n t r o d u c t i o n

Next to conventional polymer blending by melt mixing also reactor blending became attractive for the generation of heterogeneous polymer systems[1]. Especially rubber modified thermoplastics with improved impact resistance have got an outstanding importance in many fields of technical applications, e.g. automotive industry. For a successful blend development the control of the correlations between the polymer components concerning the thermodynamic interactions and the rheological behavior as well as the fields of temperature and force affecting the material system is of fundamental importance. The tightly focused and controlled adjustment of morphology in heterogeneous polymer blends provides for an adequate property level. The realization of a definite phase morphology in polymer blends made via melt mixing or reactor blending is a complex process during which the type of the resulting blend morphology, heterogeneous or homogeneous, is initially determined by the miscibility of the components.

The heterogenization of PP via controlled downstream copolymerization of ethylene and propylene has been recognized as a powerful approach for toughness enhancement. The so produced heterophasic ethylene-propylene copolymers or reactor blends consist of a PP matrix and a dispersed EPC phase. In previous studies[1–3], the effect of EPC composition as well as matrix and dispersed phase molecular weight on the property profile of such heterophasic systems have been pointed out. It could be shown that reactor blends are able to be produced both with monomodal and bimodal dispersed EPC phase. Generally, the formation of dispersed phases in multi-component polymer systems depends on the component properties, such as melt viscosity,
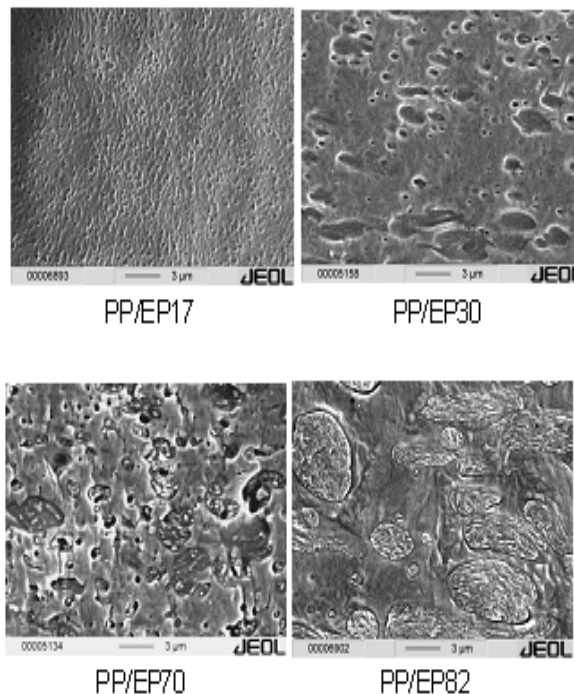

Fig. 1. **Phase morphology of monomodal dispersed heterophasic PP/EP copolymers[1];** the numbers mark the ethylene content of EPC, ω_{Et}^{EPC}

melt elasticity and surface tension. In the case of reactor blending the specific reaction conditions influence the formation of morphology primarily. On the other hand also the processing conditions like temperature, pressure, shear rate, residence time and the components ratio will influence the morphology formation process in the melt and the morphology-property relationship.

Morphology-property relationship of reactor blends

Heterophasic PP/EPC copolymers were produced by reactor blending varying the blend composition and ethylene content of EPC (ref.[1]). The studied reactor blends show a heterophasic morphology consisting of a PP matrix with dispersed EPC domains. A typical morphology of such reactor blends is presented in Fig. 1.

Normally, the EPC domains are amorphous, but they can contain a part of crystallizable ethylene-propylene copolymer incorporated as inclusions in the domains, because of interfacial energy conditions. The main influencing parameter on the overall blend morphology but also on the internal morphology of the composite dispersed phase particles is the EPC composition. A decreasing dispersed domain size is caused by a decreasing ethylene content of the EPC. The effect is ascribed from one side to the high degree of solubility of the propylene-rich EPC in the amorphous region between PP lamellae and from the other side to the decreased interfacial tension between the matrix and the high propylene containing ethylene-propylene copolymer. The reactor blend with high ethylene content (PP/EP82) exhibits coarse domains comprising a large semicrystalline core originating from crystallized EPC with long ethylene sequences. On the other hand, the ethylene-propylene copolymer with the highest propylene content (PP/EP17) organizes itself in a very fine dispersion. The domains are regularly distributed by both shape and size. The phenomenon is associated to the high degree of com-

Fig. 3. **Particle distribution of an EP reactor blend with bimodal phase morphology** at $\omega_{Et}^{EPC1}/\omega_{Et}^{EPC2}$=30/70 and $\varphi^{EPC1}/\varphi^{EPC2}$=30/70

patibility between the matrix and the propylene-rich dispersed phase as indicated by the single glass transition temperature that this material exhibits.

The pursuit of property optimization resulted in the development of reactor blends containing two different ethylene-propylene copolymers as a dispersed phase. This became possible by a two-step reactor blending procedure in which two separate EPC phases has been produced. Thus, different materials have been developed with different
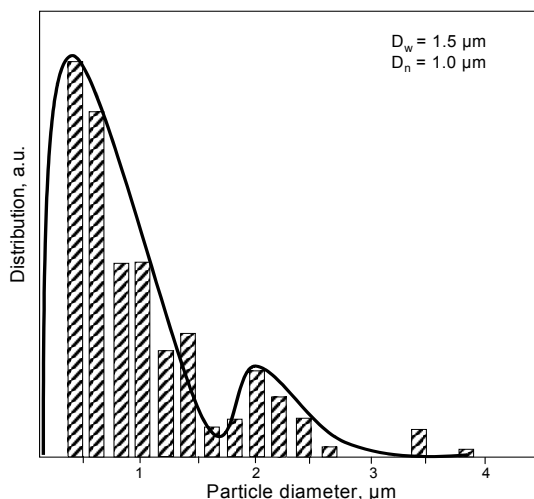

Fig. 2. **AFM micrograph of an EP reactor blend with bimodal phase morphology** at $\omega_{Et}^{EPC1}/\omega_{Et}^{EPC2}$=30/70 and $\varphi^{EPC1}/\varphi^{EPC2}$=30/70

Fig. 4. **Comparison between Charpy notched impact strength of an EP reactor blend with monomodal (PP/EP 17) and bimodal** (PP/EP 17/EP 70) **phase morphology**

weight content ratio $\varphi^{EPC1}/\varphi^{EPC2}$ and different composition ratio of the EPC $\omega_{Et}^{EPC1}/ \omega_{Et}^{EPC2}$, respectively. The design concept of such blends is to choose the elastomer components in such a way that the advantages of the one compensate the deficiencies of the other. Figure 2 shows an example of an EP reactor blend with bimodal phase morphology.

The influence of the phase morphology of the reactor blends investigated is demonstrated in Fig. 3. It becomes obvious that because of the specific technology of synthesis, i.e. the two-step reactor blending procedure in which two separate EPC phases has been produced, a bimodal particle distribution occures.

Generally can be stated that the ethylene/propylene ratio of EP is the main influencing parameter governing the phase compatibility of the investigated materials. A reduction of particle size with several orders of magnitude is caused with increasing propylene content in EP. Accordingly, increasing propylene content in ethylen/propylen copolymer was found to exert also a beneficial effect on the impact strength and the brittle to ductile transition temperature of the materials (Figure 4). The design concept of such blends is to choose the elastomer components in such a way that the advantages of the one compensate the deficiencies of the other.

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IL-08
BIOCRUDE TO BIOPLASTICS; A GLOBAL PERSPECTIVE ON EMERGING BIOPRODUCTS

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Introduction

Unprecedented climate changes of recent years and global warming issues have given yet another justification for an urgent transition from petrorefinery to biorefinery. The whole issue seems getting enough momentum in viw of scarcity and un=predictability about fossil fuel resources and at the same time availability of methods to transform abundant biomass into valuable biobroducts. Among various value-added products, the bio-plastics represent a significant potential of growth and success by utilizing renewable feedstock.

Traditionally, the bio-products made from different renewable feed stocks had played a major role in almost every area of application till the dawn of industrial revolution of 20th century when mass scale exploitation of hydrocarbon reserves led to manufacturing of petrochemical-based products for almost every industrial and consumer application. Although the current global output of biomass is about five times the world's annual need of energy and chemicals but, unfortunately, with the exception of wood and cotton, very few renewable materials are being consumed on mass scale to manufacture consumer goods[1]

Plastics, almost consumed in every segment of economy, have been traditionally manufactured from petroleum based synthetic resins. After the discovery of Beckolite in 1910, a rapid growth was seen in following decades and by 1950 a staggering amount of 2.3 million ton of synthetic resin was consumed by plastic industry in USA with a healthy 5−7 % annual growth[2].

Hydro-carbons to carbo-hydraes
A Pragmatic approach

About 150 million ton of plastic is consumed on global basis with largest application in packaging industry[3]. The overall market distribution as shown in Fig. 1. The huge amount of synthetic resins and plastics has posed a number of environmentally related hazards such as possible links between plastics and endocrine disruptors, extensive use of chlorine for PVC plastics, generation of volatile organic compounds (VOC), and solid waste disposal issues. Further, glass-fibre, the main reinforcement material has its own health and environmental related concerns. On top of this, tougher environmental regulations and public awareness has forced the plastics industry to give serious consideration to renewable carbohydrates as potential feedstock for its products.

Bioplastics
Potential growth and market trends

Recent years have witnessed a global surge in research and industrial development to introduce novel consumer bioproducts. In case of bioplastics, EU and USA has seen significant growth in this area during last decade. Aggressive initiatives have led to the development of
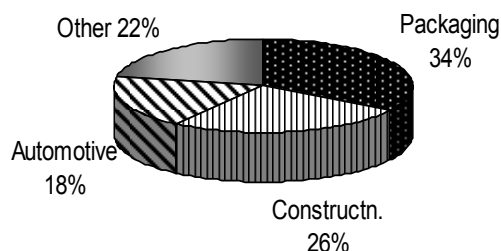

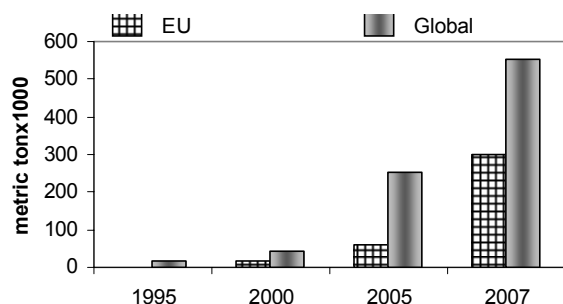Fig. 1. **Market distribution of plastic consumption**

Fig. 2. **Phenomenal growth of bioplastic industry in EU**

Fig. 5. **Starch based commercial products from EarthShell Corporation, MD, USA (ref.[8])**

a highly competitive and dynamic bioplastics market in EU, Fig. 2, which represents almost 40 % of global market[3,4].

Major chemical companies like Eastman Chemicals, BASF, and DuPoint have been responsible for most of the development of biodegradable polymers and bioplastics in Europe by spending more than 24 million US$ in recent years[4] and launching their brand name biobased resins and plastics like „Eastar", „Ecoflex", and „Biomax".

Biodegradable food packaging and beverage containers are top priority for European researchers and product developers. Mater-Bi™, a biopolymer developed by Novamont SPA Italy, comes from renewable raw materials of agricultural origin and from non-genetically modified starch. Novamont manufactures and sells various lines of

biopolymers for a variety of manufacturing processes[5]. Other major players in this area are Vegeplast S.A.S. France and Natura Packaging , Netherland.

In North America, USA multi-nationals are competing hard to install manufacturing facilities at ideal locations. Cargill Dow has installed a bio-polymer manufacturing plant in Blair, Nebraska, having a 140,000 tonnes annual production capacity of polylactic acid (PLA) from corn starch. The product, NatureWorks™, has a world market of about US$ 10 billion and is being used in the manufacturing of thermoformed trays and lids of food packaging and fibre-fill comforters and pillows[7].

Other major companies involved in commercial production of corn starch based biopolymers are Shell and DuPont, whereas the latter one has built a plant in North Carolina to manufacture a copolymer named „Sorona".

The starch-based bioplastics are gaining access into every area of commercial applications traditionally served by synthetic plastics like packaging, building and construction, automotive, electronics and agriculture. Of all these, industrial and food packaging is proving a fast growing sector with product range as diverse as biowaste bags, loose-fill/ films, and shaped/blocked packaging for electronics and toys. The bio-packaging for organic food has been received very well by consumers, especially in EU, due to its unique characteristic of water permeability which keeps fruits and vegetables fresh. Above all, being

Fig. 3. **Compostable food packaging from Natura Packaging Netherland[6]**

a   b

Fig. 4. **Products developed from PLA- NatureWorks™.**
(a) First compost-able PLA bottle by „Ihr Platz" Germany[6],
(b) Food packaging developed by „Huhtamaki", Finland[6]

Fig. 6. **TOYOTA „Ecoplastic" Tire Cover in „New Raum" Model[9]**

compost-able makes these packaging materials even more attractive as eco-friendly.

Automotive industry is another potential growth area for bioplastics and natural fiber composites which consumes about 2.5 million ton of plastic annually. However, due to some exceptional performance requirements like durability and safety, there are various challenges in developing true functional and biodegradable plastic parts fro automotive industry. So far, only Toyota Motor Corporation and GoodYear Tire have made significant efforts in this regard. Toyota is already utilizing its auto-grade bioplastic, EcoPlastic, made from polylactic acid (PLA). used for the tire cover is made from plants, such as sweet potatoes and sugarcane. Enzymes are used to break starch in the plants down into glucose, which is fermented and made into lactic acid. This lactic acid is polymerized and converted into a plastic which can be used in the manufacture of products after being heated and shaped.

Toyota is also installing a new plant in Japan to manufacture PLA from annually renewable resources such as sugar cane.

GoodYear has been marketing successfully its Eco-tyre series for the last 3 years utilizing Novamonts MaterBi.

Mazda Motor Corp. and an industrial consortium have developed a new bioplastic made through a fermentation process using natural materials such as fermented starches and sugars derived from corn. Not only is the new bioplastic carbon-neutral (with only 12 percent petroleum content and reduced energy requirements for manufacture) but it is stronger and more heat-resistant than other bio-plastics, making it a viable candidate for a wider range of automotive applications[10].

The use of plant cellulose fibres as reinforcement material in plastic composites for automotive applications is another potential area in which high energy consuming glass fibre can be replaced with renewable feedstock. The European automotive industry has taken the lead in this area and consumes about 22,000 metric tons of natural fibers annually in low-stress applications in luxury cars. In North America, industrial and research sectors are showing a great deal of interest but the market demand has been only recently picked up to modest levels of about 45,000 metric ton[3].

Challenges and future outlook

There have been significant efforts during last decade to launch new bio-products based on renewable bio-crude but unfortunately very high material development costs and small production capacities have resulted in non-competitive prices of basic raw materials for bioplastics compared to conventional plastics. Some other notable challenges can be summarized as;

− Lack of political initiative and urgency towards bio-plastics compared to biofuels.
− Need of an efficient biomass harvesting and a reliable supply chain network with adequate crop storage and
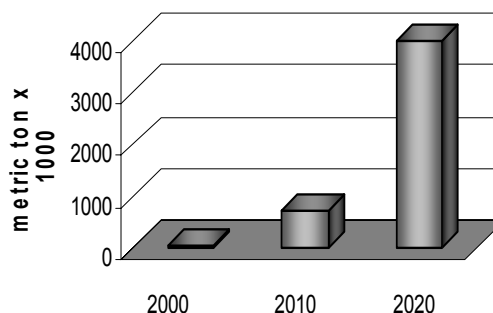
Fig. 7. **Biocrude to bioplastics;** EU projection for bioplastic growth[11]

separating systems.
− Need of same political initiative and urgency towards bioplastics as shown for biofuels.
− Need of coherent research and development efforts to solve pertinent technological hurdles like product standardization, food safety and hydrophilic characteristic of starch/protein based bioplastics.

In spite of all challeneges, there exists a tremendous potential of growth for bioplastics to replace petroleum based conventional products.

The emerging but functional bio-products also seem to have a true commercial success not very far away as their potential of saving significant amount of CO_2 emissions can be utilized as potent marketing tool and might be used as „emission trading" incentive which is going to be implemented by 2008 under Koyoto Protocol[4]. Plastics and composites manufacturing sectors need to make a cautious and smart move to drive their present technology in this transition period towards bio-based economy. A more feasible approach in the current scenario seems to remain focused on developing renewable technologies integrated to the existing manufacturing infra-structure. Only this approach will make a good economic sense.

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IL-09
SCRATCH RESISTANCE OF AUTOMOTIVE COMPOUNDS

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Introduction

The goal of our research on scratch resistance was to understand the mechanism leading to scratch visibility.

Scratch resistance is an aesthetic property that plays a major role in interior applications. It is not the target to make the material resistant towards scratches at all but to reduce the visibility of scratches. The common hypothesis to explain scratch visibility was in the beginning of this project, that scratching induces cavitation of rubber particles leading to a visible stress whitening (blushing) effect.

Approach

In order to start the research project on scratch resistance, different interior materials have been investigated in detail by using several microscopic techniques. The idea was to describe the difference in the appearance of scratches. The literature has been studied, where mainly Prof. Sue from Texas University was highly involved in introducing new test methods (ISO standard) and describing scratches in polymers. The goal of this project was to understand the origin of scratch visibility and to reduce that visibility; therefore scratches have been investigated using different techniques. A relation between ingredients and scratch visibility was established.

Experimental

In order to measure the roughness and the depth of scratches measurements have been performed using standard roughness measuring equipment (profilometer). Furthermore light microscopy, electron microscopy (SEM) and different scratch measurements have been performed. The scratch measurements were based on the Erichson test which uses a ball like tip and a fixed force and speed to scratch over a sample. The scratch visibility is then measured optically by measuring a grey scale and comparing the scratched and unscratched regions. This leads to the DL value describing scratches. Another method is based on sand paper, here one scratch with a sand paper is performed and again the grey scale difference between scratched and unscratched region is compared.

Literature

Misra et al. describe that visibility of scratches is related to the shape and size of the plastic deformation. „The light scattering efficiency was observed to depend on extent and severity of plastic deformation. Severely deformed fibrils and tearing/breaking produced greater scratch visibility than smooth and well defined grooves".

Sue et al. describe the influence of talc and slip agents on scratch visibility, scratch hardness and coefficient of friction during scratching. It is claimed that the negative influence of talc is related to the increase in rigidity and the debonding of talc and PP during scratching leading to visible deformations. Slip agents reduce the maximum tensile stress induced by the scratch. They do this by reducing the friction during scratching. The reduced tensile stress on the other hand leads to a more tough deformation meaning less visible plastic deformation (cracks, crazes, fibrils etc.).
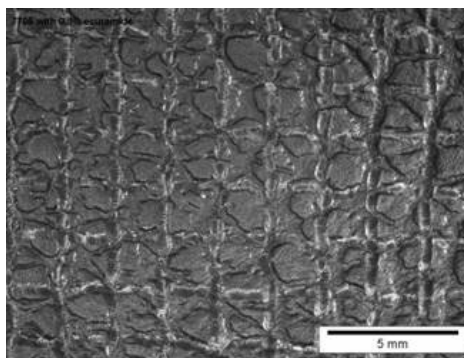
Results

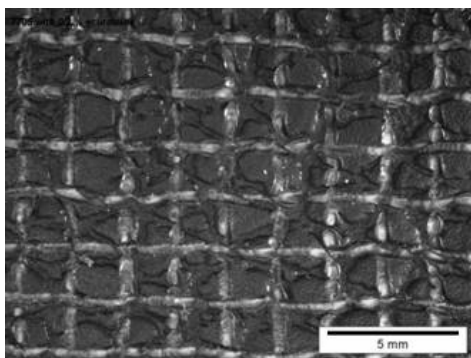Fig. 1. **Scratches on PP compound containing a high amount of slip agent**

Fig. 2. **Scratches on PP compound containing a low amount of slip agent**

Conclusions

A hypothesis to explain the mechanism of scratching and reduction of scratch visibility is being described. The hypothesis is based on the idea that scratch visibility is mainly related to surface deformation during scratching. This deformation and fracture leads to rough surfaces inside the scratch and those surfaces scatter light and appear therefore whiter than the non scratched surrounding. The hypothesis is based on microscopic observations of scratches performed under standard conditions with a nee-

High content of SL

Low content of SL

Fig. 3. **Scratch roughness in samples with high and low slip agent content**

dle like pen. Roughness and scratch depth measurements support the idea that surface roughening is responsible for scratch visibility. Based on these ideas materials with improved scratch performance can be developed. The addition of slip additives leads to major improvements. Those slip agents change the interaction of the steel pen with the material leading to a sliding movement over the surface. The material is not broken and therefore keeps, besides an indentation of several micrometers, its original roughness leading to no whitening inside the scratch. Scratch resistance is also dependent on texture and roughness of the injection moulded part. The smoother the surface the better the scratch resistance.

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IL-10

POLYPROPYLENE/ORGANOCLAY COMPOSITE FIBRES, EFFECT OF ORIENTATION ON STRUCTURE AND MECHANICAL PROPERTIES

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Organoclays are effective solid additives for polypropylene composites and composite fibres[1-3]. The development of the polypropylene (PP) based nanocomposites, containing layered silicates is focused mainly on improvement of mechanical properties of polymers, enhancement of barrier against gas permeability, thermal stability and decrease in combustibility. Nanocomposite fibres based on fibre-forming PP with improved mechanical properties are particularly interesting because of their contemporary high production and poorer elastic modulus, relative to polyamide and polyethylene terephthalate fibres.

In this paper, the polypropylene (PP)/organoclay composite fibres, their supermolecular structure and selected mechanical properties are presented. In the experimental work the commercially available organically modified montmorillonites (Cloisites) as well as selected commercial compatibilisers-dispersants were used. The effect of composition, structure and average orientation of the PP composite fibres on their mechanical properties is discussed in the paper, as well.
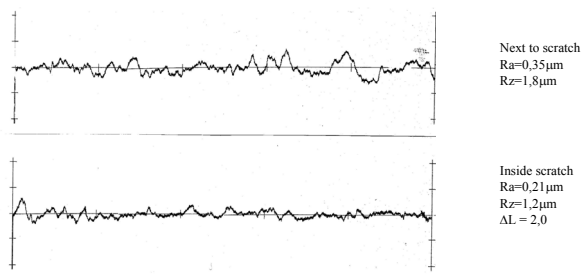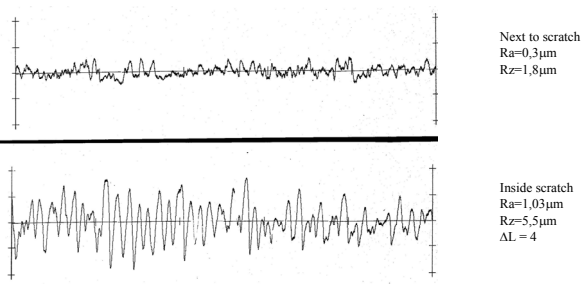
Two commercially available types of polypropylene (PP), produced by Basell Co., were used in the experimental work: polypropylene PP Moplen 500R (PP500R) in powder form and fibre-grade polypropylene PP Moplen 561N (PP561N).

The organoclays based on montmorillonitte (MMT) used in this work were Cloisite 15A and Cloisite 30B (C30B), produced by Southern Clay Product, Inc, Gonzales, TX 78629, USA.

Commercially available polyesters (PET, PBT and PTT), polymethyl metacrylate (PMMA), copolymer of ethylene and methyl metacrylate (Luc) as well as oligomeric polyester wax Licowax E (LiE) and alkylpolydimethylsiloxane (TEG) were used as other additives.

PP500R, organoclay and additives were melted and kneaded using twin screw corotating extruder ϕ 28 mm. Temperatures of the extruder zones from feedstock to head were 80, 150, 270, 280, 280, 280 and 280 °C. The extrudate was cooled and cut. The concentration of organoclay in PP500R was 10.0 wt.%. Content of compatibiliser was selected for individual samples.

The chips of PP500R organoclay concentrates and PP561N were mixed and spun using a single screw extruder ϕ 30 resp. 16 mm and a spinneret with 40 resp. 13 orifices. The spinning temperature was 280 °C. Fibres were drawn using laboratory drawing machine at drawing temperature 120 °C. Fibres were drawn for various drawing ratio including maximal one.

The PP/organoclay composite fibres were prepared. The composition and spinning condition were selected. A positive effect of organoclay on mechanical properties of PP composite fibres was found for low filler concentration about 0.1 wt.%. Tenacity and Young`s modulus are strongly affected by deformation of fibres during drawing. The main contribution of organoclay to mechanical properties of PP composite fibres consists in higher orientation of fibres corresponding with higher maximal drawing ratio (Fig. 1, 2). Besides, composite fibres exhibited lower non-uniformity as compared with unmodified fibres. MMT acts in PP as nucleating agents and increase the crystallization rate of PP. The PP composite fibres, formed at maximum

Fig. 2. **Young`s modulus versus drawing ratio of PP/C15A (0.1 %) composite fibres**

Table I
Tenacity T, elongation E and Young`s modulus YM of PP/ organoclay C30B composite fibres (maximal drawing ratio)

Content of silicate and additives	T [cN/tex]	E [%]	YM [N/tex]
PP561N+PP500R	71.7	20.7	8.26
0.1% C30B	71.1	20.5	8.18
0.1% C30B 0.1% (PMMA+TEG)	60.6	21.9	7.36
0.1% C30B 0.1% (Luc+TEG)	73.9	20.0	9.17
0.1% C30B 0.1% (PBT+PTT+LiE+TEG)	69.6	22.8	8.69
0.1% C30B 0.1% (PET+PBT+LiE+TEG)	77.8	19.6	9.68
0.1% C30B 0.1% (PET+PBT+LiE)	71.3	20.9	8.44

drawing ratio, exhibited higher tensile strength and Young's modulus in comparison with unmodified fibres, as a rule (Table I). Positive effect of ethylene acrylate copolymers and polyester additives coupling with polysiloxanes on tenacity and Young`s modulus was found.

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Fig. 1. **Tenacity versus drawing ratio of PP/C15A (0.1 %) composite fibres**

IL-11
INTERFACIAL EFFECTS IN ANISOTROPIC ELASTOMER-NANOCOMPOSITES

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The promise of Nanocomposites is to achieve combinations of properties, by exploiting interfacial phenomena or the multifunctionality or surfaces and in addition preferential orientation effects. The inherent challenge related with these goals lies in reaching an optimum dispersion of the nanoscaled fillers, tailoring the role of interfaces as well as the spatial architecture of the composite.

Functional polymeric particles, nanoplatelets, short and long nanofibers have been prepared and incorporated into rubbers in order to impart stimuli-adaptive properties to the crosslinked elastomers.

Spherical polymeric nanoparticles with variable functionality were prepared by cross-linking emulsion polymerization in the size ranging from 30-400 nm (ref.[1]).

Cellulose nanofibers were in-situ generated by an original „dynamic co-coagulation" process of water-soluble cellulose polyelectrolytes and rubber latices[2]. The size and the aspect ratio of the Cell II fibers are controlled by the shear rate applied in the flow reactor during the co-coagulation.

Alcaline suspensions of Na-Montmorilonite and rub-ber emulsions were submitted to „dynamic co-precipitation" in order to increase the degree of exfoliation.

Microglassflakes were mixed into bulk rubbers by using a two roll mill and subsequently vulcanized in a heating press at 160 °C.

Starting from properties imparted by nanoscaled fractal filler networks (carbon black and silica), the effects of in situ-formed cellulose fibers, layered-silicates and micro-glasplatelets will be presented. Physical properties, which are directly related to the interfaces between the constituents of the composites under consideration such as dynamic mechanical properties, diffusion and permeation of organic molecules will be related to the morphology of the nanocomposites.

Essential differences in mechanical properties and relaxation impacted by nanoparticles and nanofibers arise from orientational effects and direct phase bonding. The swelling behavior and diffusion of low molecular weight substances reveal high density interphases, which are more pronounced in the case of nanofibers and nanoplatelets than for silica and micro-glassflakes.

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CL-1-01
STUDY OF JUTE FIBRE-REINFORCED POLYESTER COMPOSITE

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Chemically modified Jjte fibre (Hessian cloth) and e-glass fibre (mat)-reinforced − unsaturated polyester (USP) resin composites were prepared using the hand lay up technique at room temperature (25 °C). A strong interfacial adhesion between jute and polyester was obtained using chemically modified jute fibre. This modification involves the introduction of reactive vinylic groups at the surface of the fibre and matrix through esterification of jute hydroxyl groups by methacrylic anhydride. Jute fibre content in the composite was optimized with the extent of mechanical properties and composites with 25 % jute show higher mechanical properties. The mechanical properties are found to increase with the incorporation of dissimilar portions of glass fibre into the jute-reinforced composite. Among all the resulting hybrid composites, the composite with a jute to glass fibre ratio of (1:3) demonstrate the improved mechanical properties such as tensile strength (TS) 130 %, tensile modulus (TM) 50 %, bending strength (BS) 150 %, and bending modulus (BM) 225 % over untreated jute composite. Scanning electron micrographs of tensile fracture surfaces of unmodified and modified jute-polyester composites clearly demonstrate better fibre-matrix bonding in the case of the latter.

CL-1-02
NEW GENERATION TECHNOLOGY FOR SURFACE FINISHING OF AUTOMOTIVE PLASTIC COMPONENTS

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A b s t r a c t

Decorative finishing of injection-moulded automotive components requires the application of decorative surface finishes. Currently available alternative finish technologies include: solvent- or water-born wet paints, in-mould colour achieved by pigments and dyes, or in-mould decorative films. Wet paints, most commonly used for decorative finishing of automotive plastic components exhibit very low transfer efficiency typically not exceeding 30–35 %. Consequently they constitute a major source of solid waste and emit VOC's, second only to the vehicles exhaust emission. Powder coatings, an attractive 100 % solvent-free alternative technology, achieve 90–99 % transfer efficiency. However, they require electrostatic deposition of charged particles of powder coating. Hence, powder coatings are generally only used on inherently conductive metallic components, such as in the automotive, marine and construction industries, or on relatively costly conductive polymers. A rapid increase of powder-coating technology usage is also observed in the furniture industry.

The key barriers to wide introduction of powder coating technology in plastics surface finishing are: non-conductive plastic surfaces, inadequate adhesion to commodity plastics such as polypropylene blends, and frequently − the absence of low-temperature curing powder coatings. This paper presents theoretical and practical aspects of novel technologies facilitating successful powder coating of automotive and commodity plastics, eg: (*i*) providing adequate surface conductivity of polymeric substrates, and (*ii*) coating adhesion.

T h e   p r i n c i p l e s   o f   e l e c t r o s t a t i c   p o w d e r - c o a t i n g   t e c h n o l o g y

The principles of electrostatic powder-coating technology are schematically illustrated in Fig. 1. The individual powder particles charged by a corona discharge ioniser (see Fig. 1a) form a fluidised powder cloud in which all particles, bearing identical charge, repel each other. The oppositely charged conductive substrate (see Fig. 1a) attracts all particles which electrostatically self-assemble on its surface forming a semi-continuous particulate layer. At the next stage of the process the particulate-coated substrate is admitted to a curing oven in which three consecutive processes take place: (1) particles melting; (2) fluid self-levelling, and (3) cross-linking.
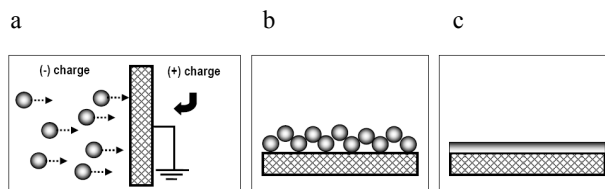

Fig. 1. **Basic principles of powder-coating technology:** (a) electrostatic powder transfer; (b) electrostatic self-assembly of charged particles; (c) self-levelled coating layer

Surface-conductive and adhesion enhancing polymer interphases

The lack of bulk and surface conductivity of polymers can be, to a limited extent, overcome by the use of either, conductive polymer blends containing adequate levels of conductive fillers, or by the use of conductive primers applied prior to powder coating deposition. These can be alternatively achieved by the addition of conductive carbon black (10−16 %), carbon nano-tubes (2−5 %), or other additives. The above solutions are, however, not sustainable due to the high material cost, and high volatiles content in commodity conductive primers.

A plausible solution of the above problems can be achieved by surface engineering of polymers with the use of specialty multi-functional molecules. Once grafted onto the surface of a commodity polymer, eg. polypropylene, nylon or other automotive plastic, they provide the following properties of the interphase without adversely affecting the bulk properties of the underlying substrate material:

−   electro-conductivity, and
−   adhesion promotion of the powder-coating polymer.

Figure 2 provides a schematic illustration of the principles underlying the design of such multi-functional interphase. A nano-layer of conductive molecules (item [2] in Fig. 2) is chemically grafted onto the surface of a non-conductive polymer at the concentration facilitating uniform charge transfer between adjacent molecular clusters. This, in turn, leads to electro-deposition of an even layer of powder coating particles across the whole surface of the polymeric substrate. The untreated polymers typically exhibit surface resistivity in the order of 10^{14} Ω/square, which completely impedes electrostatic deposition of charged particles. To achieve uniform transfer of powder coating particles, and facilitate formation of a smooth coating layer after melt-flow and self-levelling of molten particles, the resistivity of polymer surface must fall below the threshold value of approximately 10^{-11} Ω/square. Data in

Fig. 3. **Surface resistivity of Nylon 6-6:** (a) untreated; (b) conductive adhesion promoter molecules *A*; (c) conductive adhesion promoter molecules *B*

Before coating   During coating   Coating completed

Fig. 4. **The effectiveness of powder coating particles transfer onto the surface of PP-based substrate surface-modified by electro-conductive molecules *A***

Fig. 3 demonstrate significantly improved surface conductivity (i.e. reduced resistivity) of Nylon 6-6 after surface grafting two alternative types of conductive adhesion promoter molecules: '*A*' and '*B*'.

Photos in Fig. 4 illustrate, in turn, the effectiveness of electrostatic transfer and deposition of powder coating particles onto the surface of PP substrate whose surface has been modified with electro-conductive adhesion promoter molecules '*A*' providing surface resistivity of approx. $2 \cdot 10^{-10}$ Ω/square. An excellent quality of progressive powder coating deposition over the whole substrate surface is clearly demonstrated through this sequence of photos.

During the subsequent heating and melting of particles and ensuing film forming, the surface-grafted conductive molecules uncoil, as schematically illustrated in Fig. 2b, and interpenetrate the polymeric coating layer, hence enhancing the coating's adhesion to the surface of the coated product.

Fig. 2. **Schematics of design principles of multi-functional polymer interphase for surface electro-conductivity and adhesion enhancement:** (a) electro-conductive interphase with electro-statically self-assembled particles of powder coating: [1] powder coating particles;[2] nano-layer of conductive adhesion promoter; (b) unfolded molecules interpenetrating into a layer of powder coating particles

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CL-1-03
ANALYSES OF INHOMOGENETIES OCCURRING IN THE INJECTION PROCESS

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Injected plastic parts are used mainly in consumer and automotive industry, in electrotechnics, electronics and in packaging. For all these industries there is typical very fast moral product obsolescence caused by dynamics of market development and competitive environment as well as fashion and demanding consumers. Situation in a continuously changing market needs fast development and construction of injected products and tools necessary for their production.

Moreover, in the global market the teams who solve part design, tool design and production technology can be thousands of kilometers and several time zones from one another. If such teams do not have precise values describing design, tool and technology, their communication can be very complicated or conflicting and mainly it leads to increase of costs and longer time for launching a new product in the market. Mainly the second aspect can lead to big financial loss from the time when we are not the first and only in the market who offer a new product.

Analytic SW Moldflow with is complex solving of the whole injecting process offers a global service that is always a step ahead of your plans. That means that designing teams can get perfect instruments for communication in global world and precise values describing both the injected part and the tool and technical parameters.

The analytic SW Moldflow works on the basis of final elements method. The final element method is a modern, highly efficient numeric method for solving technical and scientific tasks. Nowadays it is considered one of the most effective approximate solving methods.
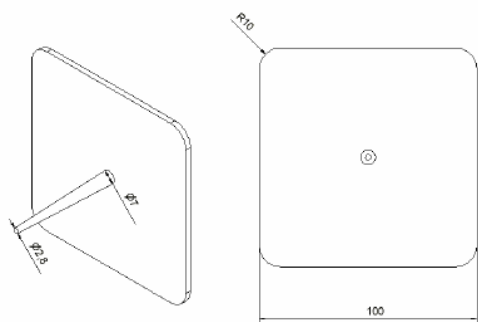
Fig. 1. **Injected sample part**

Fig. 2. **Temperature field in the section of the injected sample part**

Inhomogeneties in the injection process occur mainly due to inhomogeneous pressure and temperature field. Different temperatures in section and length of flow path lead to unbalanced changes of volume during cooling of the polymer melt and during polymer transition from visco-plastic state to the solid stage. Occurrence of inhomogeneities is affected by injection speed, packing and cooling speed. Just thanks to the Moldflow volume analysis we are able to describe these stages very well.

We described temperature field of a sample of an injected board 100×100 mm, 3 mm thick, injected in speed of 60, 100 and 140 mm s^{-1}. We took samples at four different distances from the gate. We can also compare morphologic structure of the sample in microtone cuts with temperature field in the cavity analyzed by Moldflow volume analysis. Inhomogeneous temperature and pressure field affects not only morphologic structure but also mechanic properties as we can see on the dependence of tensile module and direction of drawing force and injection speed. Also changes in morphologic structure show different values of the tensile module in the section of the product. In this case the module was measured by nanoindentation, i.e. indenting a triangular prism into the sample. The tensile module is calculated from the course of indentation.

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CL-1-04
EFFECT OF NANOCLAYS ON THE FLAME RETARDANCY OF POLYMER NANO-COMPOSITES

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Highly flammable polymers, such as polyolefins, can be produced flame retardant either by organo-halogens or metal (Mg, Al) hydroxides. Application of halogen based flame retardants, however, is accompanied by an evolution of thick smoke and highly acidic hydrogen halide gases. Large amounts (60 % w/w) of Mg and Al hydroxide required to attain acceptable flame retardancy has a negative impact on the end-use properties of polymers[1].

Unlike traditional flame retardants, flame retardancy of polymer nanocomposites is based on the char formation and its structure[2]. The char insulates the polymer from heat and forms a barrier reducing the escape of volatile gases from the polymer combustion[3]. Moreover, the filler content in nanocomposites usually do not exceed 5 % w/w[2]. Reduction of flammability together with high strengths and potential recyclability are thus the main attributes in increasing the application of polymer nanocomposites in automotive industry.

In this paper the effect of nanoclays on flame retardancy of polymer nanocomposites is investigated. In order to unravel the influence of filler and polymer matrix structure, composites based on organoclays (Cloisite 30B, Nanocor I-3TC, Nanoblend 1001) and polymer matrix (polypropylene, polyamide, polyethyleneterephtalate and polystyrene) have been investigated. The composites were prepared by melt blending in a twin-screw extruder and/or in a mixing chamber. The filler content was kept constant at 5 % w/w. The flammability behavior was investigated by the determination of limited oxygen index (LOI), ignition point (IP) and inflammability point (IFP). In addition to the above regulatory flame testing methods, thermogravimetric analysis has been also examined. The data acquired from TGA include the oxygen onset temperature (OOT), peak maximum temperature (PMT) and solid residue at 500 °C.

DTA curves and flammability measurements for PP/clay composites (Fig. 1, Table I) indicate a considerable increase in the oxygen onset temperature and 30 °C en-

Table I
Flammability data for PP/clay nanocomposites

Sample	IP [°C]	OOT [°C]	PMT [°C]
Neat PP	350	210	310
PP/ clay	380	305	380
Modified PP/ clay	–	335	405
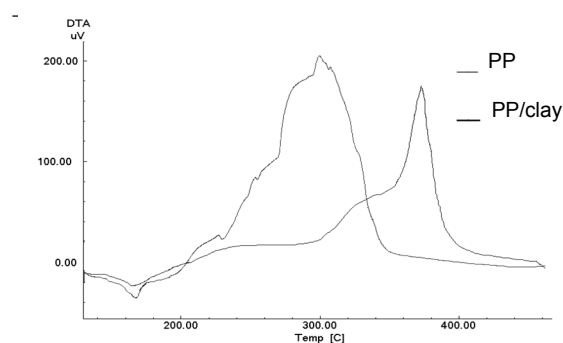
Fig. 1. **DTA curves for neat PP and PP/clay nanocomposites**

hancement of the ignition point. By the application of reactive modifier, further improvement of OOT and IP have been observed, however, only a small effect on the value of limited oxygen index (Fig. 2) was observed.

Further examination of the combustion process under fire conditions revealed a considerable different flame mechanism in both, unmodified and modified PP/clay nanocomposites in comparison to neat PP.

Whilst during burning of PP, typical polymer flow accompanied by melt dripping is evident (Fig. 2a), PP/clay composites (Fig. 2b,c) did not indicate any flow or melt dripping.
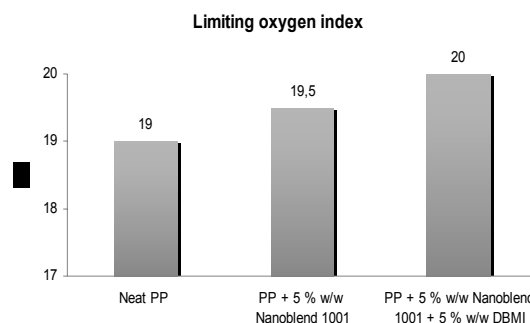
Fig. 2. **LOI of PP/clay nanocomposites**

a   b
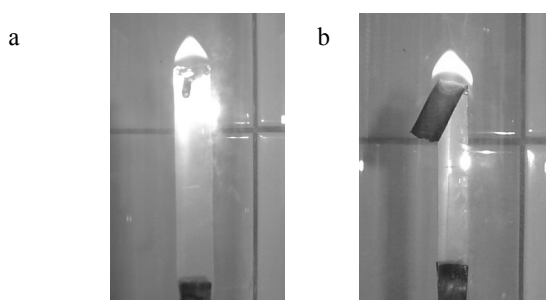
Fig. 2. **Combustion of neat PP (a) and PP/clay composite (b)**
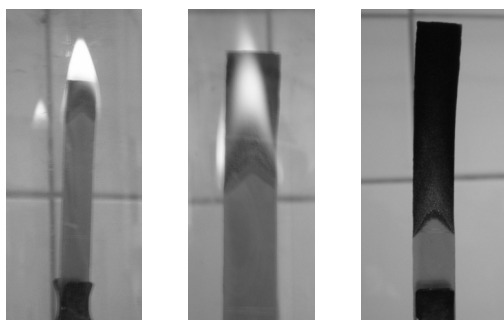
Fig. 3. **Combustion process of modified PP/clay composites**

In our recent work it was found that the application of reactive modifiers in PP/organoclay nanocomposites resulted in an extensive exfoliation of silicate platelets and a better filler dispersion[4]. Observation of the combustion process from its beginning from the inflammation point (Fig. 3a) followed by burning (Fig. 3b) up to the termination of flaming (Fig. 3c) highlight the mutual effect of the nanoclay and modifier on the flame retardancy mechanism of PP/clay nanocoposites. Unlike unmodified composites (Fig. 2b), the samples kept their original size and shape and no deformation was observed during the burning process.

From Tables II and III is evident that the most significant effect of nanoclays on flame retardancy was observed in PET nanocomposites.

In the presentation, further insight of the effect of nanoclay structure and modification of nanocomposites on the flame retardancy and combustion process will be presented.

Table II
Flammability data for PET/clay nanocomposites

Sample	LOI [%O_2]	IP [°C]	OOT [°C]
Neat PET	24,5	322	320
PET/ clay	28,0	354	390

Table III
Flammability data for PS/clay nanocomposites

Sample	LOI [%O_2]	IP [°C]	OOT [°C]
Neat PS	19.0	430	290
PS/ clay	19,5	460	365

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CL-1-05
HYBRIDE COMPOSITES OF PE WITH BIRCH FIBERS AND NANOCLAY

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Maximization of Impact strength, Tensile, Modulus of natural fibre and nanoclay filled polyethylene was studied by applying Central composite design (CCD): 2^3 + star design which studies the 3 experimental factors (NC, MAPE,DCP) in 16 tests. The order of the experiments was randomized.

M a t e r i a l s   u s e d   w e r e   a s   f o l l o w s

Thermoplastics: Linear low density polyethylene was supplied by Novacor chemicals Ltd (NPE, granular).
Fibres: As a wood fiber we used birch fibre (20−60 mesh) which was prepared in laboratory.
Coupling agents: Maleated polyethylene (MAPE) was supplied by Eastman chemical company as a coupling agent.
Initiator: Dicumyl peroxide (DCP) 98% purity, supplied by Sigma. It has a melting point of 39−41 °C and it will decompose rapidly above 120−125 °C.
Filler: Cloisite Na+ Nanoclay (NC) was used as a filler.

Compounding

A 30 wt.% PE with MAPE and Cloisite Na+ Nano-clay was melted on rollers at 170 °C at 60 rpm. Then birch fibres were added to the mix followed by the addition of the remaining PE, within 7 min. The mixture was removed from the rollers five times with 3 min mixing times. Finally the DCP was added and mixed for 3 min. The composite was then removed from the roller and cut into strips large enough to fill the moulds.

Compression moulding

The strips were pressed into the dog bone shaped moulds (ASTM D638 Type V). Twenty-two specimens (10 for tensile testing «thick» and 12 for impact strength testing «thin») were simultaneously prepared in the same mould. The mould was maintained at 170 °C, in a DAKE PRESS. The pressure was increased to 20 MPa and held for 15 min. After the high pressure stage, the press was cooled below 60 °C by circulating cold water in the platens.

The dimensions of the tensile specimens were as follows: width, 0.29−0.32 cm, and thickness, 0.29−0.32 cm. Width of impact test specimens was 0.27−0.29 cm and the thickness was 0.16−0.19 cm.

Mechanical tests

All the specimens were polished, then equilibrated in testing room overnight, and then the width and the thickness was measured with a micrometer.

Tensile testing was performed on an Instron Model 4201 at 23 °C and 50 % relative humidity, and all the broken specimens were kept for further study. Such analysis included SEM, FT-IR, TGA *etc*. Impact strength was determined by a Wick tester at ambient temperature (about 23 °C).

Summary

Maximization of Impact strength, Tensile, Modulus of natural fibre and nanoclay filled polyethylene as achieved by applying Central composite design is presented in the following figures.

In summary the Strength and Impact values of composites increased simultaneously when compare to pure PE as follows: Impact strength increased from 115 kJ m^{-2} to 171 kJ m^{-2} , Stress from 25 MPa to 49 MPa and Modulus from 555 MPa to 926 MPa. Composites samples were examined directly by ESM and explanation of presented behavior is advanced.
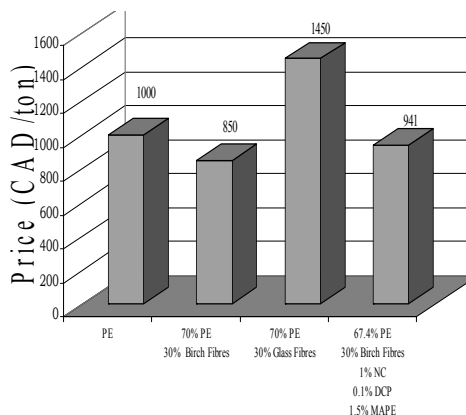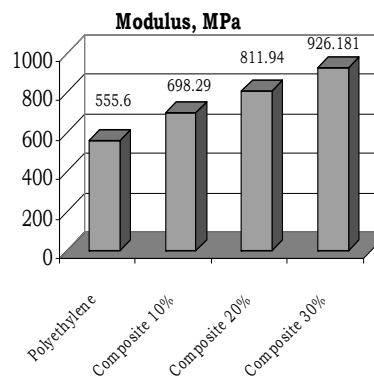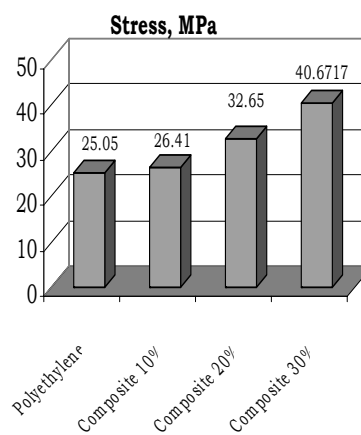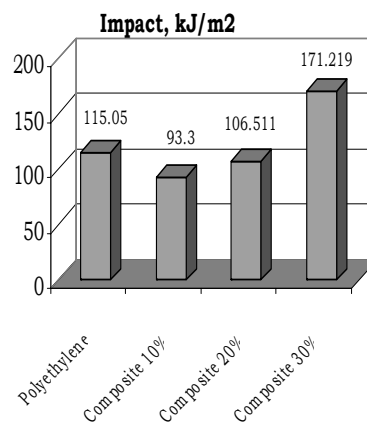
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CL-1-06
COMPUTATIONAL SIMULATION OF COMPOSITES REINFORCED BY SHORT FIBERS

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Composite materials reinforced with stiff micro/nano fibers are becoming important structural materials. Large differences in the stiffness of the matrix and fibers, large number of the fibers and large aspect ratio make the accurate analysis of such structures very cumbersome. The bearing capacity of such materials, stiffness evaluation and material design require correct analysis of the material behavior up to the micro- or nano-scale. Large gradients in displacement, strain and stress fields are responsible for low efficiency of computational methods like classical FEM and BEM. Billions of equations would be necessary to simulate accurately enough the interactions fiber with matrix, fiber with other fibers and other effects with these methods. We developed a new method, called the Method of Continuous Source Functions (MCSF) using both discrete and continuous source functions inside fibers to simulate the compatibility conditions between the fiber and matrix. It enables considerably reduce the problem.

Only straight and regularly distributed fibers are considered in the present models. Both ideal cohesion and de- and re-cohesion effects are possible to model.

The ordered fibers enable to obtain a material, which can have very attractive mechanical properties. It can be much stiffer and stronger in one direction than in other directions. The direction can be locally changed according to the loading conditions. There are some technologies like casting which enable to control the processing of the composite.

From the mechanical point of view, both near and far field are important to be accurately simulated. The near fields are responsible for the bearing capacity of the composite and the far fields are responsible for stiffening effect.

As the source functions are similar also for other physical fields like thermal conductivity, or electro-magneto- mechanical fields, the method used in the present simulation can be used also for modeling of such problems, although the singularities can be different for different fields, but the mechanical fields contain all, weak, strong and hyper-singularities and so, they can serve to be basis for numerical studies of their behaviour in different conditions. However, many studies have to be done to develop the method to manage complex behaviour like nonlinear physical and geometrical effects.

CL-1-07
SHAPE STABILIZED PHASE CHANGE MATERIALS BASED ON THE POLYETHYLENE AND PARAFFIN WAXES

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Phase change materials (PCM) are substances with a high heat of fusion which, through melting and solidifying at certain temperatures, are capable of storing or releasing large amounts of energy[1]. PCM have received great interest in many applications such as energy storage and thermal protection systems as well as in active and passive cooling of electronic devices[2].

PCM, based on low density polyethylene blended with soft paraffin wax and hard Fischer-Tropsch paraffin
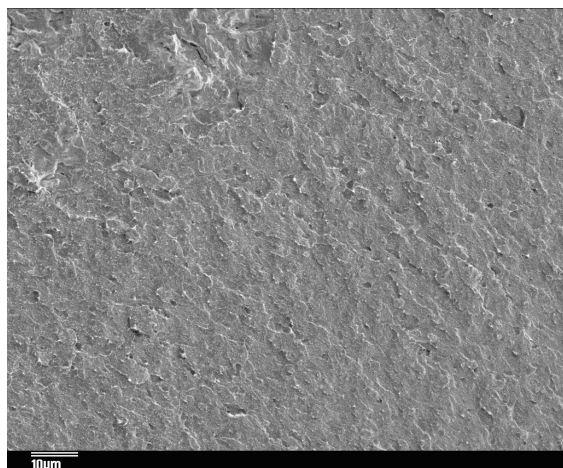
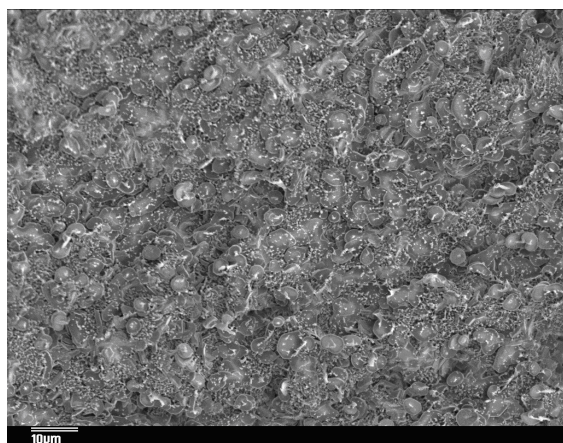Fig. 1. **SEM micrograph of LDPE/Fischer-Tropsch paraffin wax blends**

Fig. 2. **SEM micrograph of LDPE/soft paraffin wax blends**

wax respectively, were studied in this work. Differential scanning calorimetry, dynamical mechanical analysis, thermogravimetric analysis and scanning electron microscopy were employed to determine the structure and properties of the blends. The blends were able to absorb large amounts of heat energy due to melting of paraffin wax, whereas the LDPE matrix kept the material in a compact shape on macroscopic level. Different behavior was observed for the two paraffin waxes. The Fischer-Tropsch paraffin wax was much more miscible with LDPE (Fig. 1) in comparison to the soft paraffin wax (Fig. 2). LDPE blended with Fischer-Tropsch wax degrades in just one step, while blends containing soft paraffin wax degrade in two distinguishable steps. SEM showed completely different morphology for the two paraffin waxes and confirmed the lower miscibility of LDPE and soft paraffin wax. DMA analyses clearly demonstrated the toughening effect

of the waxes on the polymeric matrix. This technique was also used to follow the thermal expansion as well as the dimensional stability of the samples during thermal cycling. Controlled force ramp testing on DMA confirmed poor material strength of the blends containing soft wax, especially at temperatures above wax melting. The highest concentrations at which the polymeric material was able to sustain the external forces as well as the thermal cycling were at 40 wt.% soft and 50 wt.% Fischer-Tropsch wax.

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CL-1-08
SEARCH FOR THE STABILISATION MIXTURE WITH THE MAXIMUM STABILIZING EFFECT USING THE SIMPLEX METHOD

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The simplex method for the function minimization has been applied for finding the optimal composition of a stabilizing mixture for polyurethane coatings. Regarding the degradation of polyurethane coatings for automotive interior applications, the crucial factors are temperature and UV radiation[1]. The stabilizer mixture consisted of HALS, UV absorber and an antioxidant. The residual stability of the samples after accelerated ageing was assessed by the measurement of oxidation onset temperatures using the differential scanning calorimetry (DSC).

The stabilizing effect often exhibits the maximum for a particular composition of the stabilizer mixture. For the development of new coating formulations, the design of experiment or the trial-and-error methods are used. Both methods are quite labour- and time-consuming. It would be advisable to find the maximum more straightforwardly – by using a non-gradient optimization method. In order to find the optimal composition of the mixture, the simplex method for function minimization is employed[2].

The minimization of a function of *n* variables is based on the comparison of function values at the (*n*+1) vertices of a general simplex, followed by the replacement of the vertex with the highest value by another point. The simplex adapts itself to the local landscape and contracts on to
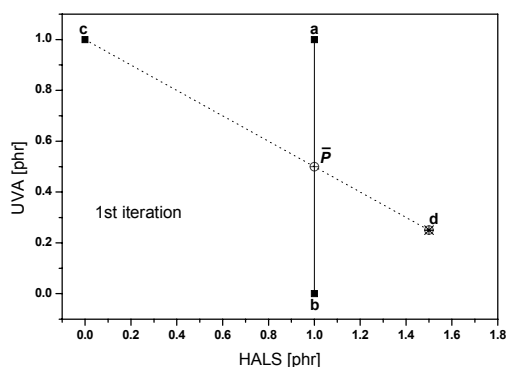
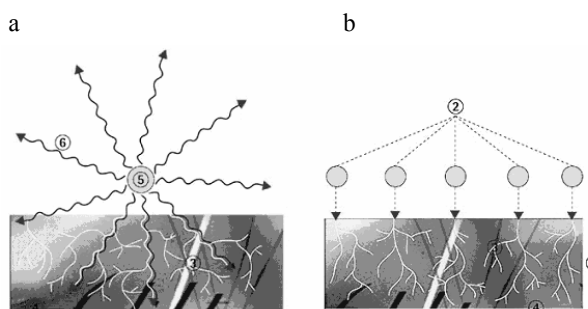Fig. 1. **First iteration of the optimization procedure**

Fig. 1. **Design of Gamma rays (a) and Electron rays (b);** (a) 3 − secondary electrons, 4 − irradiated material, 5 − encapsulated Co − 60 radiation source, 6 − Gamma rays, (b) 1 − penetration depth of electron, 2 − primary electron, 3 − secondary electron, 4 − irradiated material

the final minimum (Fig. 1).

It has been shown that the procedure provides readily the stabilizer composition with the maximum protection effect.

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CL-1-09
IRRADIATION OF POLYMERS MATERIAL

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Radiation processing involves the use of natural or man – made sources of high energy radiation on an industrial scale. The basic of radiation processing is the ability of the high energy radiation to produce reactive cations, anions, and free.

Radiations processing involves mainly the use of either electron beams from electron accelerators or gamma radiation from Cobalt – 60 sources. Radiation processing does not make product radioactive.

A major of industrial applications of radiation processing are cross-linking of wire and cable insulations, tube, heat – shrink cables, components of tires, composites, mould product, for automotive and electrical industry etc.

A second major application of radiation processing is sterilization of medical disposables.

The cross-linking of rubbers and thermoplastic polymers is a well – proven process the improvement of the thermal properties.

The irradiation cross-linking of thermoplastic materials via electron beam or cobalt 60 (gamma rays) takes place separately after the processing. The level of cross-linking can be adjusted with the irradiation dosage and in many cases with the help of a cross-linking booster.

The main deference between beta and gamma rays lies in their differing abilities to penetrate the irradiated material. Gamma rays have a high penetration capacity. In the case of electron rays, penetration capacity depends on the energy of the accelerated electrons.

With electron accelerators, the required dose can be applied within seconds, whereas several hours are required in the gamma radiation plant.any case. References should be indented to tab 7 mm and format to block, use Times 9 pt again.

Properties of natural (not irradiated) and irradiated polypropylene (PP) both unfilled and filled with 25% of glass fibres have been compared.

Used polymers:

−   PTS − Crealen EP − 2300L1 − M800 (unfilled PP),

−   PTS − Crealen EP8G5HS* M0083 (PP filled 25% glass fibres).
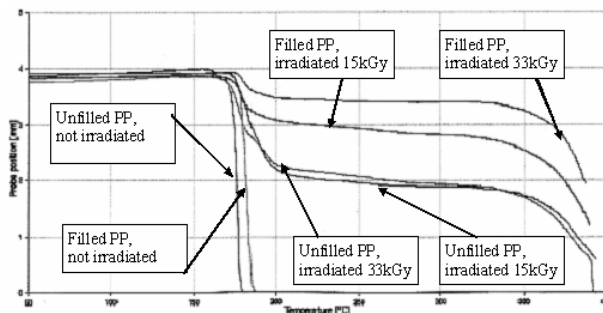
Fig. 2. **Results of thermal stability**

Irradiation was realized in the work of the firm BGS Beta Gamma Service GmbH & Co, KG, Saal am Donau, Germany with the electron rays, electron energy 10 MeV, doses minimum of 15 and 33 kGy.

The most important results have been found by TMA analyses[3]. The irradiation has enormous influence on the thermal stability of both filled and unfilled PP, as it is possible to see from (Fig. 2).

The big differences of mechanical and thermal properties of irradiated and natural PP was found. From the point of view of practise use the most important is the enormous improvement of thermal stability of irradiated PP. In next works, the further polymers will be tested.

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CL-1-10
ARE THE FILLED POLYOLEFINE A PROMISSING MATERIAL?

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The use of commodity polymers in many technical applications is limited due to its material behaviour – thermal stability, barrier properties, toughness or mechanical strength. That is the reason why to modify the basic polymer with fillers, reinforcement at different macroscale, microscale as well as nanoscale level. All the physical and chemical properties can be modified by way of fillers. Now a day there is not an exact limit between the fillers and additives. The real compounds are considered rather for composites in that the polymer serves as binding mean for fillers, pigments and processing agents.

The fillers are added in a great amount to PVC, PP, PE, and PA. Approximately 47 % of PVC-U are used for manufacture of pipes (26.5 %) and profiles (20.5 %). The content of fillers in these products is up to 15 % that represent the most import field as the volume of fillers concerns. Exclusive filler is $CaCO_3$. From the ecological view are the pipes and profile produced from PP, PE, PP foams,

(PE+PS) blends, PS and polymers filled with wood. Nevertheless there is a big economical and technological problem that explains the growth of PVC profiles in future about the 3 %. The main customer of reinforced and filled PP is the automobile industry. PE filled with $CaCO_3$ is used as sheets in agriculture and antiblock application. Semi-permeable sheets became the reality due to adding the very find grinned, surface coating $CaCO_3$ with narrow distribution. The main branch of its application is sanitary sphere. Fillers are in the form of masterbatches, content of 5 % is sufficient for most application. Among the engineering polymers only PA is modified with filler (calcining kaolin, mica, talc and wollastonite). The secular trend heads toward to minimum content of fillers and improvement of its mechanical properties. This aim can be achieve only in the way of using the selective fillers with high aspect ration or to use very fine particles or both[1]. The technologies of grinding were used for this purpose.

Nanofillers represent the particles with the size less than few nm (black, silica, whiskers and various pigments of TiO_2). Nevertheless in many cases the particles have a trend to agglomerate and built up particles with size of several μ. This problem starts to be solved some years ago[1,2] and is based on mechanisms of exfoliation of layered silicates during melt processing. In this way it is possible to prepare composites with aspect ration up to 1000. Content of such particles can be up to 80 %. The optical properties of these composites are not influenced since the particles are shorter than the wavelength of the light.

Utilization of organic fillers first of all woodfibers and sawdust particles in thermoplastics represent an attractive composite[3]. The reason is its availability, favourable ration between price and volume and further specific properties (low hardness, that minimize the wearing of processing devices, relative low density with comparison to composite with inorganic fillers, biodegradation). The problem is to achieve the necessary dispersion and strong interface, while the reinforcement is hydrophilic and matrix hydrophobic. The various surface coating of fillers (anhidride, silane, MAPA) and nucleation agents (benzoate sodium) are use to remove this disadvantage. The further problem is the great dependence on rheological properties during processing.

The system PP matrix filled with rigid submicroscopic particles was chosen to illustrate the way how to enhance the toughness of this system by keeping its stiffness[4–7]. The first step is to modify relevant parameters of the matrix at molecular as well as super molecular level (adding α and β nucleation agent). Effect of particles on the properties and behavior of system strongly depends on its size, shape, surface coating and distribution. Mechanisms of toughening (creation of shear bands) can starts after releasing the stress concentration on the interface. It can be realized under following conditions:

– size of particles < 5μm, formation of free volume,
– aspect ration narrow to 1, prevent the creation of high stress concentration,

− homogeneously distributed particles, prevent the creation of agglomerates,
− debonding at the particles-polymer interface has to be achieve before the yield stress of the matrix[6], otherwise no change in the stress state of the matrix takes place.

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CL-1-11
MODELING AND SIMULATION OF THE IMPACT BEHAVIOR OF FOAMS

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Due to there energy absorbing and dissipating capabilities, polymeric foams are frequently used in the automotive industry. They are intended to be used at relatively low stress levels, what makes them predestined for occupant and pedestrian protection. For an effective engineering and development of a new vehicle you have to be able to predict the material behaviour in crash situations. This keeps you from doing unnecessary crash-test and raising the development costs. These complex crash situations are mainly simulated with FE-programs, which are based on material models and parameter that describe the crash behaviour of the materials. The objective of this work is the development of a novel methodology for characterising the impact behaviour of polymeric foams.

At the beginning the foams were tested with a commonly used method to be able to compare with the new achieved impact data. For this purpose the foams were tested under a monotonic uniaxial compression load using testing machines, where the dependency of force and displacement was measured and transposed to stress-strain
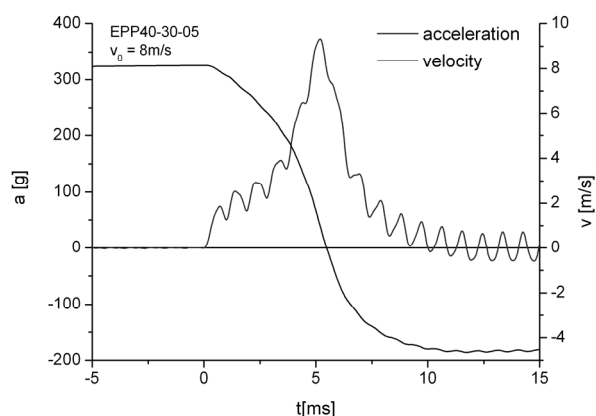
Fig. 1. **The acceleration curve measured during the impact test and the calculated velocity profile for EPP foam**

data. The new method is based on an impact test with a free motion steel plate that hits the specimen, which is mounted on the floor. To comply with the assumption of a uniaxial load case, the specimen has to have a cubical or cylindrical shape.

These tests differ from the monotonic compression tests on one hand in the loading rate and on the other in the kind of measurement. The measurement only consists of an acceleration sensor on the impacting body.

With the assumption of an uniaxial impact load and a zero Poisons' ratio one can calculate the function of stress, strain and strain rate as well as the hysteretic behaviour of the foam. The quality of this data can be instantly checked by simulating these tests with the same calculated material parameters und comparing the simulation results with the real tests.

To show that these material parameters achieved from uniaxial impact tests are also applicable to more complex load situations, test with a spherical impact body were
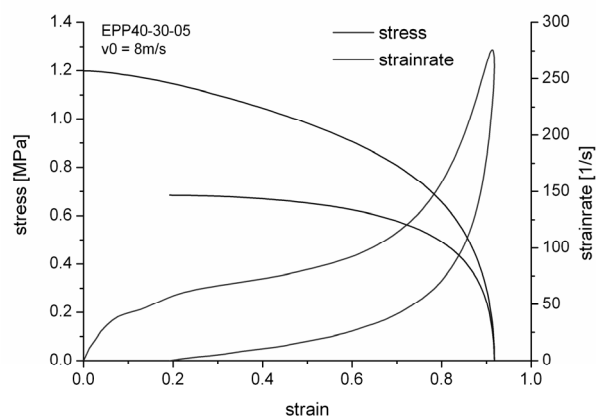
Fig. 2. **The stress-compression-strain rate diagrams of an EPP foam at loading rate of 8 m s⁻¹**

made and compared to the simulation results. Here we have a method to characterise the behaviour of polymeric foams under an impact load. The advantage is that this is a cost and time efficient method to achieve foam data, that correspond to the load situation of there intend use. Furthermore it is possible to check the quality of the material data without additional tests.

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CL-1-12
POLYMER COMPOSITES WITH *IN-SITU* POLYMERIZED CYCLIC BUTYLENE TEREPHTHALATES (CBT^{TM}) – PROMISING MATERIALS FOR AUTOMOTIVE APPLICATIONS

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Many composite applications are nowadays based on thermoset composites. Recent developments prefer, however, thermoplastic fiber reinforced composites due to recycling issues. The progress on reinforced composites is driven by aerospace industries but gains more and more importance in the industry. One of the key problem that is frequently raised when using thermoplastics as polymer matrices is their high melt viscosities (in the range of 100–10,000 Pas). This creates serious challenges for wetting and impregnation of the reinforcing fibers. One approach is to develop thermoplastic resins that have the ability to be polymerized reactively like thermosets.

One promising approach is pursued by Cyclics Cooperation. Cyclic butylene terephthalate (CBT^{TM}) shows an ultra-low processing viscosity (as low as 0.02 Pas) and can be transformed into linear high molecular weight thermoplastic poly(butylene terephthalate) (PBT) via entropically-driven ring-opening polymerization in a short time scale. Hence, new manufacturing technologies have to be adopted to deal with the low viscosity of CBT.

Static pressing, semi-continuous pressing, and RTM technologies enable fast manufacturing of plates as well as structural components, even under isothermal conditions. The fiber reinforced PBT-plates and structures can be used for further thermoforming or welding processes.

In the presentation a brief summary is given on the *in-situ* polymerization of CBT to PBT, followed by disclosing the experience gained on this material. The tensile and flexural properties of fiber-reinforced PBT composites were compared to those of traditional thermosets in order to evaluate the potential of the former systems. Finally, an outlook will be given on further steps of the R&D activities and possible applications of the CBT-based polymeric composites.

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CL-1-13
THERMAL DECOMPOSITION OF MODIFIED POLYURETHANE FOAMS

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PUR foams are used widely in many fields as structural, cushion, insulation, electrical, flotation and packing materials. Flexible PUR foams are usually obtained from the reaction between polyfunctional alcohol (polyol), diisocyanate and water as a blowing agent. Foam properties are mainly affected by the properties of raw materials and can be modified by a wide variety of additives, such as fillers, stabilizers, cross-linking agents and chain extenders.

The proposed work is focused on the investigation of a new thermodegradable flexible polyurethane (TD-PU) foams that maintain useful structural properties at working conditions (up to 160 °C) but deliberately degraded in

a controlled fashion by heating at predefined temperature (at around 180 °C). To control and enhance the thermodegradation of common PU foams at the temperatures lower than 240 °C (the initial degradation temperature of the urethane bonds) needs modification of the polymer network preferably by a thermally labile compound.

Many symmetrical, difunctional azo compounds well known as a source of tertiary alkyl or aryl radicals in thermally, photochemically and electrochemically initiated decomposition has been developed. It is known that these compounds undergo homolytic bond cleavage by a radical disproporcionation and its decomposition rate, which is independent on the medium, follows first-order kinetics[1]. Therefore thermosensitive difunctional azo initiator (TDAI), with the initial degradation temperature $T_0 \approx 180$ °C was synthesized. Additionally the TDAI was end-capped by tolylene diisocyanate 80/20 (TDI) to form azo-TDI precursor, which was consequently incorporated to the PU network via „one-shot" process. The TD-PU thermodegradation, which is mainly based on the decomposition of N=N groups in the polymer network was studied by means of Thermogravimetric Analysis (TGA) and Differential Scanning Calorimetry (DSC) methods.

Experiments showed direct proportion between the enhancing degradation rate of TD-PUR and the increasing amount of thermolabile azo-compound in TD-PUR. The thermodegradation rate enhancement at 200 °C of TD-PUR having maximum amount of TDAI in comparison with common PUR foam was found to be more than 3 fold. The initiate degradation temperature of PUR foam was lowered from 240.9 °C (without TDAI) to 177.7 °C (with TDAI) that enable the faster degradation of TD-PUR at lower temperature under the controlled conditions. Based on the TGA analysis the homogeneous system of TD-PUR network was observed and thus the synergic action between the azo-compound and the TD PUR foam was confirmed.

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CL-1-14
ENGINEERING BIOCOMPOSITES OF REDUCED FLAMMABILITY

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Polymer materials manufactured from natural resources have been characterized. Polylactid acid (PLA) was used as a matrix in the composites filled with cellulose fibers (flax, hemp, sisal). PLA is useful in the packaging, electrical and automotive industry, at which the biodegradable materials started competing with cheaper synthetic plastic.

To meet the non-flammability requirements for the electrical housings it is essential to use flame retardants. Different amount of ammonium polyphosphate (APP) and magnesium hydroxide $Mg(OH)_2$ have been used to reduce flammability of PLA-natural fibers composites.

Flammability by UL-94 tests, mechanical and thermal properties, as well as a structure of biocomposites was presented as a function of the matrix material and filler content.

Biocomposites display combined features of all components or new properties resulting from the mutual interactions between the components in mu.

Flame retardants are needed for plastics of many industrial branches: transport: 30 %, electric 26 %, industrial equipment 20 %, construction 15 %. Agents improve also the processing. Halogen free flame retardants like exolite (phosphate), magnifin (magnesium hydroxide, sodium carbonate, graphite) etc. will be used.

APP is an additive flame retardant containing nitrogen and phosphorus, typically used in a crystalline form. It is currently used to flame retard flexible and rigid polyurethane foams, as well as in intumescent laminations, molding resins, sealants and glues.

However, chemical manufactures and foam manufacturing trade groups do not consider it to be an alternative for penta BDE on a large scale. Reasons for this are that APP is typically incorporated as a solid, it has adverse effects on foam properties and processing and it is not considered to be as effective as a fire retardant compared to other alternatives.

Discussion and Conclusions

No more than two types of formulation are suited for the UL94 standard in the case of Vertical Burn Method, nevertheless most of them have passed Horizontal Burn Tests.

Material	Times		Behaviour	Class
80% HM 1011 + 70% Hemp H1	0 ⇨ 25 mm	0:17 min	burning, no flaming drips	HB
	25 ⇨ 100 mm	2:16 min		
HM1011	0 ⇨ 25 mm	0:30 min	burning, flaming drips, cotton ignition	HB
	25 ⇨ 100 mm	2:21 min		
70% NW3051D + 30% Flax F4	0 ⇨ 25 mm	0:12 min	burning, no flaming drips	HB
	25 ⇨ 100 mm	2:30 min		
65% NW3051D+25% Flax F4 + 10% Talc Crystalline	0 ⇨ 25 mm	0:28 min	burning, no flaming drips	HB
	25 ⇨ 100 mm	2:58 min		
NW3051D + 30% Hemp H1 (Pellet)	0 ⇨ 25 mm	0:18 min	burning, no flaming drips	HB
	25 ⇨ 100 mm	2:00 min		
[NW3051D + 30% Hemp H1(Pellet)] with 7,5% Flame Resistance	0 ⇨ 25 mm	0:20 min	burning, no flaming drips	HB
	25 ⇨ 100 mm	2:45 min		
[NW3051D + 30% Hemp H1(Pellet)] with 15% Flame Resistance	0 ⇨ 25 mm	0:24 min	burning, no flaming drips	HB
	25 ⇨ 100 mm	3:26 min		
[NW3051D + 30% Hemp H1(Pellet)] with 7,5% Flame Resistance; (Cryst)	0 ⇨ 25 mm	0:20 min	stops burning almost immediately	HB

Scheme 1. **Horizontal Burning results of different PLA composites**

Flammability test results have evidenced that a flame retardant content of 20 % is enough to manufacture the composites with natural fillers being suited for the flammability risk applications. Thus, further activities should focus on carrying out different tests aimed at both optimizing a formulation of new composites and demonstrating their feasibility as engineering materials.

CL-2-01
SIMULATION OF TEMPERATURE FIELDS IN CURING RUBBER

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Computation of temperatures in the heated and cured rubber is based on the Fourier equation of the transient temperature field. Important parameters in this equation are thermal diffusivity and reaction (curing) heat. Both of these quantities depend on the composition of rubber compounds but thermal diffusivity depends also on the temperature. Their values can be determined only experimentally. Because of a lack experimental data the curing process is often simulated with constant values of thermal diffusivities, and the influence of curing heat is ignored or in the better case estimated. Since the temperature fields depend on the instantaneous degree of curing equations of the curing model have to be solved simultaneously.

In order to simplify the mathematical model of rubber curing a new quantity called „effective thermal diffusivity" is suggested. This quantity includes besides thermal diffusivity also curing heat. This allows to compute the temperature fields of curing in advance and then to calculate the fields of the curing degree from them. The determination of „effective thermal diffusivity" has to be done at future technological conditions of rubber processing. In this case, the curing heat is not needed for modelling.

CL-2-02
PREPARATION AND PROPERTIES OF FERRITE POWDERS FOR RUBBER COMPOSITES

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The incorporation of magnetic polycrystalline ceramic ferrites in elastomeric matrixes produces flexible magnets or elastomeric magnets[1]. Hexagonal ferrites with magnetoplumbite structure have attracted the attention of researchers for a long time. The high values of magnetocrystalline anisotropy and saturation magnetization ensure a wide application of the M-phase ferrites as permanent magnets[2]. Several methods have been developed to prepare ferrite particles and many efforts have been devoted to the development of synthesis procedures leading to a better control of particle size ($<1\mu m$), morphology (hexagonal plates) and homogeneity. The chemical co-precipitation method[3] is a cheap and easy choice for mass production.

The aim of the study is to describe the details of co-precipitation synthesis of $BaFe_{12}O_{19}$ and detection of structural changes occurring during the synthesis process. It reports the results of an investigation of the morphological, structural and magnetic characteristics of $BaFe_{12}O_{19}$. Barium ferrite powders were prepared with molar ratio 2Fe/Ba = 5, 4 as follows:

$$12\,FeCl_3 + BaCl_2 + 36\,NaOH + Na_2CO_3 \rightarrow \text{(coprecipitation)}$$
$$BaCO_3 + 12\,FeOOH + 38\,NaCl + 12\,H_2O \rightarrow \text{(calcination)}$$
$$BaFe_{12}O_{19} + 38\,NaCl + 18H_2O\uparrow + CO_2\uparrow$$
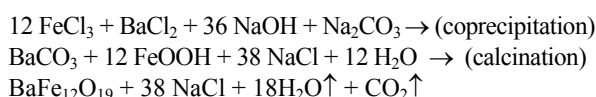
The calcining temperature was changed from 800 to 1000 °C. It was found that the co-precipitation combined with high temperature results in M-type hexagonal powders whose particles are in the range (80–250 nm) in dependence of calcining temperature. From the TEM, FT-IR and Mössbauer spectroscopy results is evident that the increasing of the calcining temperature affects a decreasing amount of $BaCO_3$ and causes better formation of hexagonal plates in magnetic phase $BaFe_{12}O_{19}$ of resulted materials.

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CL-2-03
CARBON BLACK PRODUCED BY SCRAP TIRE PYROLYSIS

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The rubber samples (cca 200 mg) from a scrap tire were pyrolysed under atmospheric pressure and different temperatures. The carbon blacks produced (CB_{p1}) were

analyzed by the measurement of BET surface area (Nitrogen sorption method), pore structure (Nitrogen sorption method), iodine adsorption number (ASTM D1510), mass loss by heating at 125 °C (heating loss ASTM D1509), ash content (Thermogravimetric analysis) and pour density (ASTM D1513). The same parameters were estimated also for commercial carbon blacks N220, N330, N550 and N660. The third studied material was a pyrolytic carbon black produced by pyrolysis of scrap tire in an industrial scale batch reactor (CB_{p2}).

The parameters of the pyrolytic carbon black obtained in our laboratory (CB_{p1}) were compared with the parameters of commercial carbon blacks and also with the parameters of pyrolytic carbon black obtained in an industrial scale batch reactor (CB_{p2}).

Specific surface area of (CB_{p1}) has the values from 70 g m^{-2} to 120 g m^{-2} dependent on the pyrolysis temperature and type of the rubber material. Compared to the commercial carbon blacks these values correspond with the specific surface of carbon blacks N330 and N220. However, the CB_{p2} sample had a specific surface area comparable with N660.

The results of the measurements of iodine adsorption number have confirmed the similarity of CB_{p1} to N220 and CB_{p2} to N660. Pyrolytic carbon blacks had much higher ash content than the commercial one. Pour density of pyrolytic carbon blacks was also higher than pour density of commercial CBs.

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CL-2-04
RUBBER RECYCLING VIA HIGH-TEMPERATURE COMPRESSION MOULDING

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Rubber waste treatment is a great problem nowadays. Millions of waste tyres are produced worldwide per year. They are often trashed to landfilles but this is both ecologically and economically unacceptable way. Regeneration of rubber is a common process but the utilization of its product is limited. Another way is to combust the tyres but only the energetical potential of rubber can be exploited in this case. To exploit the chemical one pyrolysis can be carried out. Another course is the material recycling. Waste rubber is ground and the product can be used as filler or it can be mixed with thermoplastics, liquid rubbers etc. A new material can be also obtained by compression moulding of ground rubber without any additive at high temperature and pressure[1]. This paper focuses on the latter method.

Recycling possibilities of natural rubber (NR) and styrene-butadiene rubber (SBR) and their mixtures were tested on model compounds containing various curing systems. The model vulcanizates were ground and the crushed material was compression moulded at high temperatures (e.g. 250 °C) and pressure (20 MPa) to form a new material. Tensile properties, hardness, crosslink density and retention of these properties after thermal ageing were observed and compared to those of the original material. The real ground rubber from waste tyres was tested as well.

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CL-2-05
PHASE SELECTIVE DISTRIBUTION OF CARBON BLACK FILLED RUBBER BLENDS

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The phase selective carbon black distribution plays an important role regarding the performance of rubber composites based on rubber blends.

Since 2002 we use the online measured electrical conductance for the description of dispersion and distribution processes during the mixing process of carbon black filled rubber mixtures[1–4]. Recently, we used this method also for the qualitative analysis of the morphology development of binary blends during the mixing process[5].

With our new developed method, analyzing the carbon black-rubber-gel by thermogravimetric analysis (TGA) in correlation with differential thermo analysis (DTA) it is possible, to describe the wetting behavior of the polymer chains to the carbon black and the phase selective carbon black distribution during the mixing process. The determined carbon black distribution corresponds very well with the given carbon black distribution in blends of the masterbatches, and with results from the

online conductance measurements. With this method it is possible to characterize the free carbon black portion and the portion of carbon black in the particular blend phases depending on mixing time. In the present work we have investigated the effects of the material and technological parameters on the kinetic of CB distribution in SBR/NR blends by the use of the newly developed TGA/DTA method.

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CL-2-06
ADVANTAGES OF ACTIVE ZINC OXIDE'S APPLICATION IN RUBBER INDUSTRY

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Zink oxide has showed to be the most important activator for sulphur vulcanisation of elastomers. In addition to its role as an activator, there are also evidences that the inclusion of ZnO in the vulcanizates brings also other benefits (it reduces heat-build-up, improves abrasion resistance, improves heat resistance of the vulcanizates and their resistance to the action of dynamic loading[1], helps to dissipate local heat concentrations in rubber products, it is necessary in vulcanizates for bonding rubber to the reinforcing steel cord, etc.). Besides improving the properties of vulcanised rubbers, ZnO also assists in the processing of uncured rubbers. ZnO is added to rubber formulations to decrease shrinkage of moulded rubber products and maintain the cleanliness of moulds.

Although zinc is generally considered as one of the least harmful of the heavy metals, there is an increased concern about its environmental effects[2]. Diffuse emissions of zinc from rubber products, such as the wear of tyres may enter the environment. In view of the upcoming legislations and ecolabelling requirements for vehicle tyres, for instance, it can be stated that it is desirable to keep the ZnO content in rubber compounds as low as possible, not only for environmental but also for economical reasons[3,4].

This contribution tries to summarize the efforts how to reach the above mentioned goal and presents some results from own research as well. The summarized results indicate that the same or better properties of vulcanizates can be reached by lower dosage of zinc oxide with higher specific surface.

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CL-2-07
CHARACTERIZATION OF THE FATIGUE BEHAVIOR OF ELASTOMER COMPOSITES

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In many engineering rubber applications both pure elastomeric materials as well as composites out of rubber and reinforcement materials, such as textile, polymer and steel cords, are used. Such technical rubber articles are often exposed to complex mechanical stresses, frequently in a cyclic mode, which can result in crack formation and crack propagation up to final failure of the relevant rubber article.

For example, air springs are used as structural damping elements in trucks, busses and in other heavy vehicles. The elastomer component in air springs typically consists of a multi-layer build-up, with an inner liner and outer cover of un-reinforced rubber and two fabric-ply layers containing polymer fibers of different orientations in a rubber matrix. To enhance the overall performance and life time of air springs, a more detailed understanding of the micro-mechanisms of failure under cyclic loads in such a multi-layer build-up is required. To support both mate-

rial development efforts and novel design concepts including life-time assessment, appropriate test methods and procedures to characterize crack initiation and crack growth resistance behaviour are needed.

In elastomer composites the following three basic micro-modes of failure have been identified for service relevant loading conditions: (*i*) crack formation and crack growth in the elastomer matrix, (*ii*) delamination between fabric-ply layers and (*iii*) crack initiation and crack growth at the cord (fiber)/matrix interface.

Hence, the main objectives of this paper are:

− The development and implementation of adequate test methods and data reduction schemes to characterize the crack initiation and growth resistance of multilayer elastomer composites under cyclic (fatigue) loading conditions including rubber matrix fatigue matrix/ cord/fiber debonding and delamination of cross-ply layers.

− The application of the test methods to selected elastomer composite materials.

Several elastomer types and composite layer set-ups were included in the investigations. The materials were selected, manufactured and provided as test specimens by the company partner. The experimental work on test specimen level was performed in the testing laboratory of the scientific partner.

In the fatigue process of elastomers, at least two stages can be distinguished. The first stage is related to the crack nucleation and the initial phase of crack growth initiation, the second is concerned with the period over which the nucleated crack grows either in a stable or unstable manner until ultimate failure occurs. Current methodologies for describing elastomer fatigue behavior and to predict the service life of rubber components follow two general approaches. One approach focuses on predicting crack nucleation life and makes use of continuum mechanics parameters such as stress and strain. The other is based on fracture mechanics concepts and focuses on the kinetics of crack growth using energy based fracture mechanics parameters[1].

The fatigue behaviour of the bulk elastomer was characterized using a modification of the well-known pure shear specimen (faint-waist pure shear, FWPS) configuration and applying the tearing energy concept[2]. Main emphasis was given to the characterization of the influence of preconditioning and processing parameters on the fatigue crack growth behaviour of elastomers used in real applications.

Furthermore, ring-type and peel-type specimens manufactured from cross ply laminates were used to characterize the fatigue behaviour of the elastomer composite layers. While due to the high local stiffness difference between the rubber and the cross-ply the main load for the ply interface is near mode II (shear stress) in the ring specimen, the peel test represents the mode I (opening) loading situation. A complex combination of these two basic modes may occur in a real component during service. Moreover, a novel test set-up for characterizing the

rubber matrix/cord interface under cyclic loading was also developed and implemented.

Finally, component tests were also performed. In addition to the conventional tests, novel full-field strain analysis methods were applied to characterize the strain and temperature distribution in the component under complex cyclic loading conditions. To gain more insight into the local failure behaviour, failure analysis on both test specimen and component level was carried out using various microscopy methods.

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CL-2-08
WEAR OF RUBBER COMPONENTS

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Polymer processing industry is a very branched one because of the production of a lot of products for various applications. Products from polymers and composites with polymer matrix find wide use: products for common use, sports and free time activities, domestic goods, packaging, medical applications, construction, electrotechnics and electronics, engineering and automotive industry. Rubber industry plays a very important role in the polymer processing since the tire production occupies a dominant position in this branch.

The tire is a very important part of the vehicle which is in direct contact with the road surface and responsible for the driving force transfer. In terms of design, tire is a very complicated component consisting of polymeric matrix and reinforcement. It is composed of various layers. In terms of wear, the overlayer called tread equipped with design (pattern) is the most important part.

The wear of tire treads on road surfaces is measured as abrasion resistance. The off-road behaviour of tyre treads on surfaces with sharp stones is not well character-

Fig. 1. **Sample before and after test**

Fig. 2. **Sample wearing during test period**

Fig. 3. **Comparison all measured properties**

ised by abrasion resistance as the mechanism of rubber damage is rather different here. The sharp edges of stones can cut rubber tread surfaces and tear off bigger pieces of rubber gradually. This type of wear is called chip and chunk effect in the tire processing industry and with a simplification, it is comparable to machining.

The tire wear is usually tested under running conditions, and these long-lasting tests are very expensive. Finding a fast test carried out on small samples would be very useful in practice.

The test for cutting and chipping of rubber compounds which correlates with service behaviour and provides test results at a reasonable speed and accuracy was described by J. R. Beatty and B. J. Miksch[1]. In accordance with their description we constructed a rather modified apparatus.

The tests were carried out on cylindrical samples of the Lüpke test with diameter 55 mm and thickness 13 mm (Fig. 1, ref.[3]).

This enhanced laboratory apparatus provides to take test of conditions which can be widely changed. It makes possible to measure different characteristics of chip-chunk processes.

Thirteen various types of tire tread mixtures designed for off-road tires production have been chosen for the experiments (motocross and multipurpose tires).

The presented test method shows the possibility of the evaluation of wear (chip-chunk) resistance of tire treads on small samples. This method makes possible to compare various types of compound with a standard and to observe the wear progress during the test period. The wear of the sample during the test period depends on the properties of rubber compounds and on test conditions. A significant correlation of chip-chunk resistance with the usual rubber properties was found (Fig. 2). According to the statistical calculation all the measured data are statistically significant[2].

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CL-2-09

EFFECT OF FILLING DEGREE IN TWIN SCREW EXTRUDER ON CONTINUOUS COMPOUNDING OF E-SBR/SILANIZED SILICA COMPOUND

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The paper focuses on experimental investigations of the continuous mixing of a silica filled rubber mixture with a co-rotating twin screw extruder. The rubber mixture is a free flowing Rubber/Filler Composite (RFC) based on emulsion styrene butadiene rubber (E-SBR) with silanized silica as filler. The reaction between the silica and silane is carried out during the production process of RFC and hence the rubber mixture contains completely silanized silica[1]. Continuous mixing involves compounding all the ingredients together in one mixing step. The continuous mixing of silanized silica based rubber mixture requires

optimum process parameters to assure micro-dispersion[2]. This property influences the dynamic shear modulus value at low strain measured with a rubber process analyser (RPA) which influences the Mooney viscosity of the final compound. In the experimental work, the influence of filling degree in twin screw extruder with respect to screw speed and output on the compound and product properties are analysed. The mixture characteristics shows that filler dispersion and cross-linking behaviour and the properties of the vulcanised rubber correspond to the characteristics of the reference compound mixed in the internal mixer.

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CL-2-10
INFLUENCE OF SURFACE QUALITY
ON FLUIDITY OF ELASTOMERS

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This paper shows influence of technological parameters on the flow length into mold cavity. The fluidity of elastomers is affected by many parameters (mold design, melt temperature, injection rate, pressure and curing process).

To be able to study the influence of surface quality of runners and cavities on the flow of elastomers, a special injection mold has been designed and machined. Injection
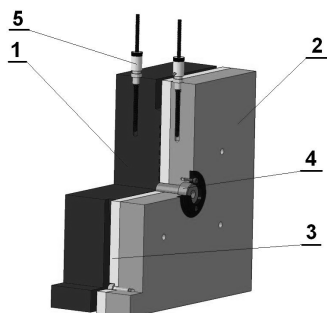
Table I
Values of surface quality of testing plates

Polished plate	Ra=0,029 μm
Ground plate	Ra=0,369 μm
Electroerosion machined plate ("fine")	Ra=3,520 μm
Milled plate	Ra=9,368 μm
Electroerosion machined plate ("rough")	Ra=17,393 μm

mold is assembled from (1) cavity plate, (2) clamping plate, (3) testing plate, (4) sprue bushing, (5) temperature sensor (Fig. 1).

The surface of the plates (bottom of spiral) is machined using various types of working technologies: milling, grinding, polishing and electro-spark cutting.

Length of testing samples has been measured by measuring jig. The experimental dates have been statistical processed and evaluated. Injected samples were prepared on injection molding machine REP V27/Y125.

For preparing of injected samples were chosen three rubber compounds with different flow properties. These compounds have to have sufficient processing safety

Table II
Injected rubber compounds

	Hardness [ShA]	Strength [MPa]	Elongation [%]	Viscosity (1+4 min/100 °C) [°MU]
A	50±5	10	300	31
B	60±5	7	250	40
C	65±5	16	300	73

Fig. 1. **Injection mold**
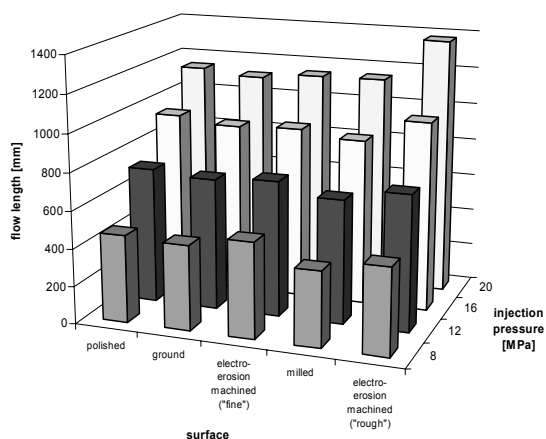
Fig. 2. **Dependence of flow length on surface quality and injection pressure (compound A)**

(scorch safety) to flow through the nozzle, runners, and gates without scorching, but still cure rapidly in the mold.

Measurement shows that surface quality doesn't have substantial influence on the length of flow. Samples which were injected into the spiral (cavity) with the worst surface quality have approximately same length of flow in comparing with the best surface fluidity. These findings are very important from the point of view of use in production. For verification of these results further experiments have to be carried out using different rubber compounds.

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CL-2-11

SIMULATION OF DEFORMATION BEHAVIOR OF REINFORCED RUBBER BY A NETWORK MODEL COMBINED WITH FEM

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A modeling of deformation properties of rubbery material was presented in this contribution. This model was designed to description and prediction of mechanical properties from its structure and material properties. The progress from simple network model (NM)[1] to the model of real polymer material was presented. In the first approximation, the model was a 3D tetra-functional network of rubbery matrix[2], in which undeformable inclusions were introduced. This network model was approached to the behaviour of real polymer material. First, the NM was combined with Finite Element Method (FEM). By the FEM, the distribution of deformation and stresses during the tensile test was analyzed.

In the second phase, the structural properties approached to the real behaviour of the rubbery material. Before, the network was fully affine. The chains were fixed in the nod. Then a portion of chains was replaced by so called free entanglements. Both fixed nod and entangle-

ments were permanent nods. That means that they did not disappear or re-appear during the virtual tensile test. The entanglement enabled slipping of the chain through the nods of the network. The third variant of a nod was a tie-point. This nod was unstable and it disappeared during the tensile test. Each variant of nod represented certain component in the structure of polymer. The fixed nod represented for example Sulfur Bridge, the free entanglement the entangled chains and the tie point represented two polymer chains adhered together by weak intermolecular forces.

Virtual tensile tests were performed on the homogenous rubbery networks and composite networks with undeformable inclusions. The stress/ strain curves until five fold elongation of sample were calculated. Some material characteristics were derived from the curves such as Young modulus, stress at break. The loading-unloading curves were calculated until the double elongation. Mainly heterogenous materials show nonlinearly elastic deformation response[3]. The energy dissipated during one loading-unloading cycle was calculated by the model.

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CL-2-12

MOLECULAR CHARACTERIZATION OF SYNTHETIC POLYMERS BY SIZE EXCLUSION CHROMATOGRAPHY

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Molecular characteristics of polymers − their molar mass, chemical structure (composition, functionality, etc.) and physical architecture (linearity, branching, stereoregularity, cis-trans isomery, etc.) − both average values and distributions co-determine the end-use properties of corresponding plastics and rubbers. Presently, size exclusion chromatography (SEC) called often also gel permeation chromatography dominates the field of molecular characterization of synthetic polymers. Besides the molar mass averages and distributions, SEC provides useful information also on the long chain branching of macromolecules, on intrinsic viscosities and gyration radii of dissolved polymer species, as well as on preferential solvation of

macromolecules in mixed solvents. Important products of SEC include also data on association, aggregation and micellization of macromolecules. SEC is fast, relatively cheap and it exhibits rather high inter-laboratory repeatability (precision). Measurements, including sample preparation are usually not labor-intensive and sample consumption is low. Based on (universal) calibration or in combination with the flow-through light scattering or viscometric detectors, as well as with ultraviolet, infrared and mass spectrometries, SEC can provide valuable additional information about numerous soluble polymer species. Modern automated and often robotized fast SEC instruments have reduced time of analysis down to few minutes so that some polymerization procesess can be on-line monitored and optimized.

At the same time, however, SEC suffers from numerous shortages. Recent series of round robin tests demonstrated surprisingly low accuracy (low inter-laboratory reproducibility) of SEC data obtained without strict protocol of both measurements and data processing. It is evident that a worldwide standardization is necessary of practical measurements (for example in terms of sample preparation, as well as of its volume and concentration), and data acquisition/calculation (for example in terms of base line and peak limit setting). The analysis of above round robin tests results clearly shows that expertise is needed for accurate SEC measurements. The approach „switch-on, inject, switch-out; computer itself and without inspection will produce SOME data", which is often applied in many universities and research institutions, may produce results differing several hundred percent from the median values. It is anticipated that the high-speed, high sample throughput SEC procedures are especially susceptible to large errors.

The intrinsic though often overlooked or ignored shortages of SEC include: low selectivity of SEC separation and imperfect column „linearity", dependence of polymer retention volume on both sample concentration and volume, low sensitivity and selectivity of detectors,

limited solubility of some polymers so that high temperature measurements or expensive eluents are needed, as well as broadening of chromatographic zones. Unavailability of the calibration standards is usually overcame applying calibration with polystyrene standards. Molar masses obtained in the latter way, however, represent only relative data and should be denoted „polystyrene-equivalent values". Important problems of SEC are caused by presence of the non-controlled enthalpic interactions between separated macromolecules and column packing, which result in shifts of sample retention volumes. Effects of enthalpic interactions are partially but often not fully suppressed by using light scattering or viscometric detectors. SEC also suffers from the low sample capacity of columns, which are easily overloaded and resulting SEC peaks are extensively broadened or deformed. This is why the minor macromolecular admixtures (1 % and less) in polymer samples cannot be directly characterized by SEC – even if their molar masses well differ from the molar mass of the major component. Possible changes of sizes of macromolecules during SEC measurements represent further shortage of SEC. The latter are caused by the (de)association, (de) aggregation or degradation of polymers species within column. The flow induced shearing leads to mechanical degradation of macromolecules with molar masses over one million and especially over ten million of g mol^{-1}. Large column packing particles and low flow rates must be applied for ultra-high molar mass polymers. Large column packing particles, however, bring about increased band broadening phenomenon.

Selected shortages of size exclusion chromatography, especially effects of un-controlled enthalpic interactions within the SEC columns will be discussed in this contribution.

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

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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 $\alpha=0.05$.

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

Temperature of vulcanization	Time of vulcanization	Static adhesion strength	Dynamic adhesion 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 ilustrated in Fig. 1.
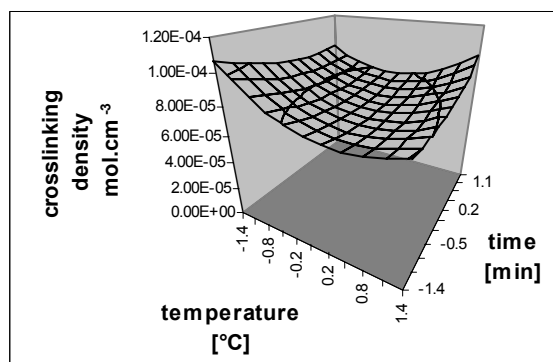
From comparison of regression coefficients of adhesion properties with its critical values is evident, that temperature and time of vulcanization statistically not influenced on adhesion properties of polyester cord to rubber.

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

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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 reaction[1]. 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 °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 mobility[2].

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

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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 automotive[1]. 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 fibers[2]. 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 University[3]. 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 surfaces[4].

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 surface[5].

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

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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 industry[1].

Since the recycling of used PU foams is complicated and expensive due to their thermosetting character[2], 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 sensitive[3] via the screening toxkit Thamnotoxkit F^{TM} (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

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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 materials[1]. One of the effective nanoadditive is TiO_2 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 nanoTiO_2 was measured by spectrophotometer Libra S12, thereafter UPF, UVA and UVB factor were calculated[2]. 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 nanoTiO_2 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 nanoTiO_2 concentration.

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P-06
APPLICATION OF LIGNIN IN RUBBER BLENDS

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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 polymer[1]. The biosphere contains $3 \cdot 10^{11}$ tons of lignin with an annual increase of about $2 \cdot 10^{10}$ tons[2]. The polymer structure of lignin is considered to be a three-dimensional network composed of phenylpropane units[3]. Lignin structure is dependent on wood species and processing conditions[4].

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]. Autors[7] 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

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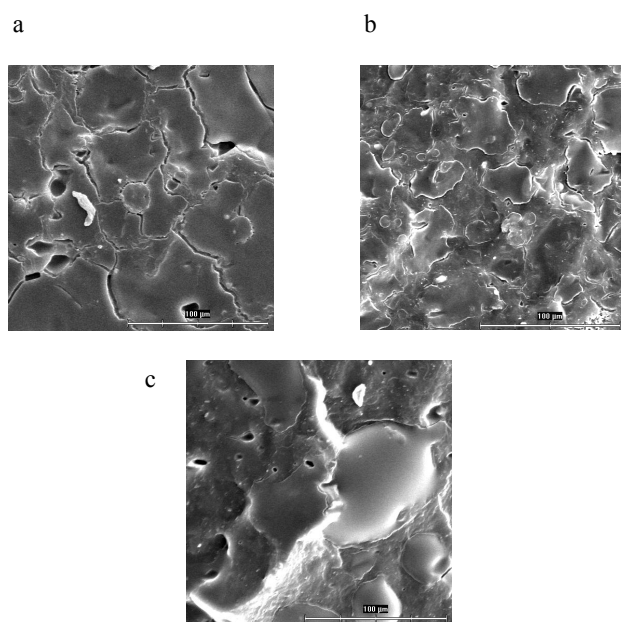
Fig. 1. **SEM of natural rubber vulcanisates filled with 30 phr of lignin containing Ca (a), Mg (b) and Na (c)**

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

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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,
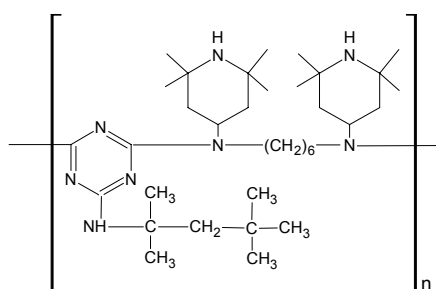
Chimasorb 944
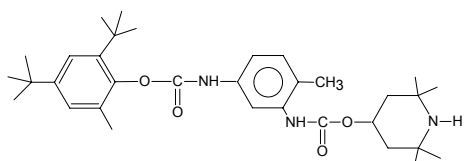
TMP

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 photo-degradation 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 photo-oxidation: 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 pro-degradation 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 nano-filler (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.

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

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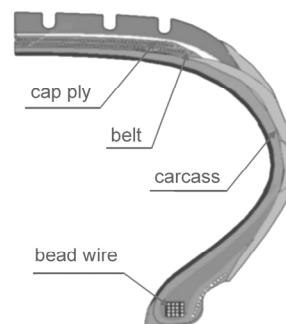
Scheme 1. **Distribution of reinforcement materials in a passenger car radial tyre**

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

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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 mono-tonic 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 μm and a length of 100 to 150 μm.

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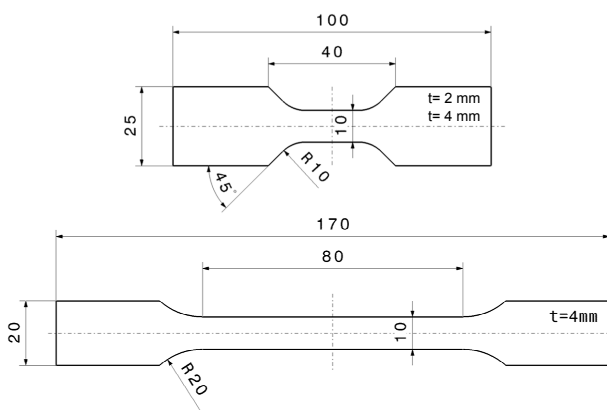
Fig. 1. **Top: short specimen, Bottom: standardized specimen**

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

molded thermosetting plates. The reinforced thermoplastic plates had a dimension of 100×100 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 servo-hydraulic 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 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 in[7]. 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.
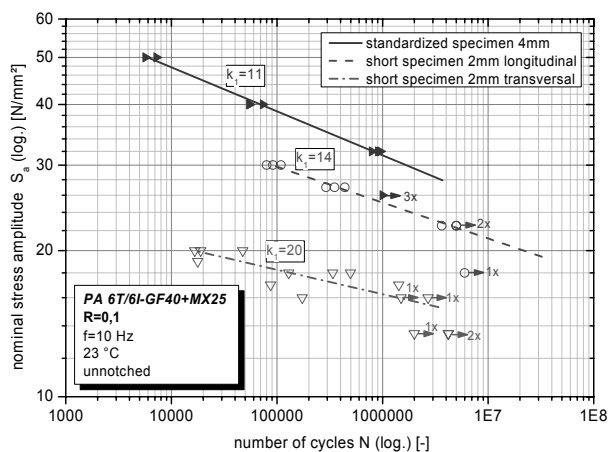
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P-10
SOME ASPECTS OF TYRE ADHESION EVALUATION

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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

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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 measured[1]. 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 $\log I/I_0$ 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
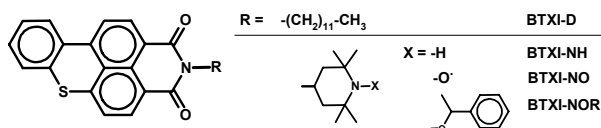
stability of the dyes was more influenced by the polymer matrix. The photolysis proceeds more rapid in the PS and PVC matrices as compared with PMMA.

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

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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 structure[1]. 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 properties[2].

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

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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

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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

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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 bis-maleimid in adhesion promoting systems.

The results also demonstrate that the presence of bis-maleimide 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)

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2-Oxazolines provide thermally initiated addition reactions with a wide range of reagents, for example with carboxylic acids, phenols, thiols and amines[1–3]. 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

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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 preparation[3] 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.
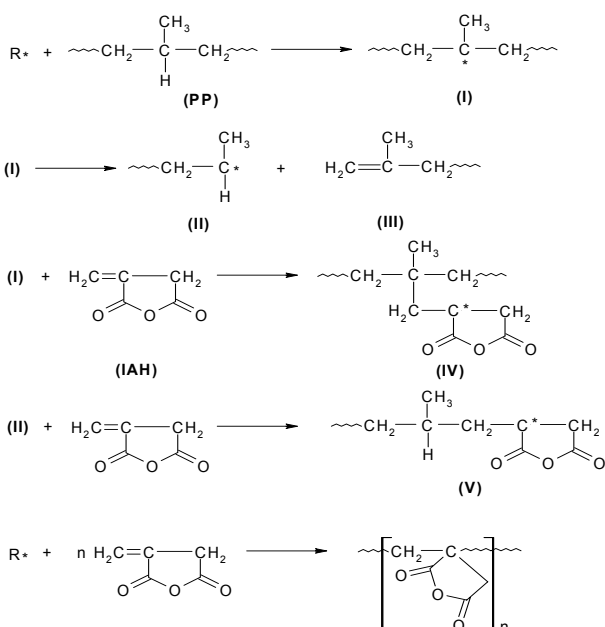
Scheme 1. **Grafting of itaconic anhydride onto PP, β-scission of PP, homopolymerization of IAH**

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_w (MFI) and α in dependence on both c_{L101} and c_{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.

M_w, observed using MFI of PP, depends strongly on
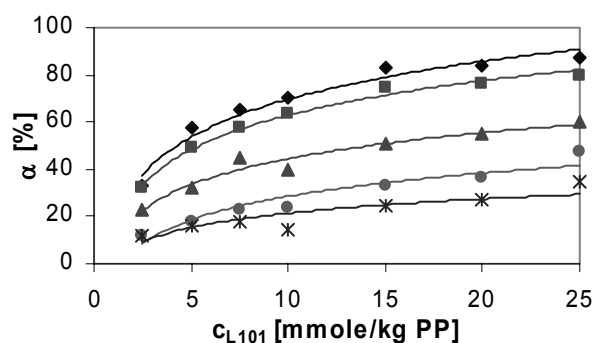
Fig. 1. **Dependence of efficiency of grafting α on Luperox 101 concentration;** Concentration of IAH ranging from 0,11 mole % to 0,75 mole %. C_{K10P} = 0,42 mmole/kg PP
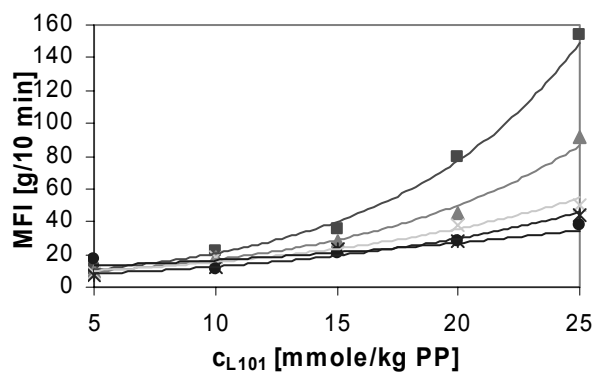
Fig. 2. **Dependence of MFI on Luperox 101 concentration;** C_{K10P}=0,15 mmole/kg of PP, concentration of itaconic acid, was from 0,5 mole % to 3 mole %
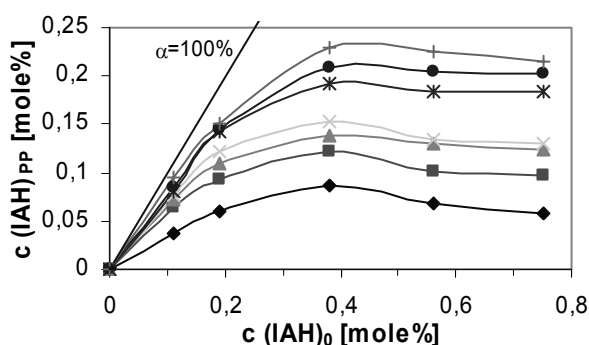
Fig. 3. **Dependence of concentration of IAH grafted onto PP versus initial concentration of IAH;** C_{L101} was 2,5; 5,0; 7,5; 10,0; 15,0; 20,0; 25,0 mmole/kg PP. C_{K10P}=0,42 mmole/kg of PP

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_w, observed by MFI, the most of all used additives. By increasing concentration of peroxide, β-scission occurs and causes decrease of M_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_w. MFI reaches in samples of high yields up to 100 times higher values than raw PP and M_w decrease form initial value 346 kg/mole to M_w of modified PP about 100 kg/mole. Also last variable, concentration of grafting agent, affects M_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

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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.
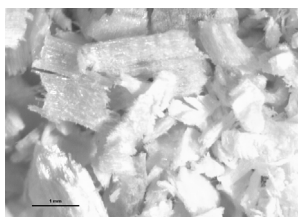
Fig. 1. **Spruce strands;**
enlargements 40×
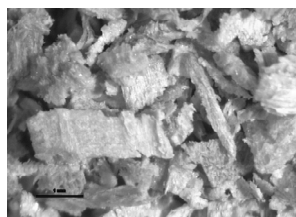
Fig. 2. **Oak strands;**
enlargements 40×
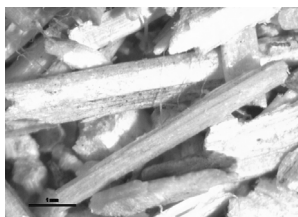
Fig. 3. **Hemp strands;**
enlargements 40×
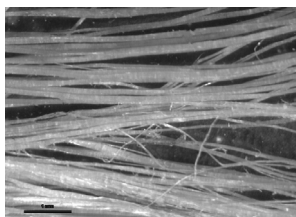
Fig. 4. **Jute fibers;**
enlargements 40×

The compounding of the components proceeded in the Brabender mixer at temperature corresponding the melting temperature of matrix. Each mixture was pre-mixed 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
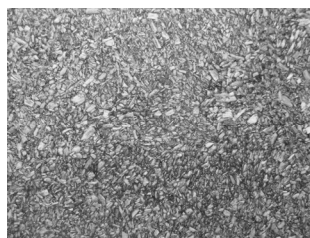
Fig. 5. **Hemp-polyethylene composite;** weight ratio: 70 % Hemp, 28,8 % PE, 1,2 % PP MA)

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.

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

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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 NH_2- and $-CO-NH_2$.

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 (N_2 and/or O_2). 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.

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P-20

IMIDIZED METHACRYLIC RESINS AS POLYMER ADDITIVES WITH IMPROVED HEAT RESISTANCE

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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 achieving of T_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-21

POLYMER MISCIBILIZERS − FORGOTTEN COMPATIBILIZERS OF IMMISCIBLE POLYMER BLENDS

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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

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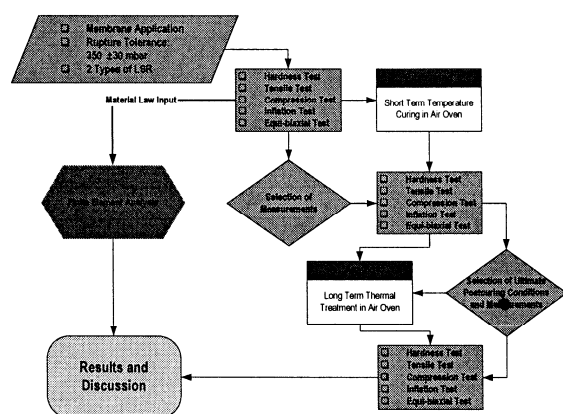
Fig. 1. **Project flow chart for the characterization and comparison of the suitability of two LSR types for the usage as a membrane application in automotive**

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 behaviour[1]. Using an adapted set-up, a friction-free stress-strain diagram was evaluated for the compression behaviour[2]. 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 code[3].

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.

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

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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 materials[1]. 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 groups[2] or coating with conductive polymers[3].

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.

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

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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 2θ 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 differences 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 amplitude[1].

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 plots[2] and by the evaluation of the frequency dependence of complex modulus.

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P-25
PHOTOCHEMICAL CURING OF ALIPHATIC URETHANE ACRYLATE COATINGS

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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-phenyl-propane-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 Δ*E* of inks after their irradiation[4] with total light dose of 20 MW m^{-2} was calculated. The urethane acrylate coatings (layer thickness 10−30 μm) increased the ink stability in about 30 %.

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P-26
MECHANICAL PROPERTIES OF ELASTOMER / LAYERED SILICATE COMPOSITES

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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.

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

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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 polymers[8], 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 N_2 and/or O_2 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

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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 reaction[1]:

$$\begin{array}{c} R \\ \diagdown \\ N-H \\ \diagup \\ R \end{array} + \; N_2O_3 \; \rightleftharpoons \; \begin{array}{c} R \\ \diagdown \\ N-N=O \\ \diagup \\ R \end{array} + \; HNO_2$$
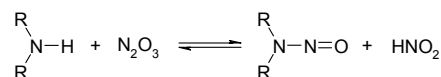
The creation of Nitrosamine-free vulcanization systems is one of the important environmental problems in the car tyres production. Present work deals with formation of Nitrosamine-free vulcanization system of rubber compond for passenger car tyres by the method of substitution of commercially used sulphenamide accelerator (Vulkacit

DZ) with some new accelerators on the base of Dithio-phosphates, that do not form dangerous Nitrosoamines. Advantages of dithiophosphate accelerators are well-known[2].

The new Nitrosamine-free vulcanization systems were prepared with the addition of three new dithiophos-phate 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 com-pared 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 DZ[4].

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P-29
STUDY OF THE ELECTRICAL PROPERTIES OF RUBBER/CARBON BLACK COMPOSITES DURING UNIAXIAL DEFORMATION AND RELAXATION

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During the past years growing interest has been de-voted to the study of the electrical properties of flexible conducting composites during mechanical deformation. Two types of deformations can be used, pressure or longi-tudinal deformation. The effect of pressure during mould-ing 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 forma-tion 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 matrices[2].

In our work the influence of longitudinal deformation on the changes of electrical properties of conducting com-posites was investigated. Two composites, ethylene-propylene rubber (EPDM Keltan 4703, DSM, The Nether-lands) 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 $2 \cdot 10^{-3}$ S cm^{-1}, while for SBR/CB composite one order of magnitude higher conductivity, $6 \cdot 10^{-2}$ 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 deforma-tion 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 re-lease of the mechanical stress.

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

We have found that different behaviours of compos-ites with EPDM and SBR matrices depend on structures of rubber matrix and on interactions between matrix and con-ducting filler. During relaxation in elongation state an increase of the current was observed which was explained by partial reconstruction of conducting paths in compos-ites. 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

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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} Ωm. 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} Ω to 10^7 Ω and decrease of volume resistivity from 10^{12} Ω m to 10^5 Ω 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

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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 silicate[1].

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 available[2].

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

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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 $SrFe_{12}O_{19}$, 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 (*1*) in the form:

$$Y = b_0 + b_1 x_1 + b_2 x_2 + b_{11} x_{12} + b_{12} x_1 x_2 + b_{22} x_{22} \qquad (1)$$

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 cross-linked 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 thermo-oxidative 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

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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 [kN]	POM Insert		PA 6.6 Insert	
	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 [kN]	POM Insert		PA 6.6 Insert	
	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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P-34

SURFACE MODIFICATION OF POLYETHYLENE IN DIELECTRIC SURFACE BARRIER DISCHARGE

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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 O_2 and/or 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 O_2 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

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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

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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 tester[5] 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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CONTENTS

Posters

AUTHOR INDEX