

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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Abstract

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.

Emerging multi-functional opto-electronic and electro-chromic materials and systems

A range of optical, electrical and other properties of functional coatings or inks can be controlled by surfacetailoring 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 by 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 electrochromic 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.

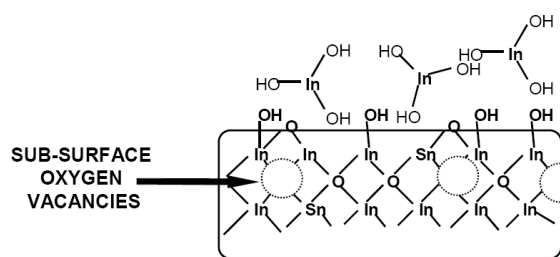


Fig. 1. Schematics of the ITO surface and sub-surface structure illustrating the following: (a) the termination of the bixeyte lattice with both, bridging and non-bridging oxygen atoms (oxygen vacancies), and (b) hydroxylated indium, $\text{In}(\text{OH})_3$, providing suitable sites for the attachment (chemisorption) of organic molecules such as dispersants and organic dopants

Flexible opto-electronic devices based on indium oxide

Pure indium oxide (In_2O_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 or 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

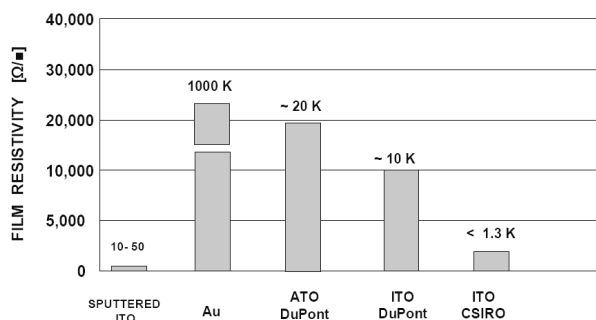


Fig. 2. Comparative data on conductivity of printable nano-oxide films on a flexible transparent PET substrate (30 μm): commercially available ITO coatings, ATO coating and a new generation CSIRO coating with ITO nano-particles doped by self-assembled electro-conductive organic molecules

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.

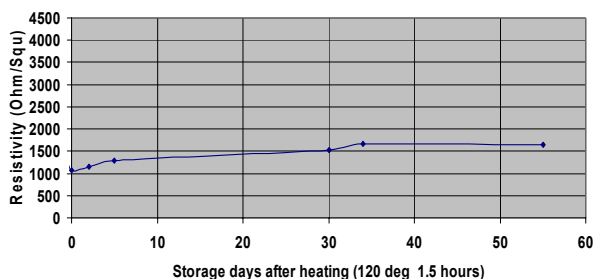


Fig. 3. Stabilisation of long-term conductivity of thin ITO film doped by self-assembled organic electro-conductive molecules

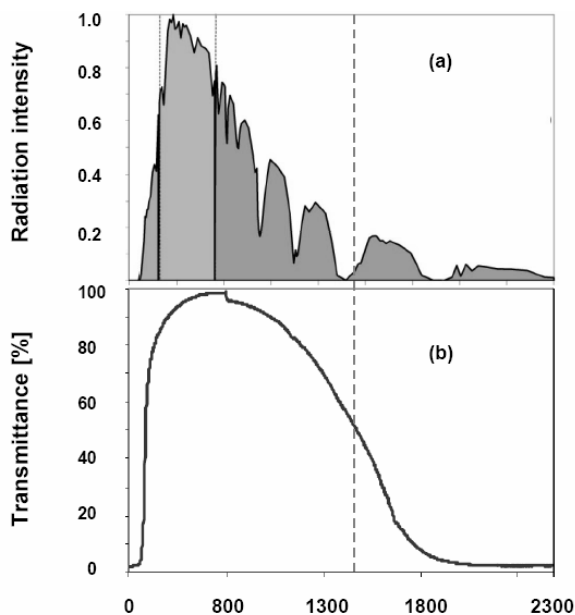


Fig. 4. (a) Full spectrum of solar radiation, and (b) UV-Vis-NIR spectrum on a nano-structured ITO coating

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 be 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 typical main features of the product tyre and about

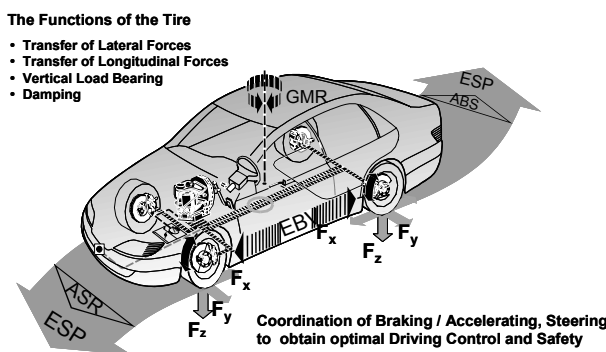


Fig. 1. Functions of a tyre

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 extent. 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

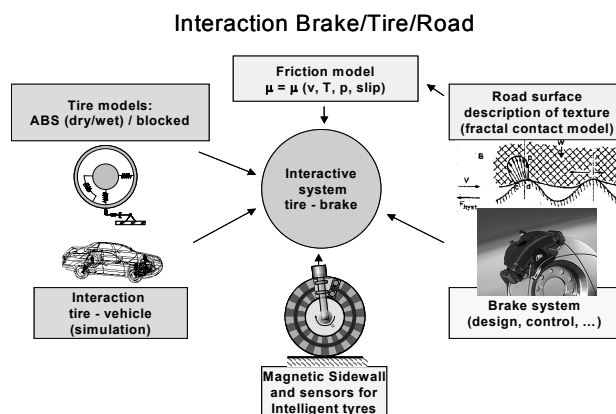


Fig. 2. Tyre as part of an interactive system

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 experiments, 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 systematic identification process in order to determine the material parameters of the models. Some basic procedures are provided by the commercial programs 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 polyurethanes¹⁻⁷. In combination with small-angle scattering, swelling experiments have been used to determine the polymer network structure and chain statistics³⁻⁵. 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 segment⁸ 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 polyurethanes¹⁰ and Pedersen's micelle model¹¹. 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 phase⁹ 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 polyetherurethane 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 ($G \approx 2.2 \text{ MPa}$) 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 CO₂ 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 2020¹. 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 elasticity⁸. 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 technology⁹. 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 filling¹⁰. *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-materials¹¹.

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 products¹³. 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 (scCO₂) was established for sulfur-cured tire rubbers¹³⁻¹⁷, 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 scCO₂. Not only NR but also synthetic rubber vulcanizates 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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Abstract

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.

Introduction

Next to conventional polymer blending by melt mixing also reactor blending became attractive for the generation of heterogeneous polymer systems¹. Especially rubber modi-

fied 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 studies¹⁻³, 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,

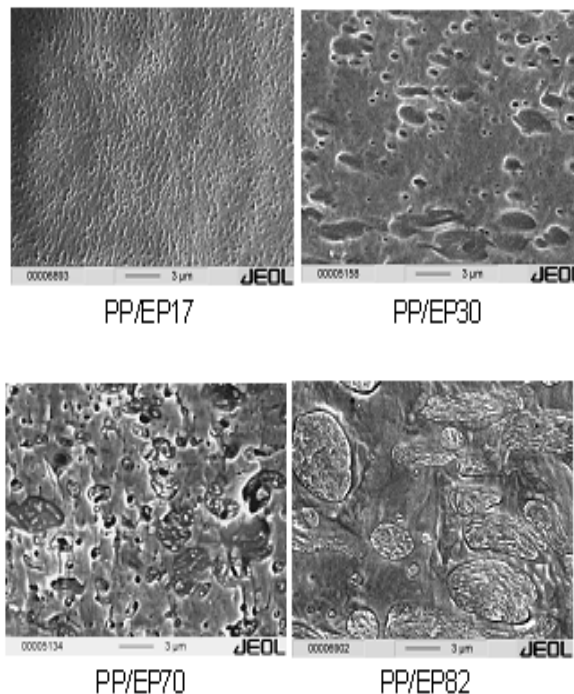


Fig. 1. Phase morphology of monomodal dispersed heterophasic PP/EP copolymers¹; the numbers mark the ethylene content of EPC, ω_{Et}^{EPC}

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 semi-crystalline 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-

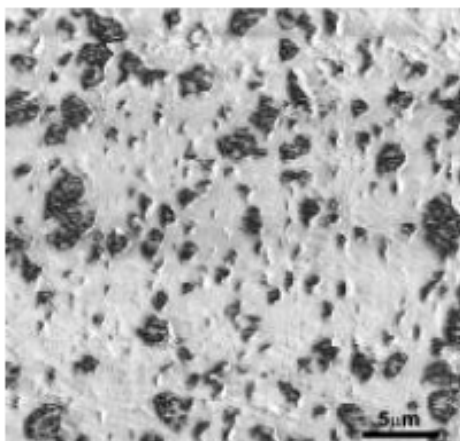


Fig. 2. AFM micrograph of an EP reactor blend with bimodal phase morphology at $\omega_{Et}^{EPC1}/\omega_{Et}^{EPC2}=30/70$ and $\phi^{EPC1}/\phi^{EPC2}=30/70$

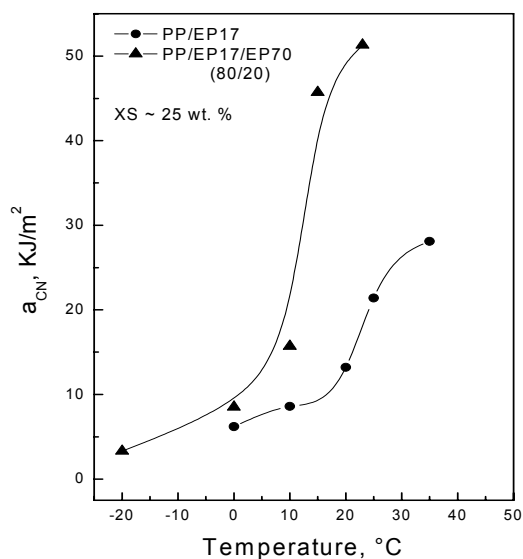


Fig. 3. Particle distribution of an EP reactor blend with bimodal phase morphology at $\omega_{Et}^{EPC1}/\omega_{Et}^{EPC2}=30/70$ and $\phi^{EPC1}/\phi^{EPC2}=30/70$

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

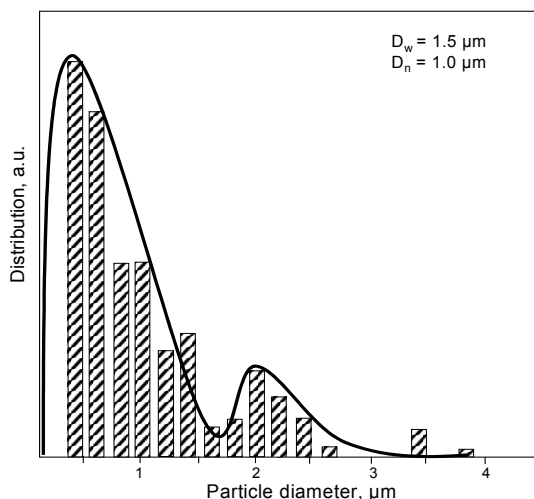


Fig. 4. Comparison between Charpy notched impact strength of an EP reactor blend with monomodal (PP/EP 17) and bimodal (PP/EP 17/EP 70) phase morphology

weight content ratio $\varphi^{\text{EPC1}}/\varphi^{\text{EPC2}}$ and different composition ratio of the EPC $\omega_{\text{Et}}^{\text{EPC1}}/\omega_{\text{Et}}^{\text{EPC2}}$, 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 occurs.

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 ethylene/propylene 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 view of scarcity and unpredictability about fossil fuel resources and at the same time availability of methods to transform abundant biomass into valuable bioproducts. 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 goods¹

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 growth².

Hydro-carbons to carbo-hydraes *A Pragmatic approach*

About 150 million ton of plastic is consumed on global basis with largest application in packaging industry³. 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

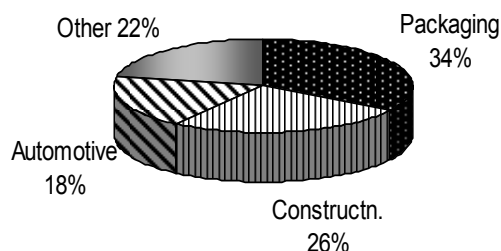


Fig. 1. Market distribution of plastic consumption

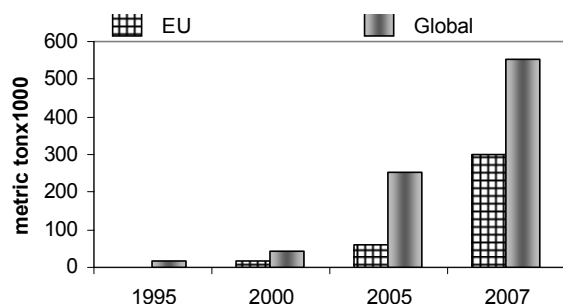


Fig. 2. Phenomenal growth of bioplastic industry in EU

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 DuPont have been responsible for most of the development of biodegradable polymers and bioplastics in Europe by spending more than 24 million US\$ in recent years⁴ and launching their brand name biobased resins and plastics like „Estar“, „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



Fig. 3. Compostable food packaging from Natura Packaging Netherland⁶

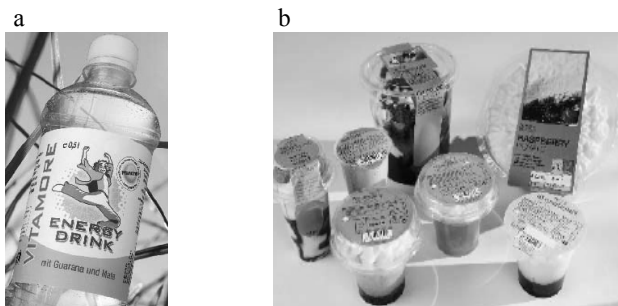


Fig. 4. Products developed from PLA- NatureWorks™. (a) First compost-able PLA bottle by „Ihr Platz“ Germany⁶, (b) Food packaging developed by „Huhtamaki“, Finland⁶



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

biopolymers for a variety of manufacturing processes⁵. 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 pillows⁷.

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. 6. TOYOTA „Ecoplastic“ Tire Cover in „New Raum“ Model⁹

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 from 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 bioplastics, making it a viable candidate for a wider range of automotive applications¹⁰.

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 ton³.

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 bioplastics compared to biofuels.
- Need of an efficient biomass harvesting and a reliable supply chain network with adequate crop storage and

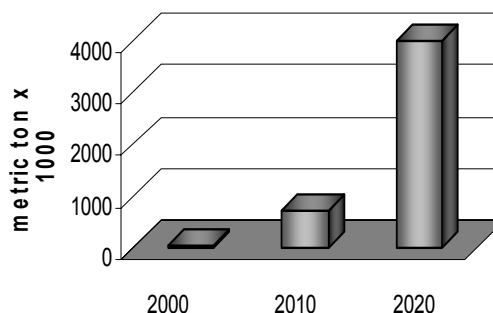


Fig. 7. **Biocrude to bioplastics**; EU projection for bioplastic growth¹¹

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 challenges, 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 CO₂ 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 Kyoto Protocol⁴. 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 infrastructure. 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

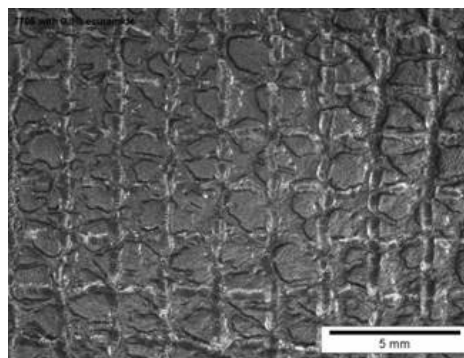


Fig. 1. Scratches on PP compound containing a high amount of slip agent

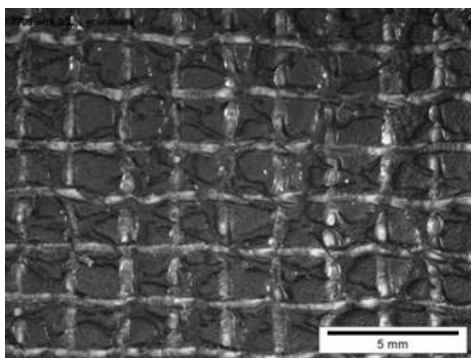


Fig. 2. Scratches on PP compound containing a low amount of slip agent

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-

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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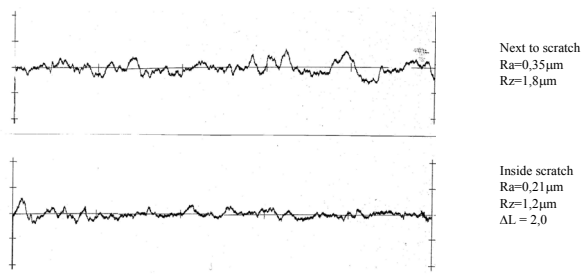
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Organoclays are effective solid additives for polypropylene composites and composite fibres¹⁻³. The development of the polypropylene (PP) based nanocomposites, containing layered silicates is focused mainly on improvement of mechanical properties of 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.

High content of SL



Low content of SL

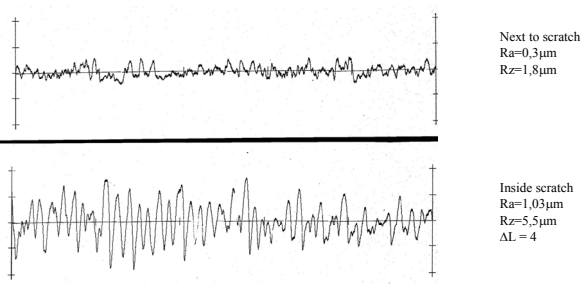


Fig. 3. Scratch roughness in samples with high and low slip agent content

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 montmorillonite (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

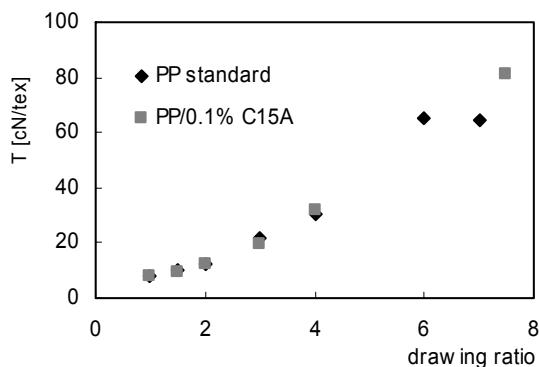


Fig. 1. Tenacity versus drawing ratio of PP/C15A (0.1%) composite fibres

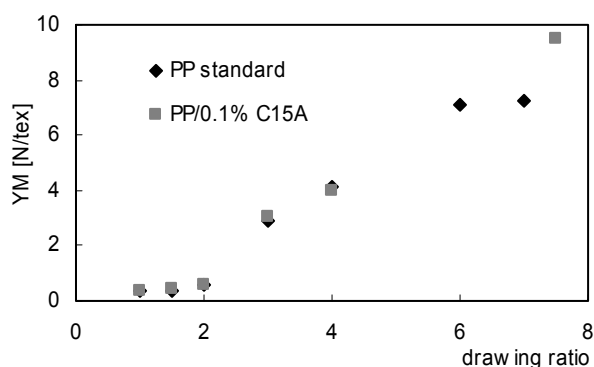


Fig. 2. Young's modulus versus drawing ratio of PP/C15A (0.1%) composite fibres

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 (PMMA+TEG)	60.6	21.9	7.36
0.1% C30B (Luc+TEG)	73.9	20.0	9.17
0.1% C30B (PBT+PTT+LiE+TEG)	69.6	22.8	8.69
0.1% C30B (PET+PBT+LiE+TEG)	77.8	19.6	9.68
0.1% C30B (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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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 of 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 latices². The size and the aspect ratio of the Cell II fibers are controlled by the shear rate applied in the flow reactor during the coagulation.

Alcaline suspensions of Na-Montmorillonite 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-glassplatelets 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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