

Slovak University of Technology Faculty of Chemical and Food Technology



Polymer Institute Slovak Academy of Sciences



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Central Europe, particularly Slovakia, has become a manufacturing hub for car production. 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 new EU emerging markets and Eastern Europe. The dominant investors in automotive industry in Slovakia and neighboring countries, namely Volkswagen, PSA, and recently Hyundai/KIA attracted a number of other companies – suppliers of plastics and rubber parts being a significant part of them – building up their new facilities and technology centers in the country.

Reflecting this development, Slovakia will host for three days the participants of the International Conference on Polymeric Materials in Automotive (PMA 2005) being a first scientific meeting on this topic in the region. 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.

Considering polymeric materials in automotive, rubber cannot be omitted. In Slovakia, traditionally this topic has been covered by the International scientific conference on rubber organized annually by the Rubber Research Institute of Matador Púchov a.s. under the name Slovak Rubber Conference. It is a privilege to have the 17th Slovak Rubber Conference as a separate session of the PMA 2005, especially, because the conference is connected with a celebration of 100th anniversary of MATADOR, the trademark of automotive - related rubber products, especially tires.

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PL-01 SURFACE ENGINEERING OF POLYMERS AND RUBBERS FOR ADVANCED AUTOMOTIVE APPLICATIONS

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Polymeric materials and rubbers are increasingly important in the manufacture of exterior and interior automotive components such as: bumper facias, protective bodyside mouldings, exterior and interior cladding, eg. door trim panels, instrument panels, seat structures and others. Another important type of materials for automotive industry are nano-composites. They exhibit significantly higher strength-to-weight ratio and stiffness, as well as higher impact strength than standard TPO's. Of particular importance are thermoplastic olefins (TPO's). The main drivers for the rapid increase in their use are: low cost, reduced specific density, easy processing and the possibility of achieving total recyclability. Standard automotive polymers are frequently chemically inert, and hence require priming or surface treatment to facilitate adequate adhesion of decorative or other functional materials.

This paper reviews the theoretical principles of macromolecular design of interfaces¹ and provides detailed discussion of industry-feasible technologies for surface engineering of polymers and rubbers for advanced automotive applications.

According to contemporary theories, significant adhesion enhancement can be achieved through the use of connector molecules chemically attached to the substrate surface¹. They act through the following mechanisms: (i) interpenetration into adjacent polymeric phase, and (ii) chemical reaction/crosslinking with the adjacent material. The effectiveness of the interface reinforcement depends on the following: surface density of grafted molecules; length of individual molecules, and optimum surface density in relation to the length of connector molecules.

Novel and relatively simple, industry-feasible technologies for surface grafting connector molecules and engineering of interface/interphase are also discussed in detail and supported by a range of experimental examples^{2,3}.

It is shown, in agreement with contemporary theories, that the use of chemically attached graft chemicals of controlled spatial geometry and chemical functionality, enables a significant increase in the strength and fracture energy of the interphase, to the point of cohesive

fracture of the substrate, or that of an adjacent medium such as adhesive, elastomer or other material. This occurs even after prolonged exposure of investigated systems to adverse environments such as hot water.

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PL-02 NON-CONVENTIONAL INJECTION MOULDING TECHNIQUES IN THE AUTOMOTIVE INDUSTRY

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Non-convention technologies in injection moulding are a major field of development in the automotive industry and in other large and technically advanced application sectors.

The main driving forces for these recent developments are associated with the attempts to reduce manufacturing costs and to improve product performance and process reliability. In fact, non-conventional moulding techniques are widening the scope of application of plastics and increasing the added-value of the produced components due to a higher level of integration of manufacturing operations.

Such technique require specific processing equipment, special moulding tools and, in some cases, a more careful selection or development of the materials to be moulded. Furthermore, the higher complexity of the processes involved present new challenges to the technical and scientific community in the field.

Within this scope, this presentation will analyse the major emerging and already available non-conventional injection moulding techniques, addressing functional and design aspects of the respective products, tooling and processing equipment. The techniques to be reviewed include: fluid-assisted injection moulding (FAIM), multi-material moulding (co-injection and over-moulding), insert and hybrid moulding, in-mould assembly, in-mould decoration, back injection, injection-welding and moulding of special materials.

PL-03 INTERFACES BETWEEN POLYMERS AND OTHER MATERIALS RELATED TO ADHESION

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Adhesion between dissimilar metals obviously depends on the interface. Therefore, understanding this interface and techniques to tailor the interfacial chemistry and properties are instrumental in improving adhesion and adhesion durability. This presentation will discuss various methods for interface tailoring and modification with emphasis on automotive materials. One process is by treatment of the substrate with organofunctional silanes. Progress has been made recently in the use of such molecules for improving adhesion between paints and metals and between rubber and metals. In addition to adhesion, such treatments also improve the corrosion resistance of the painted metal. Replacement of the phosphate conversion layer and even of the cathodic electrocoat system becomes a possibility. Another major automotive application of organofunctional silanes is that of steel tire cords. Such cords have traditionally been coated with a thin layer of brass for adhesion purposes. The rubber compounds in the critical area in the tire, the belt region, are currently formulated such that that adhesion to brass is optimized, not the compound's durability. With the use of a silane-based adhesive, it is now possible to obtain adhesion and better durability using a reformulated compound.

Another surface and interfacial modification technique that will be discussed is by plasma and plasma polymerization. This process allows one to increase the hydrophilicity or hydrophobicity of surfaces and interfaces and is, therefore, not only of great value for improving adhesion, but also in cases where adhesion or sticking needs to be prevented. One interesting application of this process is to tailor the interface between pigment particles and polymers by treatment of the particles prior to mixing. The performance of organic coatings can be greatly improved by such processes, as will be demonstrated.

PL-04 ACTUAL CHALLENGES IN RUBBER SCIENCE

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The major challenges in the upcoming decades will hinge on the availability of raw materials and energy sources. When the time frame is considerably reduced, however, and the time through to the next acute shortage is viewed, rubber technology finds itself faced first of all with the present-day orientation in the direction of high-performance products that provide high functionality under conditions of extreme dynamic stress. This assumes a more in-depth understanding of materials and realistic material concepts. This, in turn, is dependent on a step-up in basic research in the elastomer domain.

This means that it will be necessary not only to put to work increasingly profound knowledge of physical and chemical effects mechanisms in entropically elastic materials but also to develop chain architectures, including interactive monomer units and specific functionalities, aimed at improving the rubber-filler interaction.

Without the synthesis of new rubber types – e.g. by metallocene catalysis or also by hydration of already existing types – it will be difficult to solve the problem of the long-term stability and aging resistance of elastomers.

The development of modern fillers is characterized by attempts to improve the interaction among rubber types. Even if the manufacture of carbon blacks allows only limited latitude for modifying primary particles, aggregate size, aggregate shape and surface structure, the modification of reactors and processes has the effect of altering surface activity for better micro-dispersion. In the case of silica – until just a few years ago a filler of limited versatility – there are much greater possibilities for modifying surface activity with reactive compounds (e.g. silanes) during manufacture and in situ during mixing.

Proceeding on the basis of a model of chain diffusion out of tubes spatially and temporarily fixed by interhooking with adjacent chains, the viscoelastic behavior of melts can be described on the basis of the molecular structures of a polymer. The need arises to theoretically describe the dynamic mechanical behavior in the mid- to ultrahigh-frequency range. For the realization of tailor-made chain architectures, close cooperation between polymer physics and polymer synthesis is necessary here and of synergetic effect. An interesting application of this physical concept is the implementation in physically motivated material

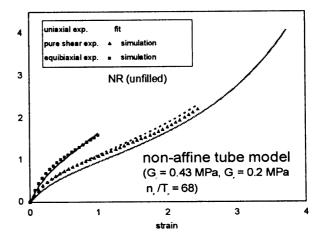


Fig. 1

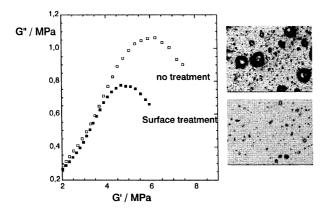


Fig. 2

laws [Fig. 1]. With the help of finite element analysis, it should be possible to provide predictive and not just adaptive descriptions of material and component properties.

A new quality in model building was achieved with insight into the fractal nature of filler aggregates and the filler networks formed from them via cluster-cluster aggregation (CCA) on the basis of a universal construction principle. This results in scale laws that describe the storage modulus as a function of the filler volume fraction or of the amplitude of deformation. Using cross-system models to describe the mechanisms of the non-catastrophic energy dissipation occurring during dynamic deformation none-theless remains a special challenge in elastomer physics.

Filler surface activity plays a big role in filler/rubber interaction. The former is composed of contributions from surface roughness, energy distribution and the type and concentration of chemical groups. For all furnace blacks, it is possible to distinguish four discrete energetic states. The share of high-energy adsorption points increases with decreasing primary particle size. This makes it possible to explain processing difficulties but also variously defined reinforcement. To ensure that the dynamic and ultimate properties are controlled in a service-appropriate manner, the surface activity of fillers can be modified in process or by means of reprocessing to more favorably accommodate the targets set [Fig. 2].

Specific functionalization of rubber (introduction of end- or side-stable amino, carboxyl, nitrile, triethoxy sylil and other groups) can make for much better use of the interaction potential of the filler surface in terms of property enhancements (traction, wear, dynamical cut-growth resistance). The further pursuit of these material concepts is clearly aimed at obtaining controllable property com-

plexes and adaptive systems. At the start, such systems are examined with polymer fillers that can be functionalized in many different ways and with correspondingly functionalized rubber types. Materials that exhibit temperature- and frequency-dependent controlled energy dissipation are expected.

One of the most desired technologies in the rubber industry is continuous mixing. Despite major advantages (steady power supply and steady process, no batch-to-batch variations, little operator attendance, reduced energy costs etc.) this technology has not been introduced until now due both to persistent equipment inadequacies and to the form in which raw rubber was delivered. Recently rubber/filler batches in powdery form were developed on the basis of rubber lattices and fluffy black or silica filter cake. Such combinations of raw materials provide higher filler dispersion, less energy dissipation and higher wear resistance in the final product. There are reasons for hoping that powder rubbers with optimized polymeric structure and filler surface activity will play a major role in the future.

Using nanoplatelets and nanotubes to realize anisotropic properties has been the subject of special interest of late, as has been surface treatment with plasma from rubber, thermoplasts and composite ingredients as a means of better controlling lubricity, adhesion and transport processes.

Another challenge is that of modifying and activating rubber and plastic surfaces by means of atmospheric plasma treatment. Applying this new technology has allowed for a cost-effective solution to adhesion problems in co-extrusion and injection molding. What's more, it has proved possible to establish friction properties, permeation barriers and anisotropic properties under controlled conditions.

The challenge in the future will be one of developing new functional raw materials, of harmonizing them and of upping the level of the utilization properties demanded by buyers (e.g. the auto industry) without, for all that, compromising quality.

PL-05 DEVELOPMENT OF AUTOMOTIVE INDUSTRY IN SLOVAKIA

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KL1-01 FLUOROPOLYMERS IN AUTOMOTIVE APPLICATIONS

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Fluoropolymers represent a family of materials available as thermoplastic resins and elastomers. The thermoplastic resins are analogous to polyethylene, in which hydrogen atoms attached to the carbon chain are replaced by fluorine or fluorinated alkyl groups. Sometimes, chlorine is also part of the molecule. Fluorocarbon elastomers are mainly copolymers or terpolymers of fluorinated monomers. The most common commercial fluoropolymers are:

- PTFE (polytetrafluoroethylene) from tetrafluoroethylene [C₂F₄],
- FEP (fluorinated ethylene-propylene) from tetrafluoroethylene and hexa-fluoropropylene [C₃F₆],
- PFA (perfluoroalkoxy) from tetrafluoroethylene and perfluoropropylvinyl ether [C₃H₇C₄OF₅],
- ETFE (copolymer of TFE $[C_2F_4]$ and ethylene $[C_2H_4]$),
- PCTFE (polychlorotrifluoro-ethylene) from chlorotrifluoroethylene [C₂F₃Cl],
- ECTFE (copolymer of ethylene and chlorotrifluoroethylene),
- PVDF (polyvinylidene fluoride) from vinylidene fluoride [C₂H₂F₂],
- PVF (polyvinyl fluoride) from vinyl fluoride [C₂H₃F],
- Fluorocarbon elastomers (copolymers or terpolymers based on vinylidene fluoride and other fluorinated monomers),
- Perfluoroelastomers (copolymers of TFE and perfluoropropylvinyl ether with a specific cure-site monomer).

Because of their high chemical resistance, and in many cases their capability of service at high temperatures, fluoropolymers are well suited to the use in automotive applications, such as hoses, *O*-rings, gaskets, electrical insulations, fuel lines, engine parts, parts of drive train, exterior parts and trim, protective coatings etc. The most recent developments are UV-curable paints, lamination films for body panels and membranes for fuel cells. This contribution will discuss the main automotive applications of fluoropolymers in some detail.

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KL1-02

EFFICIENCY AND FLEXIBILITY OF THE DIRECT PROCESS LFT-D-ILC FOR THE MANUFACTURING OF LONG FIBER REINFORCED AUTOMOTIVE PARTS

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The relevance of long fibre reinforced thermoplastics in the automotive sector has grown significantly over the past years. State of the art technologies are processing of semi-finished products like glass mat reinforced thermoplastics (GMT) by compression moulding and long fibre granulates (LFT-G) mainly by injection moulding. However, the so-called "Long fibre direct process technologies" (LFT-D) are about to gain growing market shares. These technologies enable manufacturers to produce components directly employing the base materials such as glass fibers, thermoplastic resins and additives by utilizing an in-line compounding process prior to compression moulding.

Concerning the selection of materials, the LFT-D-ILC process technology with in-line compounding of the matrix polymer offers added value in terms of flexibility, single heat exposure and costs. The matrix polymer is tailored directly within the process by adding modifiers to adjust mechanical and specific properties, e.g. heat stabilization, for each application individually.

The object of this paper is the introduction of the process technology and its advantages. Compared to injection molding, compression molding offers the possibility to achieve large area thin walled parts avoiding weld lines and offering very short cycle times and a high productivity. A large scale production of underbody panels will be presented.

Furthermore the combination of long fiber-reinforced thermoplastics with local continuous fiber structures or fabrics, referred to as Tailored LFTs, represents a further development of fiber-reinforced thermoplastic materials. Local reinforcements of LFT components for the automotive industry lead to mono-material composite hybrid structures with an optimized performance/weight ratio.

Integrated process technologies lead to a cost efficient large scale production with a high grade of automation to ensure reproducibility. A prototype production of a hybrid front end structure will be presented.

KL1-03 CLARIANT MASTERBATCHES, A CHALLENGE FOR AUTOMOTIVE APPLICATIONS

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To attract today's critical customer, automotive industry offers various brands with numerous models with a lot of different options. The different colors of the car and his components are also an important criterion for the potential buyer.

Polymers have become an important material to be used for automotive applications. More than 100 kg plastic material per car is used for various interior and exterior applications like: bumpers, side protection, dashboards, door panels, upholstery, tissues for chairs, carpets for floor covering etc. Plastic materials are used as polymers, compounds, blends, alloys or composites, all customized to meet the specific requirements according their applications. Intensive research in this area has opened more and more applications for these materials but also the number of available grades has enormously increased. For esthetic parts a great variety of grades and a large scale of colors is applied. CLARIANT DIVISION masterbatches offers products to customize all these plastic materials regarding colors and physical properties.

Products of Clariant Masterbatches are on the market under the following brand names:

- OMNICOLOR: color concentrates for universal purposes to be compatible with most of the resins.
- REMAFIN: color concentrates or multifunctionalbatches (combination of colorants and additives) for Polyolefin applications.
- RENOL: color concentrates or multifunctionalbatches (combination of colorants and additives) for PS, ABS, PA, POM, PET, PETG, PET, PMMA, PC etc.(non Polyolefin applications).
- CESA: additives concentrates, UV stabilizers, anti blocking agents, anti slip agents, anti oxidants, anti static, flame retardants, anti microbial, purging agents.
- HYDROCEROL: Chemical blowing agent (CFA) concentrate.
- ENIGMA: Special effects concentrates like glitter, interference, irrisend, luster, metallic, splash, thermo chromic, laser marking.

Besides his products, CLARIANT masterbatches offers also a wide range of services to his customers. As masterbatch house CLARIANT is specialized in the development of colors. Clariant Masterbatches are composed out of colorants and upon request they can also contain combinations of additives to improve the properties of

the resin. Supported by extended color libraries and colourmatching soft-ware, trained and experienced colorists match colors for every commercial available resin. As a Masterbatch house Clariant is a well known partner for designers in automotive industry for developing new colors. Starting from a color idea realized on paper, tissue, leather, plastic or other support, Clariant colorists transfer the color into plastic materials or synthetic fibers. Clariant color laboratories are equipped to produce standard color plaques for RENAULT, PEUGEOT, CITROEN, VW, SKODA, NISSAN and D/C MERCEDES. Tools to produce color plaques for other OEM will be soon available. Because CLARIANT is independent, there is no preference to use any particularly product form a defined resin producer. Clariant color formulations guarantee to be composed of the optimal colorant selection to be compatible with most of the used resins to avoid metamerism.

In collaboration with leading companies for color design and creation, CLARIANT participates in the well known "PERCEPTIONS nr. 5". This presentation tool for color forecast 2006, will assist designers to get new inspiration. Clariant's COLOR WORKS design and technology centers are meeting places for color specifiers, customers and business partners. Designers, marketing specialists and brand managers can use Clariant expertise and design tools to develop colors and technological solutions to color challenges.

Math Fouarge (1959) started his professional carreer in "plastic" industry in 1985. He joined Clariant in 1992 as laboratory manager for colourdevelopment. Since 1995, he works for CLARIANT MASTERBATCHES as specialist for the automotive market.

KL1-04 ADVANCED SCATTERING REFLECTOMETRY METHODS FOR CHARACTERIZING THE STRUCTURE OF POLYMER COMPOSITES

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Nanocomposite polymers comprised of two chemically linked, immiscible components with very different physical properties derive beneficial properties from the separation of the components into nanoscale domains. The problem is to determine the structure-property relationships of these materials to understand performance and the effects of aging. A case in point is thermoplastic, segmented poly(ester urethanes), used as adhesives, binders

and coatings, consisting of crystalline and rubbery segments that phase separate into hard and soft segment-rich nano-domains, resulting in an extended, crosslinked, network. We seek to address the domain composition and structure and the network structure, how these relate to the domain micromechanical properties and the overall mechanical properties of the material. We used contrast variation methods with small-angle neutron scattering on deuerated/protonated blends and network swelling with mixtures of deuterated and protonated solvents and with anomalous x-ray scattering and reflectometry measurements on thin films. In poly(ester urethanes) with low hard segment content used as adhesives and binders there is considerable mixing of the hard and soft segments, resulting in a small population of hard segment-rich domains. Thin films of poly(ester urethanes) may be significantly different that that of the bulk material.

KL1-05 USE OF HIGH MODULUS DEFORMABLE INCLUSIONS TO ENHANCE IMPACT RESISTANCE OF BRITTLE PLASTICS

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In most automotive and appliance applications of plastics, the ductile-brittle-transition (DBT) temperature below -30 °C is desired. In order to obviate the problem of relatively high DBT temperature of brittle polymers, elastomer inclusions are commonly added in an amount ranging from 10 to 30 wt %. The mechanism of toughening involves secondary deformation mechanisms and to extend volume of material undergoing plastic deformation during critical loading (delocalization of plastic deformation at the crack tip). The increase in DBT temperature is balanced by a substantial reduction of the elastic moduli, reduction in Vicat softening point and heat distortion temperature greatly imparting utilization of such a material for under the hood applications (needed both low and high temperature performance).

In our previous work, we have shown that one can achieve both increase in fracture toughness (lower DBT temperature) and increase in elastic modulus of isotactic polypropylene (iPP) by incorporating low volume fraction of complex rigid core-soft shell inclusions. Delocalization of the plastic deformation at the crack tip region is believed to be the most probable mechanism for the observed behavior. One can enhance fracture resistance of iPP even further via incorporation of a new deformation mechanism in addition to the shear yielding of iPP matrix. It is our

hypothesis that such an additional mechanical energy absorbing mechanism is cold drawing of thermotropic liquid crystalline polymer (TLCP) inclusions under shear stress field in the region near crack planes. This will result in consumption of deformation energy ahead of the crack front resulting in a reduction of the crack driving force and, at the same time, in a stabilization of formed microcracks through bridging the crack planes with the drawn microfibrils, providing the TLCP-PP interphase can be engineered to achieve optimum stress transfer from PP to the TLCP. Similar approach can be utilized to enhance fracture resistance of poly-methylmethacrylate (PMMA) via incorporating poly-vinylalcohol (PVA) fibers. In this case, the fibers oriented properly in respect to the crack plane can contribute to dissipation of mechanical energy localized close to the crack tip.

In this contribution, preliminary results from a study investigating effects of structural variables such as inclusion size and properties of the engineered interphase on the DBT temperature and high temperature elastic modulus of PP/TLCP blends for the LCP content ranging from 0 to 20 vol % will be presented. Fracture behavior of PMMA containing various volume fractions of PVA fibers of two aspect ratios will also be presented. Fracture mechanics will be used to analyze experimental data obtained in instrumented Charpy notched impact test. Finite element analysis model has been utilized to predict deformation response as a function of the interphase properties and size of the inclusions. Reasonably good agreement between the experimental data and theoretical predictions has been achieved. for both TLCP/iPP and PVA/PMMA systems. It has also been concluded that the response of these materials to fracture occurs only near the crack planes and the local damage can be thermally healed to a great extent. This feature placed the materials investigated among the "smart materials" holding a promise for applications in automotive industry.

KL1-06 POLYPROPYLENE /ASPEN/ LIQUID POLYBUTA-DIENES COMPOSITES: MAXIMIZATION OF IMPACT STRENGTH, TENSILE AND MODULUS

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BY STATISTICAL EXPERIMENTAL DESIGN

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A systematic study of the effect of concentration of maleated polypropylene MAPP, dicumyl peroxide DCP, polyisobutadiene isocyanate PBNCO and fiber content on the mechanical properties of Aspen-PP composite was undertaken with the objective to protect or increase the impact strength without losing tensile strength reinforcement. Using STAGRAPHIC Plus, the central composite design it was possible to determine the optimum concentration of additives and to maximize both the impact as well as tensile properties well above that of pure polypropylene.

Statgraphics Plus is a very powerful program for the statistical evaluation. It can be used to determine the effects (main and interactions and optimize the correlations between independent variables (MAPP, PBNCO, DCP...) and dependent variables (properties).

The STATGRAPHIC Plus enables us to calculate estimated maximum property values as well as values of independent variables necessary to use to maximize properties.

Results at this study confirm trend, that Aspen Fiber reinforcement of polypropylene composites could be made without the loss of the impact strength and achieve. The tensile strength properties increase at the same time.

To be more precise, values of max stress (stress at yield) could be increased from 32 MPa of PP to more than 60 MPa for the composite, values of Young modulus from 700+ of PP to 1700+ MPA for the composite; values of Impact strength from 52 J m $^{-2}$ of PP to 60–62 J m $^{-2}$ for the composite.

The authors would like to thank to Network of Centres of Excellence, AUTO 21 (The Automobile of the 21st Century) and the NSERC for the financial support.

KL1-07 BIOCOMPOSITES FOR AUTOMOBILE APPLICA-TIONS

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Parts made of polymer composites filled with natural fillers (biocomposites) currently constitute constantly growing share of components used in automobiles, electronic equipment housings and other large size products. Some examples of such applications have been presented in the paper. Mechanical and damping properties as well as the processability of biocomposites have been discussed in the paper. Properties of composites based on PP, PE and soft-PVC filled with cellulose fibers of different origin have been presented. Increase in the mechanical properties and higher melt viscosity in comparison to the net polymers have been evidenced. Resulting composites contain up to 50% of a wood filler, looks like wood and exhibit advantageous properties:

- high stiffness;
- enhanced Vicat softening temperature;

- lower mass in comparison to glass reinforced composites;
- safety in case of crash;
- higher comfort;
- sustainability.

Critical conditions for the high quality products manufacturing have been discussed, future trends and possible research areas have been proposed.

KL1-08 CONTEMPORARY DEVELOPMENT IN RE-SEARCH AND PRODUCTION OF INDUSTRIAL FIBRES

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The contribution gives a review on the latest development in three generations of industrial technical fibres and deals with their structure, properties and application.

With the introduction of manufactured fibres in the first half of the twentieth century they offered besides new high performance qualities for fashion fabric also superior technical properties. Nylon, polyester and steel replaced step by step the cotton cords and dominated the market till now. Mechanical-physical properties of the conventional industrial yarns are getting higher and higher mainly the tenacity and the elastic modulus. Their tenacity has increased about 50 % during the past three decades. Moderately high strength and high elongation gives a very high energy to break. They have also good recovery properties. However increase in stiffness with rate of loading reduces their performance in ballistic application.

In the last quarter of the last century a second generation of manufactured fibres became available. They are called high tenacity and high modulus fibres (HT-HM), and they are based mainly on full aromatic polymers (aramide, acrylates and others). The tenacity of these high performance fibres has increased up to 5 times and the modulus has climbed up to 17 times of polyester technical yarn. Furthermore, many technical yarns made of new materials such as polyphenylene sulphides, polyether ketons and others were introduced in the market. They are high thermo-stable fibres.

To understand the relationship between mechanical properties and molecular structure of polymer fibres, many molecular models were introduced. Extended chain structure (ECS) gives strong fibres and chain folding structure (CFS) is characteristic for conventional fibres. There is a third generation of fibres, which is appearing at the beginning of twenty first century. These smart (intelligent) fibres with some special physical or chemical properties

give a new dimension to the use of textiles. There are many applications for smart fibres in technical textiles.

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KL1-09 IMPROVING DIMENSIONAL STABILITY IN PP WITHOUT SACRIFICING THE PROPERTY BALANCE

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The importance of dimensional stability for the automotive industry is evident from the fact that a car consists of a combination of metal, fiber reinforced composites and polymer blends. Metals have a coefficient of linear, thermal expansion (CLTE) in the order of 25×10^{-6} K⁻¹ (aluminum) or $12 \times 10^{-6} \text{ K}^{-1}$ (iron). Design and construction requires an optimum set of expansion coefficients. Typical requirements for a tough polypropylene are coefficients of linear thermal expansion below $90 \times 10^{-6} \,\mathrm{K}^{-1}$ and shrinkages, 24hours after moulding at room temperature, below 0,9 %. Standard ways to reach those requirements are for example the addition of fillers; this leads to an increase in weight and a different property balance concerning E-modulus and impact strength. In this paper, new concepts to combine low weight, good mechanical properties and dimensional stability are shown. The basis of a changing dimensional stability lies in the surface morphology and is achieved by introducing a layered rubber-PP structure. This change in morphology reduces the expansion coefficients in the important length and width direction, which is accompanied by a slight increase of CLTE in the direction of the thickness. This can be explained by a different stress distribution, which is achieved during the injection moulding process. Our goal is, to achieve a material with a very good dimensional stability without loosing primary properties.

Changing the skin morphology of rubber-toughened polypropylene blends leads to improved dimensional stability of such a material. By reaching such morphology an overall superior property balance can be reached.

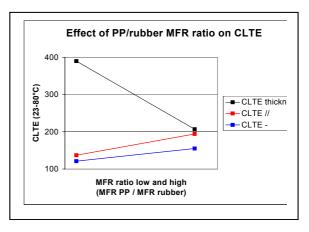


Fig. 1. Changing the morphology leads to anisotropic properties and therefore to an improvement in expansion coefficients in the parallel and perpendicular direction

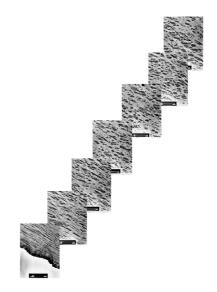


Fig. 2. TEM micrographs from surface to bulk of copolymer sample with a low MFR ratio

KL2-01 CONCEPTS IN THE COMPOUND REINFORCE-MENT: A REVIEW FROM FULLERENE-LIKE STRUCTURES TO NANOSTRUCTURED FILLERS

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The role of fullerene-like structure in carbon black reinforcement mechanism will be reviewed together with the new tools in achieving anisotropic reinforcements, barrier effects and additional reinforcement using nanostructured fillers.

Starting from the definition of fullerene-like structure, from the experimental detection of these sites and from general properties of fullerenes, it is shown the electron affinity of fullerene-like structures in carbon black should exceed that of C60 fullerene. Therefore the fullerene-like sites in carbon black should act as free radical acceptor sites where the rubber chain macroradicals formed by chain scission or hydrogen abstraction during mixing could add in competition with other known sites, to form chemical bonds, grafting the rubber on the carbon black surface. Fullerene-like structures in carbon black play a crucial role in bound rubber formation.

The discussion will be moved to the application of new nanostructured fillers in rubber compounds covering the benefits deriving from the application of this new technology.

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KL2-02

SILANE COUPLING AGENTS FOR MECHANI-CAL RUBBER GOODS BASED ON SPECIAL PURPOSE ELASTOMERS

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The use of sulfur-functional organosilanes like bis

(triethoxysilylpopyl)tetrasulfide (Si 69) as coupling agents in silica-filled rubber compounds is well known¹⁻³. Main application of these silanes is the use in sulfur-vulcanized diene rubbers for tire tread compounds. Besides diene rubbers the MRG industry uses a variety of special purpose elastomers. There, depending on the type of elastomer other vulcanization systems like peroxides or metal oxides as curing agents are required. The choice of the silane coupling functionality depends strongly on the elastomer and the vulcanization system.

This presentation demonstrates the potential of special silane coupling agents for special purpose elastomers. Apart from sulfur-functional derivatives, also silanes with unsaturated double bonds or with hetero functional groups are presented. Application examples are given and the influence of the amount of silane on the in-rubber properties is demonstrated. Proposed reaction mechanisms are discussed.

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KL2-03

RUBBER/(ORGANOPHILIC) LAYERED SILICATE **NANOCOMPOSITES:**

STATUS AND FUTURE TRENDS

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Layered silicates (LS) are unique as their layers are hydrophilic and can be broken down into their constituting platelets of ca. 1 nm thickness. Exploiting their cation exchange capability and using suitable surfactants they can also be rendered hydrophobic (organophilic).

Polymer/organophilic layered silicate (OLS) nanocomposites of outstanding mechanical and barrier properties were initially developed by researchers at Toyota Central Research Laboratories (Japan). As follow-up of this pioneering work vigorous R&D activity started in the world. The concept of nanoreinforcement has been successfully introduced in thermoplastics and thermosetting resins. The reader is addressed to some valuable reviews on this field¹⁻⁴.

Interestingly, less work was performed on rubber/ OLS systems although rubbers are predestinated for this

kind of nanoreinforcement due to the high shearing during melt compounding, low vulcanization temperature and favorable chemical interactions between the organophilic (onium) surfactants and recipe components⁵. To produce rubber/(O)LS nanocomposites various strategies can be followed, such as in-situ (intercalation) polymerization, melt intercalation, solution blending, latex coagulation etc⁶.

The lecture surveys the preparation and properties of rubber nanocomposites. Special attention will be given to the latex and melt compounding techniques, the author's group is mostly dealing with.

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KL2-04 MATADOR IN AUTOMOTIVE - FROM VISION TO MISSION

Š. ROSINA

KL2-05 A NEW ERA FOR RECYCLED MATERIALS

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More than 100 products used in the construction of a vehicle are currently manufactured from rubber or rubber composites. In addition to tyres, these products include interior housings and mats, exterior trims and seals as well as a broad range of belts, gaskets and caps under the hood. Today, the preponderance of these products are produced from virgin materials.

The mandates of the End-of-Life Vehicle Directive coupled with the increasing costs of virgin materials has begun to focus attention on potentials for the use of recycled materials. Research during the past decade has resulted in an array of new and/or improved materials and applications which can offer viable alternatives to costly, difficult to obtain virgin materials.

A new gereration of recycled materials has evolved. Dependent upon the technology used, these materials can exhibit many of the same characteristics as virgin rubber, EPDM, carbon fillers or TPEs. The materials can be adapted or modified to meet stringent industry standards and, thus, can effectively substitute for traditional materials

Many of the issues that limited the use of these materials have been resolved. Even the odor has been removed and fogging is no longer a problem.

Post-consumer tyre materials are readily available throughout the EU. A continuous supply is guaranteed. The quality and consistency of the materials produced is also assured. The industry has worked closely with CEN and the Swedish Standards Institute to prepare a European Norm for the production of post-consumer tyre materials. PrEN 14243 End-of-Life Tyre Recycling, is poised for a final vote. The EN will afford automotive parts producers the confidence to select the appropriate materials to attain their designs and specific performance requirements.

CL1-01 NOVEL TPOS FOR AUTOMOTIVE FROM SLOVNAFT, BRATISLAVA

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Slovnaft, a.s., Bratislava a member of MOL Group is the Refinery and Petrochemical Company producing from plastics LDPE and PP. Increased production of propylene monomer in MOL Group after year 2000 ended in a strategical decision to construct a new PP Unit:. In the time the tender process for new PP technology was ongoing a new investment of PSA (PEGUET& CITROEN Automotives) in Slovakia was officially announced. The contract for new PP Unit was signed with DOW CHEMICAL in November 2004 with scheduled start up April 2005. When New PP unit was under the intensive construction period in February 2004 a further automotive project in Slovak Republic – was announced. Existing Volkswagen Bratislava with continuously spreading demands for local suppliers was only the natural development.

This positive coincidence created a further prospects for the PP products from New UNIT.

New PP Unit in Slovnaft Bratislava will have the UNIPOL TM Process with nameplate capacity of 255kt/y. Unit is licensed for production of homo, random and impact PP copolymers. What is a specific feature of the Unipol TM Process? The specific feature of the UNIPOL TM process is enhanced convenience for the copolymer grades production including TPO products. Copolymers namely impact copolymers are in a majority applications targeted for injection moulding. And automotives are the challenge for TPO products.

Slovakia except of having 3 car producers will have at the same time new PP UNIT including TPO production convenient for automotives. The first compounding facility to make the requested TPO compounds is on the way.

By these projects the demand of automotive industry – to have local suppliers as much as possible is becoming realistic .

TPO products from Slovnaft Bratislava will be characterised by extra high impact properties specially under low temperatures. This excellent performance will be a result of specially controlled microstructure of rubber phase in homopolymeric matrix. Due to that ductile brake temperature will be lower than with the other source TPO grades.

The product performance expectations are high.

CL1-02 DEPOSITION OF THIN SIO_X FILMS FROM RF PLASMA POLYMERIZED HEXAMETHYLDISILAZANE (HMDSN) ONTO ALUMINIUM ALLOYS: XPS AND CONTACT ANGLE MEASUREMENTS STUDIES

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Deposition of thin films from plasma polymerized hexamethyldisilazane (HMDSN) onto aluminium alloy (Alclad 2024-T3) has been investigated in-situ and ex-situ by X-ray photoelectron spectroscopy (XPS) and contact angle measurements, respectively. Plasma polymerized thin films from (HMDSN/O₂) were deposited on substrates cleaned with 13.56 MHz argon plasma. In the absence of oxygen, a superhydrophobic ($\Theta > 100^{\circ}$) film is formed. Whereas, a hydrophilic ($\Theta = 30^{\circ} \pm 3$) film is formed with the introduction of oxygen. The decreasing of the N/Si ratio and the increasing of the O/Si one with oxygen content indicates the formation of thin polysiloxane-like thin films. This is confirmed by the calculation of the surface free energy of the deposited film at high oxygen content (HMDSN/O₂: 1/20). The surface tension components (γ_s , γ_s^d , γ_s^{AB} γ_s^+ and γ_s^-) are in excellent agreement with those of reference silica based materials (ex., silicon wafer, cleaned glass¹ and O₂ plasma treated ITO (ref.²).

This work is supported by Région Wallonne (RW n 021/5208) in the framework of a collective reasearch project "ECOPO" in collaboration with Université de Mons-Hainaut and Coating Research Institute (CoRI)

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CL1-03 APPLICATION OF RADIATION MODIFIED POLY-MERS IN AUTOMOTIVE INDUSTRY

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Modification of polymers by radiation involves the following chemical processes: polymerization, curing, grafting, crosslinking and degradation. Polymers treated

by radiation due to their modified (usually improved) properties found to be useful in many areas of application.

Automotive industry is one of the most significant consumers of radiation modified polymers. Usually required properties such as temperature resistance, mechanical strength, chemical resistance etc. are very often easily reached with radiation crosslinked polymers. In many cases components made of polymer materials have excellent, even unique properties and sometimes they are literally irreplaceable.

In this survey, main applications of radiation modified polymers in automotive industry are presented as well as the possibilities for further development which are practically unlimited.

Recently radiation has been used for improving compatibility of different polymers which are incompatible or partly compatible. By radiation supported compatibilization even radiation noncrosslinkable polymers could be used for new multicomponent polymer materials. This technique gives also some opportunities how to qualitatively use recycled polymers. Besides that, radiation is also efficient in modifying polymer composite materials and can advance their application.

CL1-04 LATEST DEVELOPMENTS IN FLUID ASSISTED MOULDING FOR AUTOMOTIVE APPLICATIONS

RAYMOND FOAD

Cinpres Gas Injection Limited, Units 1–4 Prosperity Court, Prosperity Way, Midpoint 18, Middlewich, Cheshire, CW10 0GD, England

Undoubtedly one of the most significant developments in automotive plastic part manufacture over the last 20 years has been the growing use of "Fluid Assisted Moulding" techniques.

Developed in the early 1980's by the British based company Cinpres Gas Injection Limited the process is now in common use for the manufacture of numerous internal and external plastic automotive components.

The paper will cover the three basic process methods currently used to produce automotive parts, (Short Shot, Full Shot and Plastic Expulsion Process), and will discuss the benefits (and limitations) of each process.

Recent process developments will also be covered including the use of External Gas Moulding (EGM), Gas Cool technology and Water Assisted Moulding (WAM).

Throughout the lecture various important automotive applications and case studies will be high lighted and discussed in some detail.

CL1-05 INFLUENCE OF WALL SHAPE AND TECHNO-LOGICAL CONDITIONS ON WARPAGE DURING INJECTION PROCESS

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The situation on the dynamically changing market requires faster development and design of the injection molded parts and molds which are necessary for their production. Injection molds manufacturing is very precise, demanding and high-priced. Then any changes of the molding shape or mold design after trial operation have to be paid by production costs and time loss of the new product introduction to the market.

One of the very carefully watched parameters of the injected plastic parts is warpage. Warpage is part deflection and deformation after ejection of the part from the mold cavity. It leads to shape and dimension changes which can be out of toleration field borders. If some of part dimensions are out of tolerance, it is necessary to reset injection conditions at first and being the step without sufficient results, then there have to be changed shape and dimension of the mold cavity in this case.

Warpage is primary caused by residual stresses generated during the injection cycle. We distinguish two kinds of residual stresses. Injection inducted residual stress generated during the filling and packing stage and thermal inducted residual stress rising during the packing and cooling stage. The injected part is constrained by the cores and cavity in the mold and both the stresses can not deflect the part. After ejection of the part from the mold the stresses have to rich the balanced state and deflect the injected part.

As it has been written above any reparation of the mold shape increases the production costs and prolongs production time of the mold. There are the solvers being able to count and predict the warpage during the part and mold designing. The prediction calculated from polymer properties, shape of the part and injected conditions.

One of the world wide performed solver is Moldflow MPI. There was solved the warpage and air trap (air closing in the part) of the automotive engine cylinder head cover injected from PA 66 filled with glass fibers. The deflection was reduced by part wall shape optimization and the air trap as well.

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CL1-06 PP/WOOD FLOUR COMPOSITES OF ENHANCED IMPACT STRENGTH

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Compatibilization of polypropylene/wood flour (PP/WF) composites by means of maleated polypropylene (PP-g-MAH) brings about an enhancement in the tensile strength and bending, but also a drop in the impact resistance. In order to improve this parameter a set of functionalized elastomers (SEBS-g-MAH) was implemented.

Influence of these compatibilizers on the processability (expressed by melt viscosity and MFI) and end-use properties of PP/WF composites was estimated. Tensile, bending and Charpy impact characteristics have been presented, as well as DMA results. In parallel to the enhancement of impact strength of the materials, a lower stiffness was observed.

Selected materials were subjected to the accelerated ageing for 720 h. Influence of UV and temperature on the mechanical strength and melt viscosity was estimated. The most sensitive method to detect structural changes has been tensile impact. The compatibilized materials were quite stabile against UV, but exhibited more pronounced drop in the impact strength after thermal ageing.

CL1-07 POLYAMIDE AND POLYPROPYLENE/CLAY NANOCOMPOSITES: TAILORING OF PROPERTIES BY MALEATED POLYMERS

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Remarkable improvement of material properties together with significant weight savings is the major motivation why in automotive industry polymer nanocomposites are increasingly replacing the conventional composites. Typical examples of a significant enhancement of whole complex of material parameters are polyamide/clay nanocomposites. The only limitation in potential industrial applications of these materials is their insufficient toughness. The work explores the way how by using of reactive copolymers to overcome processing/property disadvantages

of melt prepared polyamide and polypropylene/ montmorillonite (PA6/MMT and PP/MMT) nanocomposites.

It was found that by application of maleated ethenepropene elastomer (EPR-MA) toughness of PA6/MMT nanocomposites is several times higher compared to respective neat nanocomomposites. Moreover, variation of clay and EPR-MA content lead to a broad range of materials with well-balanced mechanical behaviour.

In the PP/MMT nanocomposites the main experimental effort was aimed on the explanation of comprehensive influence of maleated polypropylene (PP-MA) on the filler dispersion as well as transition from intercalated to exfoliated nanocomposites structure. The work further analyse the role of PP-MA on final physico-mechanical properties of composites. It was found that in PP/clay nanocomposites PP/-MA provides considerable benefits on exfoliation rate, filler dispersion and barrier properties, however, no substantial improvement of mechanical properties has been observed.

The work was supported by Scientific Grant Agency of the Ministry of Education of Slovak Republic VEGA 1/2110/05 and by Grant Agency of the Czech Republic $(N^0, 106/03/0679)$.

CL1-08 INTELLIGENT TEXTILE STRUCTURES AND THEIR APPLICATION IN AUTOMOTIVE INDUSTRY

J. MILITKY, V. BAJZIK, V. KOVACIC

CL1-09 POLYPROPYLENE WITH MICROFILLERS - THE WAY OF ENHANCEMENT OF THEIR TOUGH-NESS

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The fillers are more often used to fulfill a functional role, e.g. CaCO₃ was originally used to increase the stiffness or to improve the dimension stability of the products. On the other hand the embrittlement of composites was observed as a consequence of stress concentration on the relatively large particles of the filler. The new concept is the usage of filler particles as toughening agent.

Commercially available polypropylene (MOSTEN) supplied by Czech company Chemopetrol Litvínov and two types of calcium carbonates (precipitated and micro ground) were used for this study. The CaCO₃ particles were coated with different surface agents improving their dispersion. PP with different melt flow rate (MFR=2.9,

3.5, 16.9 g/10 min) and with three levels of isotacticity index (I.I. = 95.3, 97.0, 98.2%) were used.

The effect of the PP structure and the size of particles and their surface coating on the decisive mechanical properties (dynamic modulus of elasticity and dynamic fracture toughness) was evaluated by means of instrumented Charpy tester. The dispersion of the filler particles was qualitatively estimated by SEM. The change of solid phase PP ratio was evaluated utilizing the pulsed ¹H-NMR.

The composites in the study demonstrated the enhanced toughness with respect to the native PP. The correlation between the structure and fracture parameters was confirmed.

CL1-10 SURFACE MODIFICATION OF WASTE-GYPSUM FILLERS USING STEARIC ACID IN PVC/WASTE-GYPSUM COMPOSITES

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The surface modification of waste-gypsum (WG) using stearic acid as surfactant was investigated. The maximum amount of stearic acid (SA) that can be attached to the surface of the fillers was determined around 1.8 wt %. The formation of a calcium stearate layer on the surface of fillers was elucidated by FTIR analyses, X-ray diffraction spectra, and thermal analyses (TGA)¹. Polymer composites based on poly(vinyl chloride) (PVC) and coated WG fillers were prepared by the different processing equipment: extruder, injection molder and tworoll mills with various contents of the WG fillers. The effect of the addition of uncoated and coated WG fillers on rheology, physico-mechanical properties and morphological development of composites was discussed. The presence of coated WG fillers in the mixture strongly affected the processing parameters resulting in the decrease of mixing time during processing and the lowering of melt-viscosity in comparison with uncoated WG fillers². The dispersibility of coated fillers is also better than uncoated ones resulting in the higher toughness. Among these composites investigated, PVC/coated WG composite showed the optimum properties with the addition of 22.56 wt % of coated WG fillers.

This work was supported by Korea Industrial Technology Foundation (KOTEF) in 2004.

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CL1-11 BITUMINOUS AND NON-ASPHALTIC DAMPING TREATMENTS FOR AUTOMOTIVE APPLICATIONS

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In automotive industry the control of vibration at resonant frequency is typically achieved by using damping materials adhered to metal panels. Premanufactured sheet damping products and spray-on damping coatings are the most common alternatives. Today, spray-on approach that utilizes recent advances in robotic systems and certain progress in materials research is gaining an increasing popularity among automotive manufacturers. In this presentation, the merits of sheet damping vs. sprayable technologies are reviewed. The emphasis is made on the development of new materials with enhanced damping performance, new damping applications, advanced design approaches, and opportunities that sheet dampers offer when compared to the alternatives. Both traditional bituminous and novel polymeric compositions are reviewed. Particular attention is given to the development of multifunctional materials characterized by multiple damping performance.

The authors wish to express their gratitude for the support and cooperation from Rieter Acoustics laboratory and Development Center associates.

CL1-12 UV CURING ON 3-DIMENSIONAL PARTS IN THE AUTOMOTIVE INDUSTRY

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UV curing is widely used in many printing and coating applications. More recently it has been adopted by many industrial applications where the advantages of improved coating performance, high throughput, small compact units and economical use of energy have been drivers for change in these industries. The latest industry to adopt UV curing technology has been automotive. Applications such as headlamp lenses and reflectors, SMC body panels and a range of car interior parts are already manufactured successfully using UV light energy to cure coatings applied to these parts. The latest development has been the creation of projects to develop UV curable clear coating for car bodies.

There are considerable challenges associated with the UV curing of high value, three-dimensional shapes such as car bodies. Successful UV curing polymerization processes that yield consistently high quality film properties require:

- uniform irradiation of the UV-curable coating on the substrate,
- minimization of shadow areas,
- uniform and stable UV energy at wavelengths consistent with the coating needs.

Typically the lamp set up to meet these requirements would be determined by "trial and error" during the process development stage. Whilst this works for smaller objects such as headlamp lenses it would not be acceptable for complete car bodies at the OEMs. To overcome these challenges Fusion UV Systems has developed a 3D modelling software package that determines the optimum process solution; including the number, position and power of the lamps to deliver uniform UV light over the entire part.

This paper will review current and future applications of UV curing in the auotmotive industry and describe the latest in 3D modelling software.

CL1-13 EFFECT OF FILLER GEOMETRY ON THE PROPERTIES OF POLYMER NANOCOMPOSITES

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Fillers are widely used in thermosets, thermoplastics and elastomers. Current estimates put the global market for fillers at between 12 and 18 million tonnes per year. Originally, their main function was seen as reducing the cost of the compounds. However, in recent years it has been evidenced that fillers can enhance the processability and mechanical properties of composite materials. In current work the influence of three different mineral fillers on the properties of polymer composites has been investigated:

- montmorillonite (MMT) with plate-shaped particles,
- nano-precipitated calcium carbonate (NPCC) with cubic shaped particles,
- spherical nano-silica.

Common polymers were used as the composite matrix-polycarbonate (PC) and polyamide (PA). Mechanical and rheological properties of such composites have been evaluated and referred to the filler geometry.

CL1-14 THERMOPLASTIC COMPOSITES: ADDED VALUE ON AUTOMOTIVE PLASTIC PARTS

S. TOURSEL

CL1-15 LIGHT STABILIZATION OF AUTOMOTIVE TPO: FROM TRADITIONAL TO NOVEL APPROACHES

WOLFGANG VOIGT

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The presentation discusses the aspects of safeguarding automotive TPO parts against the negative aspects of UV light exposure. In this respect both reactor grade and compounded TPO Materials are considered, as well as their use in exterior or interior applications respectively. Solutions with novel, advanced stabilizer systems are compared to those applying traditional approaches.

A special low-basicity, non-interacting additive not only provides excellent UV stabilization, but is furthermore capable of preventing specific problems of paint adhesion, mold deposit, gas fading, etc, which are encountered in certain applications. Not only additivation is of importance for molded-in-color parts, but likewise the performance of the pigments plays a dominant role, compared to parts with black or dark gray colors.

CL1-16 COMPOUNDS FOR ADVANCED APPLICATIONS

GUNTER LUX

INNOCOMP Kft, Tiszaújváros

Polymers and the automotive industry show a long fruitful history regarding development, innovation and success in the implementation of new ideas, products and applications.

But in the last 15 years dramandeous changes in each individual industry have taken place.

The automotive industry had to restructure itself and the trend of moving to production sites with cost advantages regarding labor work and infrastructural issues was undertaken. In the same way efficiency improvement led to new structures in the chain of supply.

At the same time an outstanding concentration process took place in the polymer industry. Compared to the structure 15 years ago more than 50 % of the individual producers disappeared and moved into joint-ventures or have been taken over, mainly in the field of the polyole-fins, which is still the most important group of polymers for the automotive applications.

How to deal as an independent compounding company in this challenging surrounding in the fields of product development, customer service, logistics issues and so on will be part of the presentation.

CL2-01 BIOPOLYMERS AS A COMPONENT OF RUBBER RLENDS

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Typical rubber blend consist of elastomer as polymer base, vulcanization system, fillers, antidegradants and modifiers. Biopolymers, except the natural rubbers are not usually used in typical rubber composition. Some earlier patents¹⁻³ described the methods for utilization of lignin as a filler or antidegradant, but its application in practice was not widely realized. Celluloses as biopolymer, preferably in fiber form are relatively frequently used in rubber industry as reinforcing materials for tires or conveying belts. From this point of view, the main interest in this field was focused on improving of compatibility (adhesion) between rubber matrix and cellulose fiber. In the last years also the examination of cellulose short fibers as fillers for elastomers is described in literature⁴⁻⁸. Starch has a special position in the last years as biopolymer, which is used in polymer processing including biodegradable thermoplastics as well as rubber industry. In the last years, many patents and some scientific journal publications were dedicated to application of starch in native or plasticized form in rubber blends⁹⁻¹⁴.

Our work is focused on testing of chosen types of biopolymers on basic properties of rubber blends and vulcanizates. Two kinds of starch in native as well as in plasticized form, two types of proteins and lignin were tested in rubber blends based on various types of elastomers, including synthetic and natural rubber. Reinforcing filler silica was chosen as comparative substance. The vulcanization properties and final properties of vulcanisates strongly depend on combination biopolymer - elastomer. In the screning five types of elastomer were used - one type of natural rubber, three types of styrol-butadiene rubber and one type of butadiene rubber. The same biopolymer can exhibit absolutely different trends of blend properties in dependency on type of elastomer basis. Also origin of native starch and protein determines their influence on mechanical properties of vulcanizates. The suitable plasticization process and application of suitable type of plasticizer for starches and lignin can significantly improve the mechanical properties of final products. Collagen hydrolysate and lignin exhibit very good compatibility

with the polymer matrix. These two substances do not decrease the crosslinking density in comparison to other conventional fillers. This fact indicates that collagen hydrolysate and lignin can to play active role in vulcanization process.

Addition of biopolymer as a filler or modifier to rubber blend modifies also dynamical – mechanical properties of vulcanizates. It indicates, that driving properties of tires can be modifying by application of biopolymers in composition of tire rubber blends.

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CL2-02

PHYSICAL DATA OF PLASTIC AND RUBBER MATERIALS FOR MATHEMATICAL MODELING OF INDUSTRIAL HEAT TRANSPORT PROCESSES

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Mathematical models of rubber curing, tire deformation and plastic material shaping became common tools of industrial product development and design. A set of model equations, which was put together to describe these processes, contains physical properties of used materials. Values of these quantities have to be inserted into the mathematical model. To be representative and accurate these physical data have to reflect temperatures and pressures changes in the process.

A curing model of heat transport in a tire contains thermal diffusivity, thermal conductivity, specific heat, reaction heat and density of each material which is in the tire. Since the effect of temperature upon these quantities is significant. All these quantities should be measured under pressure because the volatile components can originate during heating or they are in the rubber compound. To simulate curing condition in a press, the advanced laboratory methods were developed by which these physical quantities were measured.

Thermal diffusivity of rubber compounds decreases up to 20 % with the temperature increase in the interval 20 °C to 180 °C. Thermal diffusivity of rubberized cords changes significantly not only with temperature but with the direction of the heat transfer as well. The method of linear temperature increase of sample surface was used to measure this quantity.

On the contrary specific heat of rubber and rubberized cords increases with the temperature increase. Some rubber compounds change the value of their specific heat by 50% during the curing. Differential calorimetry with continuous increase of the sample temperature was used to determine specific heats of green and cured rubber and composites.

Values of reaction heats of individual rubber compounds are really diverse and they are higher for rubberized cords than for rubber. It is a difficult problem to determine the real value of the reaction heat (curing heat) of rubber. The way of processing and aging of a green rubber compound has a great influence on it. The values of reaction heat were measured by differential calorimetry.

To increase the accuracy of measured data and to avoid the influence of heterogeneity of rubber compounds and rubberized cords the sample cells of used instruments have quite large volume (100 to 200 cm³). The influence of data errors on temperature and curing degree was computed from a mathematical model of tire curing.

CL2-03 FUNCTIONAL RAW AND AUXILIARY MATERIALS FOR THE RUBBER INDUSTRY

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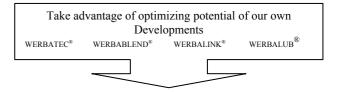
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On demand of our customers from tyre and technical rubber industries, our "Rubber Team" has developed different additives on the base of mostly environmental-tolerable raw materials.

These new products enable a significantly more effi-

cient compound preparation and facilitate the processing: preparing of compounds, calendering, injection moulding, extrusion and confecting.

It has been proved in praxis that our processing aids optimize the processes which were difficult to perform before and in some special cases, they enable the processes which were impossible to perform before.



- Reduced energy costs and less wastage during mixing and cooling of compounds
- Shorter processing time due to higher flowing properties
- Higher filling grades bring more cost reduction
- <u>Less "reject"</u> due to higher quality of extrusion and injection articles
- Higher building or green tack of semi-finished products; supports also the reduction of solvents during processing

CL2-04 TYRE RECYCLING SYSTEM IN SLOVAKIA

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End-of-life tyre is defined according to CWA 14 243 as a tyre which has been permanently removed from a vehicle without the possibility of being re-mounted for further road-use.

Tyre recycling is any process by which post-consumer tyres or materials derived from post-consumer tyres are converted into useable material or product.

The above are EU averages for the five principal disposal routes for post-consumer tyres. The actual breakdown in each state varies in function of national policy and regulations concerning material recycling and/or energy recovery, specific needs and treatment capacity. Traditionally, there have been five basic disposal routes¹:

Exporting of part-worn tyres is generally directed from wealthier towards poorer countries. Although it is expected that this practice will be limited in future, the export of tyre casings for retreading will continue.

Retreaded tyres ensure the same standards of use and

wear as new tyres.

Material recycling is comprised of two parts: the production of materials from post-consumer tyres, and their use, according to European standards, in civil engineering, construction and rehabilitation applications, and in the manufacture of industrial products.

Energy recovery facilities including electricity generation plants, cement kilns, paper or pulp mills, etc., use tyres as a secondary non-fossil fuel. Pyrolysis combines the benefits of energy recovery and material recycling obtaining carbon materials, oil and steel.

Landfilling, the disposal of waste onto or into land, is no longer an option in the EU for post-consumer whole tyres (2003) or shredded tyres (2006) under the Landfill Directive (199/31/EC).

In Slovakia tyre recycling is from 2001 year organised by Recycling found and its used tyre section. According to waste management policy of Slovakia material recycling of post-consumer tyres is valorized. The goals of post-consumer tyre policy in Slovakia are: 100% collection of post-consumer tyre in 2005, more than 95% of post-consumer tyre arising by material recycling and zero whole tyres and shredded tyres landfilling by 2006 year.

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CL2-05 EXPERIMENTAL STUDY OF WASTE RUBBER PYROLYSIS AND COMBUSTION

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Disposal of waste tires is a serious environmental problem. The impact of waste rubber on the environment can be minimized by material recycling and/or energy recovery. However, during processing and moulding are rubber materials crosslinked, and therefore they cannot be simply again softened and remoulded by heating. The high volatile carbon content and heating value make the scrap tires an excellent material for energy recovery. For this reason, both pyrolysis and combustion are currently receiving renewed attention.

This paper investigates pyrolysis and combustion behaviours of a single rubber particle in a Differential Thermogravimetric (DTG) apparatus. The Influence of temperature (400–850 °C), oxygen content in gas (5–21 %) and gas velocity (0.2–0.5 m s⁻¹) on combustion behaviour of both rubber samples and solid products of the pyrolysis process

(chars) was studied. Combustion gases were analysed by gas chromatographgy/mass spectroscopy (GC/MS).

Pyrolysis of scrap rubber sample was carried out under nitrogen atmosphere over a temperature range of 20-850 °C using a heating rate of 5 °C min⁻¹. The measured DTG curves show two different weight loss regions over a temperature range of 250-600 °C. Based on the evaporating characteristic of individual rubber components, at the temperature range of 250-380 °C, additives, oils and plasticizers are lost. At the temperature range of 400-550 the NR, SBR and BR are decomposed. In all, 52-55 % of the samples weight was lost during the pyrolysis process and another 40 % during the combustion of char. Ashes create approximately 8 % of the samples weight. Using the thermogravimetric data and a mathematical model for thermal decomposition of samples, the kinetic parameters of both pyrolysis and combustion reactions were estimated.

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CL2-06 DYNAMIC-MECHANICAL PROPERTIES OF FILLED STYRENE-BUTADIENE RUBBER COMPOUNDS

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Most rubber articles are prepared on the basis of filler-elastomer systems. Behaviour of such systems is complex because their properties are significantly dependent not only on properties of elastomers but also on properties of fillers. Differences in properties of individual fillers for rubber compounds are substantial and influence of both polymer and filler properties have to be considered in detail.

Dynamic-mechanical data of filled rubber compounds can give valuable insight into the behaviour of filled rubber systems. In this work we prepared styrene-butadiene compounds with different carbon blacks and different white fillers. For testing and evaluation of vulcanised styrene-butadiene rubber behaviour we used dynamic-mechanical properties in both shear and tensile deformation mode.

CL2-07 TRENDS TO MINIMIZE ZINC LEVEL IN RUBBER PRODUCTS

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Zinc oxide is a common ingredient of rubber compounds because it has showed to be the most important activator for sulphur vulcanization of elastomers. In addition to its role as an activator, there is also evidence that the inclusion of ZnO in the vulcanizates reduces heatbuild-up and improves abrasion resistance. It has also been found that ZnO improves heat resistance of the vulcanizates and their resistance to the action of dynamic loading¹. The high thermal conductivity of ZnO helps to dissipate local heat concentrations that might otherwise affect the properties of rubber. The thermal properties of ZnO are particularly beneficial in applications such as rubber vibration mounts, where loading and cyclic stresses would otherwise generate heat and degrade the rubber. ZnO is also needed for bonding rubber to the steel cord of tyres and for bonding between metal and rubber in technical goods.

Besides improving the properties of vulcanized rubbers, ZnO also assists 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 one of the least harmful of the heavy metals, there is an increased concern about its environmental effects². Diffuse emissions of zinc from 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 not only tries to summarize the efforts how to reach the above mentioned goal but presents some results from own efforts as well. The results indicate, that the same properties of vulcanizates can be reached by lower dosage of ZnO with higher specific surface.

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CL2-08

CONTACT-LESS MEASUREMENTS OF THERMAL PARAMETERS IN LOW CONDUCTIVE DIELECTRIC MATERIALS

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In the presented work we are dealing with the contactless measurements of thermal parameters of rubber blends. The results are compared with those obtained by DSC and contact measurements of the same values. The precision and repetition ability of presented flash method is fully comparable with independent methods.

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CL2-09

SURFACE MODIFICATION OF REINFORCING MATERIALS BY PLASMA TREATMENT AND PLASMA POLYMERIZATION

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In this work, the adhesion strength between poly (ethylene terephthalate) (PET) cords and styrene-butadiene rubber (SBR) was studied. The effects of atmospheric plasma treatment, used to increase adhesion strength be-

tween PET cords and the rubber matrix, were investigated and compared. It was confirmed that lubricants on the fibres caused a decrease in adhesion strength between the plasma treated reinforcing PET fibres and the SBR rubber matrix. Concerning to plasma polymerization, the PET cords were treated by an aborted arc discharge generated at atmospheric pressure. The PET cords were modified by plasma polymerization in a mixture of nitrogen and butadiene. The gaseous products arisen by decomposition of butadiene during the plasma polymerization were observed by UV-VIS emission spectroscopy. The chemical composition of deposited layer was examined by Fourier transform infrared spectroscopy (FTIR) adapted for the rough surfaces (diffusion reflection spectroscope EasyDiff). The topology of deposited polymer layer was investigated by scanning electron microscopy (SEM).

CL2-10 COMPARISON OF ANTIOXIDATIVE ACTIVITY OF p-PHENYLENEDIAMINES IN POLYISOPRENE STUDIED BY DSC

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The antioxidative activity of eight N,N'-substituted p-phenylenediamines in polyisoprene rubber matrix has been studied by differential scanning calorimetry (DSC) under non-isothermal conditions. For obtaining the parameters from non-isothermal DSC measurement^{1,2} a method based on the dependence of the onset temperature of the oxidation peak on heating rate was used. The results show that the values of protection factor decrease with increasing temperature and decreasing concentration of the antioxidant. Using two proposed criteria³ the tested antioxidants were ranged based on their effectiveness at 180 °C. The obtained order is proportional of their structure, specifically depends on the substitution of hydrogen atoms at the carbon atom in the alkyl substituent in the neighbourhood of the nitrogen atom of N-phenyl-, N'-alkyl-p-phenylenediamines.

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CL2-11 BACK TO THE TYRE

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The European legislations on landfill of waste and on end-of-life vehicles are forcing the tyre industry, and, in particular, the rubber industry, to come up with solutions for the problem of end-of-life tyres. A (obvious) way to cope with this problem is to recycle the rubber and to reuse it in new tyre compounds. Some recycling possibilities include the devulcanization of the rubber to produce reclaim, and the reduction of size of the rubber to make fine powders. These recycled materials are valuable products, provided that the raw materials used for their production and the manufacturing process itself are consistent enough to deliver high quality final products. Both the rubber reclaim and the fine rubber powder, when added at the right concentrations, are proven to have a relatively small impact on the properties of the new rubber compounds. The use of reclaimed rubber and fine powder in several tyre compounds (innerliner, tread and sidewall) is described in this paper, together with their influence on the properties and on the cost of the compounds.

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CL2-12 NEW METHOD OF JLB MANUFACTURING

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In the paper is presented positive effect of JLB (cap ply) on the tyre properties. Then is described the traditional method of JLB manufacturing and is presented the

new method of JLB manufacturing. Traditional method of JLB manufacturing is 3-stage production process, new method of JLB manufacturing is single stage on-line process with plasma treatment of the single cords before their rubberising instead of traditional chemical treatment. On the base of this method is presented concept of machine for JLB manufacturing. Application of new method of JLB manufacturing results in reduction of the cord costs, reduction of the energy costs, reduction of the tyre weight, increase of effectiveness of the working process and positive effect on the living environment.

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CL2-13 EVALUATION OF EFFICIENCY OF PROCESSING AIDS IN RUBBER MIXTURES

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The work is concerning to evaluation of flow properties of rubber mixtures using rheological equipment Plastograph 19/10 DW from Brabender using different types of processing aids. From viscosity dependence from shear rate the deviation from Newton flow – the index "n" were calculated.

CL2-14

THE EFFECT OF THE FREQUENCY OF OPEN-MILL ROTOR ON PHYSICAL-MECHANICAL PROPERTIES OF CLOISITE-FILLED RUBBER

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At present, the rubber industry pays great attention to the research of light fillers. Cloisite 15A is a modified smectic clay whose particles are of the size of nanometres. In our study it is used as standard filler and compared with common types of commercial fillers.

Cloisite is used for its large surface area, which

enables to substantially decrease the amount of filler in the compound compared to carbon black, thus resulting in cheaper products. Moreover, "dirty work" is eliminated from the process, and worth mentioning also is the ecological aspect. Furthermore, the articles filled with the clay are expected to have better properties.

However, to reach good properties, the filler must be properly delaminated and exfoliated. This can be influenced by the way of the compound preparation. In our research one factor is followed – the roll frequency of the open mill in the process of mixing – and related to physical-mechanical properties of vulcanizates.

CL2-15

NAPHTHENIC PLASTICISERS, AN ENVIRON-MENTALLY CONSCIOUS ALTERNATIVE TO AROMATIC EXTRACTS

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The environmental impact of chemical products is an increasing concern among both authorities and chemical industries. In February 2004, the EU adopted a proposal of legislation to ban the use of distillate aromatic extracts in tires. Although the industrial rubber segment is not directly concerned by this directive yet, it is likely to experience its effects due to the lower demand on aromatic extracts and the consequent changes in the oil industry.

Naphthenic plasticisers are one of the environmentally conscious alternatives to aromatic extracts. Their chemical nature gives them a good solvent power and good compatibility with most elastomers. Their performance in industrial rubber compounds will be compared with that of aromatic extracts and other possible alternative plasticisers.

CL2-16 COPOLYMERIC SULFUR AS VULCANIZING AGENT

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Authors inform on preparation of multicomponent copolymer of sulfur prepared by addition or polyaddition of cyclooctameric sulfur to low molecular weight polybutadiene (Krasol LB 9000) and with mixture of unsaturated

carboxylic acids from rapeseed oil (acids: oleic, linoleic, linolenic, stearic) similarly as at substitution of polybutadiene with mixture of dimers of pyrolitic C5-fraction. The most appropriate content of organic fraction in copolymeric sulfur is 10–30 wt %. The temperature of copolymerization lies in range 125–150 °C, with optimal one at 135 °C.

Vulcanizing characteristics of rubber mixtures (side wall mixtures) and physico-mechanical properties of cured rubbers prepared with above mentioned ternary or multicomponent copolymers of sulfur and with quality commercial sulfur (Crystex OT 33) as well are stated.

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CL2-17 TIRE DEVELOPMENT AND THE VERIFICATION OF THE MATHEMATICAL ANALYSES

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This paper presents a partition of the tire development. The partition includes FEM analyses (Finite Element Method) and the verification of the CAD model, the tire production and of the tire properties. FEM analyses are calculated in the static and dynamic state. The results from the mathematical analyses are the stresses, strains, footprints, deformation energies and fluid flow. One of the important inputs for FEM analyses is CAD model. The difference between CAD model and real tire is very interesting for the tire development. The prediction and verification of the tire properties include the measurements of the tire deformations in dynamic state and the termodynamics. In static state we measure the footprints of the tire and the tire uniformity, the wearing and the tread mileage.

CL2-18 BENEFITS OF MODERN ANTITACKS

WOLFGANG RUSCHIG

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The traditional slab and pellet dips are:

- 1. Water Soluble Soaps
- 2. Water Insoluble Soaps Metal Stearates
- 3. Carbonate Dispersions / Slurries
- 4. Clay Dispersions Slurries
- 5. Combination of Different Pigments

These traditional antitacks showed various disadvantages when used for modern compounds in modern production technology, such as hard particle contamination, wear of equipment, contamination of equipment, corrosion, foam and settlement. The impact on compound properties (e.g. steel cord adhesion) was high.

HANS W. BARBE CHEMISCHE ERZEUGNISSE GmbH has developed a full range of products under the low solids concept for the different applications in the rubber industry:

Tyre Compound

Technical Rubber Goods

Custom Compound

Each application requires specific considerations. "Low Solids Concept" is the description for:

- advanced formulated composition of selected raw materials,
- in a very controlled application of the antitack,
- to achieve an optimum in quantity and pick-up (consumption).

Considerations are:

- compound compatibility,
- process compatibility,
- cost efficiency,
- other requirements.
- □ To search for a compromise

The target is to

- minimize the impact on physical properties
- lower the consumption of antitack
- improve the cleanliness of the equipment
- achieve cost savings in production

HANS W. BARBE CHEMISCHE ERZEUGNISSE GMBH is developing these new products for the "Low Solids Concept" together with our customers to achieve a maximum in performance and application. This process is ongoing.

BARBE basic research	\Box	External studies (research institutes, customers)	\Box	Customer application and verification	\Box	Approved products
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CL2-19 PROCESSING PROMOTERS WITH MULTIPLE EFFECTS

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WERBALINK® 3 – is a multifunctional white filler on unique mineral base for bead profile compound of tyres. The subject of this part of lecture is the comparison of the original compound on one side and the compound modified with WERBALINK® 3 on the other side.

The main goal of testing was to increase rigidity of bead profile with keeping its flow and using properties at the same level. The selected compounds may content a higher dosage of fillers without negative effects on final quality of product. Content of processing aid material gives positive properties to compounds and facilitates the next technology step (extrusion).

WERBATEC® P250 – is a high performance tackifying resin with homogenous properties, modified with effective peptizer. It is recommended for compounds on NR-base or NR-blends with other elastomers like SBR, IR, BR, NBR containing different fillers like carbon black, mineral fillers, silica or pigments.

The main goal is to combine the high and long term tack property with better homogeneity for the production of compounds on natural rubber base where very low viscosity is needed. WERBATEC® P250 is recommended for example for side-wall and cushion gum compounds.

WERBALUB® ZP – is zinc soap on a base of specially chosen, high molecular, mostly saturated fatty acids for high quality compounds like tread or side-wall compounds in tyre industry.

Such compounds content two or more elastomers and high active fillers like carbon black or silica. Those materials must be fast and homogeneously dispersed in the compound. The extruded tread, side-wall and other semi-finished products must not have any flaws on the surface.

The main goal is to achieve the homogeneity and very good flowing properties of the compounds at the same time. WERBALUB® ZP guarantees higher uniformity of all compounds and thus it keeps the total reject at very low level

Special thanks to: Vipotest s.r.o. Puchov for laboratory tests and for verifications.

CL2-20 ON-LINE EXTRUSION MONITORING SYSTEM USING LASER LINE TECHNOLOGY

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With the development of the laser line sensor the possibility to accurately measure flat, round and complex

profiles became available without intricate mechanical devices as is necessary with fixed-point laser. The Bytewise Profile360 and On-Line Profiler, OLP, systems measures extruded profiles without the use of moving parts, which assures for long-lasting use and minimum of service requirement.

Both systems encircle the passing profile with a laser line and produce a dimensional recording up to 7 times a second. Because of the entire profile is recorded during a fraction of a second, a true width measurement is achieved, rather than a calculated width that is the result due to the zigzag pattern created by scanning devices.

With easy to use calipers the profiles thickness, width, angles and radius can be measured. Volume can be calculated and with treads for tires the conicity can be shown. For each caliper the nominal value, out of specification and warning level can be programmed. The measured values can be stored either locally or central. To warn an operator visually or audibly, analog outputs are also available. The system also provides dimensional feedback for manual or automatic process control, but each extruder needs the expertise from the supplier how the loop can be used.

By using On-Line Extrusion Monitoring System the user have continuously information of the process and will be warned when the profile exceeds the specification. Start-up scrap is reduced by faster on-line recognition of the profile that is in control, and by immediate feedback of the start up phase the machine adjustments can be made to get under control faster.

The results from each batch is presented in a Production Run Report showing the distribution of the measurements and the trend of each calliper, that can be provided to the end-user to demonstrate high performance standards.

CL2-21 DIMENSIONAL STABILITY OF POLYESTER CORDS

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Cord-rubber composites find applications in automotive and aerospace engineering industries. Automotive tire, made of vulcanized rubber and a reinforcing carcass (synthetic cords), is a highly anisotropic, viscoelastic and composite structure. Large strains, displacements and rotations encountered during normal service conditions, temperature dependent material properties of rubber as well as reinforcement complicate the evaluation of properties these materials in their preparation and using. The me-

chanical, deformation and elastic properties of the synthetic cords have a key role at the deforming behaviour of tires. It is possible the evaluation these properties of synthetic cords with variable dynamometric measurements and methods, such as stress-strain dependence, the relaxation and creep methods or the elastic recovery testing, etc. These methods provide the various stress-strain characteristics and the parameters based on them such as tenacity and elongation at the break, Young's modulus, deformation work, degree of elasticity. These quantities depend on the used equipments and on the measurement conditions.

In this paper the effects of measurement conditions (various gradient deformations) on mechanical properties of polyester cords are presented and discussed. The polyester cords were treated at different temperature and time. The basic mechanical properties and dimensional stability were evaluated.

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CL2-22 UTILIZATION OF ORGANOCLAYS AS A NANO-FILLER IN RUBBER INDUSTRY AND THEIR PREFERENCES IN COMPARISON WITH SILICA FILLERS

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Nanofillers play a key role in several industrial and academic research fields. Generally, fillers modify the properties of different materials to increase their performance and provide improving durability of composites, polymers and rubbers. Improvements in the physical properties are directly related to particle size. In the case of rubber compounds the smaller particulate of fillers lead to the greater reinforcement. The new way could be producing the rubber – nanocomposites.

The term "nanocomposite" describes a two-phase material where one of the phases is dispersed in the second one on a nanometer level (10°9m). Nanocomposites are commonly based on polymer matrices reinforced by Nanofillers such as montmorillonite, vermiculite and many others. These polymer – clay composites can be divided into three general types: conventional composite where the clay acts as a conventional filler, intercalated nanocomposite consisting of a regular insertion of the polymer in between the clay layers and delaminated nanocomposite where 1nm-thick layers are dispersed in the matrix forming a monolithic structure on the microscale. Delaminated nanocomposite should lead to most dramatic changes in mechanical and physical properties.

The paper deals with utilizing of natural Smectic clay (mainly montmorillonite) as a filler for rubber compounds with the aim to improve physical and mechanical properties at decreased level of filling. Many times large surface of these organic fillers compared to commonly used white active fillers is supposed to increase modulus, hardness, tensile strength and tear strength at the same high level of elasticity.

P-01 RECYCLING OF PUR SCRAP FROM CAR SEATS- GLYCOLYSIS OF FLEXIBLE PUR FOAM

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The polyurethane materials (especially PUR foams) form a significant part of plastics waste from end-of-life vehicles. In 1998 in European Union countries, the total amount of shredded cars was about 8 millions and it presented around 50 000 tons of flexible polyurethane foam's scrap from car seats. This amount is increasing and is expected to be between 70 000 and 100 000 tons in 2006¹. In contrast to other automotive plastics, PUR material from used cars can be easily dismantled- approximately 72 % from the total amount of PUR. Thus PUR scrap contains minimal amount of contaminants and therefore is suitable for chemical recycling².

The aim of chemical recycling of flexible PUR foams is to regain the polyols suitable for manufacturing of new polyurethane foam. Glycolysis gives a mixture of original polyol, low molecular urethanes with hydroxyl-end groups and other secondary products such as free aromatic amines, etc^{3–5}.

We have studied the possibility of carrying out the glycolysis of commercially manufactured flexible foam in order to obtain directly polyol product that can be used in the production of new foam (either flexible or rigid). Industrial scrap of flexible PUR foam based on polymeric diphenylmethane-4,4'-diisocyanate and polyether polyol has been used for glycolysis. Diethylene glycol, dipropylene glycol, ethylene glycol and propylene glycol were tested as reagents. The experiments show that it is necessary to maintain the reaction temperature above 200 °C for the sufficient course of the glycolysis. The PUR-foam/ glycol ratio 1/1 [wt./wt.] and the reaction time 2.5 hours were determined as optimal conditions. The glycolysis products were tested in manufacturing of rigid foam. The mixture of the recycled and fresh polyols was used as a raw material for further foaming. New rigid foams had fine cellular structure; the value of thermal conductivity was practically the same in all cases (around $0.026 \text{ W m}^{-1} \text{ K}^{-1}$).

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P-02 ELECTRIC PROPERTIES OF A RUBBER COMPOUND USED IN THE TYRE INDUSTRY

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It is important to know the processes running during preparation and development of new materials and the influence of the processes on inner structure and requested properties of the materials. In complex systems such as glasses, ceramics, plastics and rubber, as well, it is possible to use the methods of measurements of electrical properties to determine the changes in the structure of material¹. These methods are suitable for the mentioned purpose with respect to their effectiveness and sensitivity. The measurements of electrical properties enable to optimize their technology procedures and the composition with respect to requested properties^{2,3}, too.

The aim of this paper is to determine the possibility to study the processes running during the vulcanization of rubber compounds. The samples of a rubber compound used in the tyre industry were investigated experimentally. Time dependences of direct electrical conductivity and alternate electrical conductivity were measured. We measured real part of permittivity and loss factor in frequency range (0.02–100) kHz, where temperature was the parameter (100, 110,120, 130, 140, 150, 160, 170, 180, 190 and 200) °C. The found out results confirm, that using the showed electrical measurements it is possible to study the structural changes in this material.

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P-03 POTENTIAL ECOLOGICAL PLASTICIZERS RUB-BER BLENDS

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The contribution deals with the impact of potentially ecological suitable plasticizers on resultant physical-mechanical and dynamic-mechanical properties of vulcanizates. Parafinic plasticizer, naphtenic-parafinic plasticizer, naphtenic-parafinic modified plasticizers with polyolefinic component, rape oil and their cross-combination were used as the suitable types. Compounds were compared with the standard tread compound with used aromatic plasticizer used in the rubber industry. Plasticizer modified with polyolefinic component show improving physical-mechanical properties with unmodified plasticizers. Aromatic content which is environmentally hazardous the problem¹.

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P-04 SURFACE MODIFICATION OF POLYPROPYLENE NONWOVENS

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Polypropylene is one of the most attractive polymers for a wide range of applications. The reasons for its success are mainly due to its excellent chemical, mechanical and processing properties. Together with its relatively low cost, as well as good safety performance, long service life and harmonious appearance, materials based polypropylene has become very popular in automotive industry.

In the last decades an increasing penetration of nonwovens in automotive sector was observed. Nonwovens are used in automotive industry for a variety of purposes due to their advantages: lightweight, sound efficiency, flexibility, versatility, easily tailored properties, recyclability, and attractive cost/ performance racio¹. Principal polypropylene applications for nonwovens in automobiles are interior fabrics used in or on kick panel, package shelf, seat construction, truck liners, load decks, cabin air filters etc.

In general, a hydrophobic characteristics of polypropylene surfaces are limiting factors for some applications. Many studies have been done to overcome these problems through plasma treatment. As plasma can penetrate only a limited depth (several molecular layers), bulk properties of the most delicate materials remain unchanged. The final chemical composition of the treated surfaces is influenced by the used gas, the energy density of the plasma and many other variables. It was confirmed that various polar functional groups, such as –CO, -C=O, -C(=O)O were introduced on PP after plasma treatment². Due to this modification the surface energies of materials treated by atmospheric plasma have been shown to increase substantially, thereby significantly enhancing the wettability, printabillity, and adhesion properties of these materials.

Plasma treatment of nonwoven substrates provides four primary beneficial effects³:

- Cleaning effect combined with changes in wettability and texture for improved print quality, devability, and adhesion.
- Etching effect increases the micro-roughness of fiber surfaces.
- Free radicals induces secondary reactions, such as intermolecular cross-linking.
- Depositions enables the deposition of chemistries with desired properties onto substrates.

In our work the so called Diffuse Coplanar Surface Barrier Discharge (DCSBD)⁴ devise generating a thin layer of extremely dense diffuse atmospheric-pressure plasma in any

working gas was used. The aim was to hydrophilize polypropylene nonwovens⁵ for better water-based ink adhesion on polypropylene surface.

Plasma chemical modification of polypropylene surfaces enabled to prepare new material, polypropylene non-wovens surface coated with natural polysaccharide chitosan. It was found that chitosan immobilized on polypropylene can be covalently bonded to the plasma pre-treated surface⁶. Due to its unique molecular structure chitosan has an extremely high affinity for many classes of dyes, including disperse, direct, reactive, acid, sulfur and naphthol. Polypropylene nonwovens coated with thin chitosan layer can be surface coloured very homogeneously. Nonwovens with immobilized chitosan exhibit antibacterial properties.

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P-05

RESIDUAL STABILITY OF POLYURETHANE AUTOMOTIVE COATINGS MEASURED BY CHEMILUMINESCENCE AND EQUIVALENCE OF XENOTEST AND SOLISI AGEING TESTS

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Degradation of poly(ester-urethanes) and poly-(acrylic-urethanes), as a base for automotive paintings in interior applications, has been studied by chemiluminiscence. The samples were clearcoat and black-pigmented paints, unstabilized and stabilized with HALS Tinuvin 292 and UV absorber Tinuvin 1130, exposed to various doses of artificial weathering in Xenotest and Solisi. Chemiluminescence has appeared a powerful tool to characterize the oxidation stability of various polyurethane systems. From the dependences of oxidation onset temperatures on heating rates, the kinetic parameters describing the dependence of induction periods on temperature have been obtained. The kinetic parameters enabled to calculate the length of induction period for a chosen temperature, to evaluate the protection factors of various additives and to evaluate the residual stability of the polymer after an artificial ageing stress. It has been shown that the extinction of residual stability with ageing dose obeys a first-order kinetics. Equivalence between the two methods of artificial ageing has been determined. It has been indicated that the equivalence depends on the polymer composition. The procedure presented here can also be applied for the determination of equivalence of accelerated and field tests so facilitating to

establish a reliable correlation between them.

The authors express their gratitude to Carla Höppner (company Mankiewicz) for valuable discussions and supply of the samples. Our thanks are also extended to Andreas Kühlen (company Atlas) who provided the device Chemilume 400. Special thanks to Dr. Josef Rychlý (SAV Polymer Institute) for his help and collaboration.

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P-06

INFLUENCE OF THERMAL AND MECHANICAL LOADS TO TYRE TEXTILE REINFORCEMENT MATERIALS

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In this paper the results of influence of temperature load to tyre reinforcement materials properties are presented. Chosen textile reinforcement materials were loaded by different pretension and temperatures by different time period. Physical properties like the breaking strenght, elongation at break, shrinkage etc. of the materials were evaluated before and after loading. Testing conditions corresponded to the material conditions during its production and processing. Polyester, polyamide and aramide textile cords were tested during the experiment.

Reached experimental results shows minimal influence of thermal and mechanical load to tyre textile reinforcement materials generated during the materials production and processing.

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P-07

PROPERTIES OF POLETHYLENE REGRANULA-TE OBTAINED DURING THE PRODUCTION OF FUEL TANKS OF CARS

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Polyethylene regranulate obtained during the production of fuel tanks of certain Volkswagen and Porsche models was used as experimental material. The fuel tanks are made by blow moulding of 6-layer extruded semiproduct. These layers are made of HDPE, LDPE, LLDPE and the barrier layer is made of EVOH co-polymere. The aim of the experiments is to determine the possibility of regranulate processing by injection molding^{1,2}. Parameters of granulation and processing are set. Final mechanical properties of the recyclate were determined from the injection moulded parts; these properties included strength, toughness and hardness^{3,4}. From the dimensional characteristics, attention was paid to production and supplementary shrinkage⁵.

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P-08

MODIFICATION OF ETHYLENE-NORBORNENE COPOLYMER BY GAMMA IRRADIATION

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The possibility of crosslinking polyethylene and many other polymers with high energy radiation, primarily fast electrons and gamma rays, has led to many useful applications and to understanding of how radiation interacts with large molecules-polymers and to how they can be modified beneficially¹⁻³. However, in spite of the tremendous number of investigations devoted to this topic, there still remains great interest in the study of radiation effects in polymers because radiation processing of polymeric materials is a main step in certain modern technologies. Due to their interesting, new combination of properties and shortage of the experimental data, the radiolysis of a new class of materials known as cyclo-olefin copolymers (COC), which are polymerised from norbornene and ethylene using metallocene catalysts, is of prime interest to the study of radiation chemistry and physics of polymeric systems.

Ethylene-norbornene copolymer, TICONA TOPAS 6015 S-04, bare and containing an antioxidant, were subjected to gamma irradiation in the presence of air and in water. The irradiated copolymer was studied using IR and UV spectrophotometric analysis. The crosslinking efficiency was determined by measuring the gel content by extraction with solvent. The radiation induced changes in the molecular structure were correlated to the changes in glass transition temperature measured by the DSC method.

Radiation induced effects in different mediums in ethylene-norbornene copolymer are compared to the radiation effects in polyethylene and are discussed in terms of the heterogeneous nature of the radiation effect in polymers.

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P-09 INFLUENCE OF CONSTRUCTION VARIATION ON DISPLACEMENT CHANGES ON PERSONAL TYRES

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Reinforcement materials influence on a functional

properties of a tyre. Reinforcement materials are in composite form with rubber mixtures. A composite rubber – cord is tested by tensile test. This method is described in¹.

Behavior of tyre under dynamic loading is influenced by rubber mixtures properties, by sort of reinforcement materials and construction of a tyre². The aim of this research is an investigation of tyre construction changes (replacement of breaker plies) on behavior of tyre under dynamic loading. The paper deals with non-contact and non-destructive measurement of a tyre sidewall. The optical system with two cameras is based on stereovision³. It makes it possible to scan spatial deformation.

After 20 min of run-in a state of equilibrium arrives between temperature and pressure. A dimension changes during run-in was measured by profilometer. A temperature inside a tyre is possible measure by new tyre pressure sensor placed on a rim⁴.

Three tyres of the same sort were studied. By using optical system we determined a displacement in z direction

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P-10 NOVEL HYPERBRANCHED POLYMERS FROM AB $_2$ MONOMERS OF 2-OXAZOLINE TYPE WITH NON-EQUIVALENT B UNITS

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During last several years preparation of tailor made polymers and new polymer architectures received a big attention. Especially, chemistry of dendrimers and hyperbranched polymers is the strongly developing field. Dendrimers have perfect, monodisperse structure while hyperbranched polymers also contain linear segments and they are polydisperse. Various hyperbranched polymers have been prepared, for example poly(ester)s, poly(ether)s, poly(urethane)s, poly(amide)s, poly(alkylene imine)s, poly(ester amide)s, etc. 1.2. Recently, we have prepared hyperbranched poly(ether-amide)s by thermally initiated polyaddition reaction of a symmetrical compound of the AB₂ type containing 2-oxazoline structural unit and two

phenolic groups³. There appears a question what would happen in the case if B groups would be the same but not equivalent.

The presented polymerization reactions represent a new method for the preparation of hyperbranched polymers. It has been proved that also derivatives with nonequivalent B units can provide hyperbranched polymers and the degree of branching depends on the reactivity of the particular group.

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P-11 ELECTRO-CONDUCTIVE POLYMERIC COM-POSITES FILLED WITH METALLISED FILLER

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The physical properties of composites formed with reactive resins as epoxy and polyurethane, filled with silver-coated basalt particles and fibers are reported in this presentation.

The electrical conductivity measurement indicated percolation concentrations of ca. 28–29 vol. % of the filler for all the investigated systems. Different shapes of filler did not significant influence the percolation threshold¹.

A decrease in impact strength with an increase in filler content was observed for both epoxy-based composites and polyurethane-based composites. The impact strength of the composites decreases as follows: epoxy/silver-coated fibers > polyurethane/silver-coated fibers > polyurethane/silver-coated particles > epoxy/silver-coated particles.

Epoxy as well as polyurethane resins filled with silver-plated particles and fibers were investigated as tentative adhesives for the bonding of aluminum plaques. The strength of the adhesive joint decreases with an increase in filler content in all concentration regions, and for all investigated adhesives. The strongest adhesive joint was found for epoxy/silver-coated fibers adhesives¹.

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P-12 SYNERGISTIC ACCELERATOR COMBINATIONS FOR SULFUR CURING OF NATURAL RUBBER

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The metal salts and disulfides of dialkylthiophosphoric acids are able to accelerate the sulfur curing of the unsaturated elastomers and of the elastomer blends comprising highly unsaturated natural, styrene- butadiene or acrylonitrile-butadiene rubber (NBR) and ethylene propylene diene rubber (EPDM) of low unsaturation content, too. Bis (diisopropyl)thiophosphoryl disulfide (DIPDIS) was also using as an efficient coupling agent for the covulcanization of polar NBR and non-polar EPDM rubbers^{1,2}. Organophosphoric accelerators have no amine structures in their molecules and consequently they are not the potential sources of dangerous *N*-nitrosamines. In the combinations with the suitable conventional accelerators (thiazoles, sulfenamides, safe amine-based accelerators) they generate the synergistic accelerate systems.

The aim of this work is the study of the structure of the chemical crosslinks in the networks of unfilled sulfur vulcanizates of natural rubber obtained in the presence of organophosphoric accelerator as DIPDIS or zinc di-n--butylthiophosphate (ZDBP) and 2-mercaptobenzothiazole (MBT) combinations. The obtained experimental results showed that the polysulfidic and monosulfidic crosslinks between the rubber macromolecules are predominantly formed at the higher DIPDIS content in the rubber compound. However, the monosulfidic crosslinks are not practically presented in the vulcanizates prepared with low DIPDIS content. In the networks of DIPDIS-MBT or ZDBP-MBT vulcanizates the polysulfidic and disulfidic crosslinks are presented. The monosulfidic crosslinks were identified only in the vulcanizates with the high total content of accelerators in the rubber compounds and with the high molar ratio of phosphoric accelerator in the accelerator combinations. The differences in the structure of chemical crosslinks of the network are also showed in the physical-mechanical properties of vulcanizates and in their residual values over the thermooxidative ageing.

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P-13 POLY(ESTER-AMIDE)S OF THE AA+BB TYPE ON THE BASIS OF 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 amines¹. These reactions can be used for the preparation of tailor made materials by polyaddition reactions of bis-(2-oxazoline)s with difunctional reagents or by the construction of AB_x monomers containing a 2-oxazoline unit and another functional group which reacts with 2-oxazoline^{2,3}.

The reaction between 2-oxazolines and acids results in opening of oxazoline ring and formation of esteramide structure. When bis(2-oxazoline)s and dicarboxylic acids are used for the reaction, poly(ester-amide)s are formed. This mode represents a typical polyaddition reaction of the AA + BB type. We used 1,3-bis(2-oxazolin-2-yl)-benzene (IBOX) and 1,4-bis(2-oxazolin-2-yl)benzene (TBOX) and aliphatic dicarboxylic acids with different alkyl chains for the preparation of these materials. Properties of the designed materials can be adjusted with the choice of bis(2-oxazolines) as well as dicarboxylic acids.

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P-14 THERMOPLASTIC ELASTOMERS VERSUS RUBBER COMPOUNDS

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Due to easier processing the thermoplastic elastomers (next only TPE) are more and more desired on market like replacement of several rubber compounds.

Last results in the development of thermoplastic elastomers get near the performance strict requirements for thermosetting rubber compounds. The big advantage of these materials is their recycling.

But some customers in automotive industry give incomplete technical requirements of these materials if they want to identify the material for ready parts. This study gives the basic overview TPE – their system of dividing, sorts and properties.

It is showed a few types of TPE like representative of common and new range TPE that is comparable to more exacting requirements in the area of higher temperature and more oil and fuel resistance. These types are compared to common and special rubber compounds meeting hard specification. There is the discussion about right choice of TPE if it is the replacement of rubber parts. It depends on the comparison of physical properties, customer's specification and finished application of ready parts.

P-15 SYNTHESIS AND CHARACTERIZATION OF A SILANE-BASED THERMAL STABILIZER CON-TAINING THE 2,6-DI-*tert*-BUTYLPHENOLIC GROUP

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Compounds based on hindered phenols are considered as very effective antioxidants. However, low molecular weight antioxidants are easily lost from the polymers by the physical loss such as migration, evaporation and extraction. One possibility how to suppress a loss of antioxidants is based on their covalent bonding onto polymeric chains or – in the case of composites, onto inorganic fillers

The present work was focused on the preparation of a new thermal stabilizer, consisting of hindered phenol group, joined into an appropriate silane precursor.

Thermal stabilizer (antioxidant) based on a hindered phenol, containing a triethoxysilyl group was synthesized and characterized. 2,6-Di-*tert*-butyl-4-methylphenol (BHT) was oxidized to form a 3,5-di-*tert*-butyl-4-

-hydroxybenzaldehyde (*I*) and by coupling reaction of benzaldehyde (*I*) with 3-aminopropyltriethoxysilane (APTES) a corresponding 4-((*E*)-(3)(triethoxysilyl)propylimino)methyl)methyl)-2,6-di-*tert*-butylphenol (*II*) was prepared.

This type of molecule can be easily grafted onto different organic or inorganic species as a consequence of reactivity of alkoxy groups with hydroxy groups of substrates. Among other applications belongs a formation of different organic/inorganic hybrid structures based on the co-condensation of molecule (*II*) with various alkoxysilanes. The preparation of thin films, coatings and nanoparticles consisting of hindered phenol groups in their structure by using the sol-gel technology will be concerned in our forthcoming work.

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P-16 COMPATIBILIZATION OF COMPOSITES LDPE/ ORGANIC FILLER VIA CROSSLINKING

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Composites polymeric matrix / organic filler have poor mechanical properties due to low adhesion between hydrophobic polymer matrix and hydrophilic filler surface. In our previous work some improving of properties was achieved by modification of these composites via crosslinking initiated by organic peroxide.

In this work low density polyethylene was used as a polymeric matrix and two various fillers were compared. Properties were investigated in a large scale of a filler concentration, up to 70wt.% and they were compared for unmodified samples and those modified by peroxide-initited crosslinking. The effect of a peroxide concentration was evaluated at a constant filler content. Mechanical properties, insoluble crosslinked portion and equilibrium swelling were measured.

Generally, modification of materials by crosslinking leads to an improving of properties. This can indicate a formation of covalent bonds between filler surface and polymeric matrix that results in an increase of adhesion on the polymer-filler interface. The extent of these effects depends on the nature of the filler.

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P-17 INVESTIGATION OF PROPERTIES OF HYBRID ELECTRO-CONDUCTIVE COMPOSITES WITH

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IMPROVED TOUGHNESS

The incorporation of electro-conductive filler into a polymeric matrix dramatically increases the electrical conductivity of the material, but the mechanical properties are often deteriorated, especially the elongation at break and toughness. To improve the compatibility between polymer/polymer or polymer/inorganic filler phase, the impact modifiers are frequently functionalized. Maleated polymers are among the widest known family of the functionalized polymers used as compatibilizers and adhesion promoters as well as impact modifiers^{1–3}.

The influence of both carbon black (CB) and an ethylene-propylene copolymer, grafted by maleic anhydride (EP-g-MA), on the static mechanical properties, impact strength, peel and shear strengths as well as electrical conductivity, of composites based on the high density polyethylene (HDPE) matrix, was investigated in this contribution. It was found that CB improves the stress at yield, the stress at break, and the Young's modulus, as well as the shear strength and the peel strength of the HDPE/CB composites. The addition of EP-g-MA to the HDPE/CB composites improves their impact strength, the peel and shear strengths as well as the electrical conductivity.

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P-18 METAL DITHIOCARBAMATES AND THEIR INFLUENCE ON THE CURE SYSTEMS EFFICIENCY

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Special interest in the study of metal dithiocarbamates was aroused because of its diversified applications and

also because of the striking structural features presented by this class of compounds. *N*-ethyl-*N*-phenyldithio-carbamates (epdtc) used in the process of vulcanization of rubber compounds form a group of ultra-accelerators of the curing process^{1,2}.

The present paper is devoted to the synthesys of *N*-ethyl-*N*-phenyldithiocarbamates Co(III), Ni(II), Cu(II), Zn(II), Cd(II), Hg(II) and Pb(II) and study of their influence on the kinetics of cure and physical properties of rubber compounds with the addition of studied dithiocarbamates³.

Kinetic study of the cure process suggests a dramatic change in the reaction mechanism of vulcanization in the presence of accelerators. All studied dithiocarbamate accelerators decrease the reaction order and the values of rate constants increase by order: $\{\text{Zn}(\text{epdtc})_2\} < k\{\text{Cd}(\text{epdtc})_2\} < k\{\text{Pb}(\text{epdtc})_2\} < k\{\text{Ni}(\text{epdtc})_2\} < k\{\text{Co}(\text{epdtc})_3\} \text{ (ref.}^4).$

Study of the physical-mechanical properties of rubber compounds was provided with using of standard methods: Determination of density; Determination of indentation hardness by means of durometer; Determination of tensile stress-strain properties; Determination of tear strength; Determination of vulcanization characteristics on a vulkametr and Determination of Mooney viscosity⁵.

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P-19 CARBOXYLATE COMPLEXES AS RUBBER-TO-METAL ADHESION PROMOTERS

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The rubber to metal adhesion is one of most important problems in rubber industry¹. Transition metal derivatives of saturated carboxylic acids rank among abundant groups of compounds that are of interest from the viewpoint of inorganic, macromolecular and coordination chemistry. This is determined in many respects by the practical significance of carboxylates, which are used also as adhesion promoters in rubber technologies^{2,3}.

This paper is devoted to the synthesys of carboxylato-complexes Co(II), study of their influence on the values of rubber-to-steel cord adhesion and also study of physical and mechanical properties of rubber compounds. Vulcanizates studied were prepared according to standard formulations. The values of adhesion of the rubber compounds to the brass-plated steel-cord for the passenger radial tyres and the values of adhesion of the rubber compounds to the zinc-coated steel-cord for the steel-rope conveyor belts were measured.

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P-20 RESEARCH OF INFLUENCE OF TYPE OF TIRES TO STABILITY AND STEERABILITY OF AUTO-MOBILE

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The great part in creating automobile steerability and stability characteristics is contributed to tyres. Their features essential from the point of active safety of vehicle are following: lateral stiffness which has influence on vehicle drift resistance, circumferential stiffness – on which longitudinal forces depend during driving and braking, type and tread pattern – on which road adhesion (road ability) and longitudinal and lateral forces above mentioned depend.

Examination of steerability and stability performed on different tyre types according to methodics applied to the whole vehicle can provide valuable information referring to tyres. Having stated changes in car properties we concluded about tyre properties.

The results of such examinations performed at the Cracow University of Technology in co-operation with Research and Developing Centre of the Tyre Industry "STOMIL" Poznań are presented in this paper. The recovery type vehicle 12 000 kg total mass and 4250/7070 kg mass distribution on the front/rear axle was tested. This vehicle was equipped (by turns) with two various type of tyres with dimensions 365/80 R20. The first tyres were MPT (Multi Purpose Tyres)-designated as A and second

one the standard type (with highroad tread) -designated as B. Inflanation pressure was additionally changed in tyres type B. The pressure was increased in proportion to nominal values- for front/rear wheels of 0,5/1,5 bar) The series of Steady State Circular Tests (ISO 14792) and Severe Lane Change Manoeuvre (ISO/TR 3888) tests were carried out. The second type of mentioned test reflect the real manoeuvre of overtaking (or by-passing) in road conditions.

Steerability evaluated on the basis of steady state tests on the circular path didn't demonstrate the basic differences and tendency to changes of quasistatic movement characteristics of vehicle. But transient response tests on the basis of severe lane change manoeuvre demonstrated the tendency to loss of stability for tests velocities 70–75 kmph (dry asphalt road). Vehicle equipped with tires B with increased inflanation pressure demonstrated the tendency to skidding of rear axle i.e. loss of stability.

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P-21 THERMOSTABLE BIOPOLYMERS PREPARED FROM VARIOUS XYLANS

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In the last years, an increasing interest has been observed both on the synthesis and the non – food applications of fatty acids esters of polysaccharides. These materials present improved and/or new properties as waterproof character, termal stability and thermoplasticity. Acylation of different types of xylans with higher fatty acylchlorides inorganic solvent (DMSO or DMF) in the presence of pyridine and dimethylaminopyridine as catalyst will be described.

Prepared esters of xylans with high degree of substitutions were characterized by spectral methods (FT-IR).

Thermal properties were studied by TG and DSC methods. The thermal stability of the prepared esters increased slightly upon chemical modification.

This work was realized with the support of the Slovak Grant Agency VEGA project No. 2/3162/23 and project APVT –51-015802.

P-22

2K-PUR SYSTEMS FOR PROTECTIVE AND DECORATIVE COATINGS OF STRUCTURAL PLASTICS

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High quality of surface is of a great importance in transportation markets, especially in car production and refinish. Quality of paints should be, of course, balanced with important requirements regarding environmental protection. Therefore, low VOCs are required. High solids or water borne PUR coatings combine very effectively both these requirements.

2K-PUR system AKRYLMETAL, developed and manufactured by Synpo in Pardubice, offers a complete assortment of primers, primer surfacers, base coats and clear coats for different structural plastics, which are currently very often used in the transportation market. Two basic product lines are manufactured. Solvent borne product line is coded LV and the water borne is coded AQ. Synpo Pardubice has experience and is sufficiently equipped to select an optimal coating system from its own production and test it in its laboratories, which are accredited according to ČSN EN ISO/IEC 17025.

AKRYLMETAL coating system has been used for more than 10 years by many leading Czech companies like JAWA, Adast, Karosa, Rim-Tech (supplier of plastic components for Škoda), etc.

P-23

STUDY OF ADHESION OF LOW-DENSITY POLY-ETHYLENE PRE-TREATED BY BARRIER DISCHARGE PLASMA

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Low-density polyethylene (LDPE) dispatches excellent physical-mechanical properties. Due to low surface free energy (SFE) of LDPE its surface and adhesive properties are insufficient for bonding or printing. To obtain a higher strength of adhesive joint of LDPE to more polar polymers, it is necessary to increase its SFE by specific modification methods. The most advanced method of

LDPE surface modification is based on pre-treatment by electric discharge plasma¹. The LDPE foils were modified using barrier or radiofrequency discharge plasma^{2,3} in O_2 or N_2 at atmospheric pressure at various conditions.

The surface and adhesive properties of plasma modified LDPE were assigned by goniometric measurements of contact angles on the LDPE surface using a set of testing liquids, by peeling of adhesive joints and also using ATR spectroscopy and AFM microscopy. The SFE and its components of plasma modified LDPE were calculated by modified Owens-Wendt equation³. Evaluation of obtained results led to the conclusion that the most significant increase in hydrophilicity in comparison with unmodified polymer was reached after modification of LDPE in $\rm O_2$ atmosphere.

The research was supported by the Slovak Grant Agency VEGA (grant No. 2/4042/04).

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P-24 MEASUREMENT OF RUBBER COMPOUNDS FAILURE PROPERTIES

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Nonlinear dynamics of crack propagation are investigated experimentaly with the goal of clarifying the failure properties of special developed tread rubber mixtures for personal tires in Matador a.s. This paper presents results and evaluations of crack propagation and crack nucleation caused by flex cracking under various teperature conditions according to STN 62 1488, testing of dynamical and mechanical properties. Obteined data were evaluated and comparised.

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P-25 STRUCTURE AND PROPERTIES OF FERROMAGNETIC RUBBER BLENDS

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The present work is focused on the investigation of the influence of hard magnetic strontium ferrite filler on the structure, vulcanization charakteristics, magnetic and mechanical properties of rubber blends.

The variations in characteristics of rubber – ferrite composites were evaluated as a function of ferrite loading. Results shown that the vulcanization time is influenced by ferrite and carbon black content. The saturation magnetization is linearly dependent on the mass fraction of the magnetic filler, while the tensile strength, elongation at break and modules are influenced with the size, shape and volume friction of ferrite particles.

P-26 FORMATION OF NEW PHASE BOUNDARY LAYERS ON POTENTIAL FILLERS FOR POLY-OLEFINS AND RUBBER COMPOUNDS

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New trends in the types of fillers used for these applications indicate new posibilities not only in modifications of precipitated SiO_2 or in the use of electrical conductivity of the material by using polyaniline¹, but also in the use of new, non-traditional fillers.

The use of organoclays^{2,3} is one of the new applications showing a promise. Organoclays are produced by treating bentonites, minerals occurring in the nature, by certain organic compounds, e.g. quaternary ammonium salt. Their structure is formed by montmorillonite that can be used as a filler after specific modifications.

Environmental issues pertaining to the tire industry are forcing the use of technically accessible biodegradable natural polymers. One such biodegradable natural polymer used in rubber compounds is corn starch^{3,4}.

The main focus of our investigation reported in this contribution is the comparison of selected modified fillers as to their effects on the vulcanization characteristics and on the typical physical and mechanical properties, such as strength and hardness of the vulcanizates. The fillers used in these studies were: precipitated SiO_2 , bentonite and starch.

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