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9TH INTERNATIONAL CONFERENCE ON POLYMERIC MATERIALS IN AUTOMOTIVE PMA 2023

AND

THE 25TH SLOVAK RUBBER CONFERENCE SRC 2023



BOOK OF PROCEEDINGS



SLOVAK UNIVERSITY OF TECHNOLOGY IN BRATISLAVA FACULTY OF CHEMICAL AND FOOD TECHNOLOGY



EDITORIAL

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Slovak University of Technology, Faculty of Chemical and Food Technology Polymer Institute, Slovak Academy of Sciences

Foreword

In 2005 the first International Conference on Polymeric Materials in Automotive was organized in Bratislava starting a new tradition of events that reflected steeply rising importance of automotive industry in Slovakia. That is related to the presence of dominant investors in Slovakia, namely Volkswagen, PSA, Kia and Jaguar Land Rover and including a number of other companies – suppliers of plastics and rubber parts being a significant part of them – building up new facilities in the country. The appreciated feature of the PMA series consists in a fact that, although targeted to polymeric materials used in automotive industry, the scope of the conference is kept highly scientific. Thus, new ideas have been presented, many of these being far away from industrial application, still contributing significantly to a progress in the area.

Similar to the first International Conference on Polymeric Materials in Automotive PMA 2007, PMA 2009, PMA 2011, PMA 2013, PMA 2015, PMA 2017 and PMA 2020 the upcoming International Conference on Polymeric Materials in Automotive PMA 2023 is targeted on various aspects related to plastics and rubber in the automotive industry, with the aim to present and discuss innovative approaches towards new polymer products increasingly having a decisive influence on the design and appearance of new generation of cars. Almost 1000 participants from 27 countries attended the PMA conferences, ranked as successful and interesting.

The international scientific conference on rubber, Slovak Rubber Conference, used to be organized every year by the Rubber Research Institute of Matador Púchov. From 2005 this traditional event is held as a part of the International Conference on Polymeric Materials in Automotive and this will be the case also for PMA 2023 organized together with the 25th Slovak Rubber Conference in Smolenice Castle.



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CONFERENCE PROCEEDINGS

CHALLENGES FOR THE RUBBER INDUSTRY – REACH, CIRCUALR ECONOMY, CO₂ -FOOTPRINT

Ulrich Giese

Deutsches Institut für Kautschuktechnologie e. V., Eupener Str. 33, Hannover (Germany) Email: <u>ulrich.giese@Dikautschuk.de</u>

The conversion of the automotive industry from combustion to e-mobility, or new regulations in REACH on the handling of raw materials and chemicals, CO₂ footprint and abrasion as a contribution to microplastics pose major challenges for the European rubber industry, especially in the increasing implementation of the EU's "Green Deal" agenda published in 2021, whose projects are intended to combine projects on climate protection, energy supply, digitalization, the internal market and industrial policy¹. Corresponding projects are aimed at decarbonization and modernization of energy-intensive processes² as well as access to resources, value chains, an effective circular economy and a turnaround in transport and mobility towards more environmental and health protection. Thus, there is also a great need in the rubber industry to avoid greenhouse gases and reduce the CO₂ footprint (CFP) of elastomer products by substituting raw materials of fossil origin with renewable materials² and taking measures to save energy, especially for high-energy processing steps such as mixing and vulcanization. The environmentally sensible demand for the implementation of the circular economy represents a future problem for the rubber industry and its products that has so far only been partially solved in technical terms. The use of thermal, mechanical or physical recycling processes in accordance with the state of the art and quality requirements currently result in only a relatively small amount of waste rubber or its ingredients being used in new products.

New regulations and efforts in REACH lead to high requirements regarding substitutes for indispensable elastomer ingredients. Special attention is paid to substances from the class of antioxidants⁴, bisphenols, polyfluorinated hydrocarbons, including polymers, polyfluorinated carboxylic acids, but also polycyclic aromatics, especially with consumer products and rubber granulates.

All these demands for the protection of man and the environment are on the one hand reasonable and on the other hand need solutions, which in many cases are a big problem as long as one wants to keep the properties and application areas of elastomers on today's level.

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TUNING THE ADHESIVE PROPERTIES OF PEO-MODIFIED SURFACES IN THE PRESENCE OF FREE PEO CHAINS: A MOLECULAR DYNAMICS SIMULATION STUDY

Zuzana BENKOVÁ^{*,1} and M. Natália D. S. CORDEIRO²

¹Polymer Institute, Slovak Academy of Sciences, Dúbravská cesta 9, 845 41 Bratislava, Slovakia ²LAQV@REQUIMTE, Department of Chemistry and Biochemistry, Faculty of Sciences, University of Porto, Rua do Campo Alegre 687, 4168-007 Porto, Portugal email: <u>zuzana.benkova@savba.sk</u>

Polymers grafted onto solid surfaces can be useful in a large diversity of technological applications ranging from the stabilization of colloidal suspensions, the reversible tuning of wetting and adhesion, to friction, lubrication and wear.¹ Of special relevance is the polymer-coated surface immersed in a melt of chemically identical free polymers. Besides the technological utilization, such systems turn out to be a mathematical model for intriguing systems of two opposing surfaces grafted by polymers and exposed to a matrix of chemically identical polymers. At certain conditions, it is entropically more convenient to replace two brush-melt interfaces by a single brushbrush interface. The penetration of free chains from the matrix into a layer of end-grafted polymers is capable of repelling two opposing polymer-grafted surfaces. On the other hand, the expulsion of free chains from the layer of end-grafted chains triggers the attraction of two opposing polymer-grafted surfaces. These two entropically controlled phenomena are termed as the wetting and dewetting, respectively. In the case of repulsive surfaces, the wetting regime is located between allophobic dewetting regime at low grafting densities and the autophobic dewetting regime at high grafting densities.² The transitions between these regimes depend on the grafting densities of and the number of monomers in the grafted and free chains N and P, respectively. A theoretical schematic diagram (P, σ) for fixed N based on simple scaling arguments is shown in Figure 1.³⁻⁶

The transition between the allophobic dewetting and wetting regimes is approximately identified with the transitions from the non-stretched to the stretched regimes (4, 5). The transition between the wetting and autophobic dewetting regimes conforms to the transition to regime 7 when the density of grafted chains attains the density of a melt of free chains. An alternative definition of autophobic dewetting is based on the spreading parameter when the transition to the dewetting regime is identified with the change of the sign of the spreading parameter from positive to negative values.⁶



Figure 1. Schematic $(P, \sigma' = a^2 \sigma)$ diagram in the logarithmic scale for grafted polymers of fixed N monomers exposed to a matrix of free homopolymers of P monomers, where h denotes the height of the grafted layer and a is the size of a monomer. 1) Mushroom regime of non-overlapping grafted chains with excluded volume interactions between grafted and free chains, 2) mushroom regime with ideal behavior of non-overlapping grafted chains, 3) non-stretched brush regime with ideal behavior of grafted chains, 4) stretched brush regime with excluded volume interactions, 5) stretched brush regime with ideal behavior of overlapping grafted chains 6) pseudo-ideal regime, and 7) dewetting regime with only marginal overlap of free and grafted chains at the interface. The predicted transitions shown as lines in the logarithmic plot correspond to $\sigma(1 \leftrightarrow 4) \sim P^{2/5}N^{-6/5}$, $\sigma(2 \leftrightarrow 3) \sim N^{-1}$, $\sigma(3 \leftrightarrow 5) \sim PN^{-3/2}$, $\sigma(4 \leftrightarrow 5) \sim P^{-2}$, $\sigma(5 \leftrightarrow 6) \sim P^{-1/2}$ and $\sigma(6 \leftrightarrow 7) \sim P^{-1/2}$. The dashed line delineates the region of partial and complete dewetting characterized by positive and negative spreading parameter *S*, respectively.

The theoretical studies of the interface between a layer of grafted polymers and chemically identical chains based on scaling arguments have been mostly focused on the analytically solvable limits of densely grafted chains

with $\sigma >> N^{1/2}$ and of either P << N or $P >> N^7$ though this is far from experimental and application conditions. To study systems where $P \approx N$ theoretically, one is left with a numerical self-consistent-field (SCF) approach.⁸ However, the numerical approaches have been mostly elaborated for either very low or very high coverage densities, again far from real systems. The comparison of the theoretical predictions with the experimental results, on the other hand, is restricted only to a few combinations of N, P and σ parameters because of the difficulty to prepare grafted polymer layers of high enough and often even of well-defined grafting densities.² Moreover, the theory assumes completely flexible chains, sharp boundaries at interfaces and homogenous distribution in the plane parallel to the supporting substrate. Observed discrepancies between theoretical and experimental findings originate from phenomena that cannot be incorporated on a theoretical level. This is indeed a field for employing atomistic molecular simulations as a bridge between the theory and experiment. However, almost all simulations have been based on coarse-grained approaches.⁹⁻¹² Since coarse-graining neglects the specific interactions between atoms one of its shortcomings, relevant to surface-grafted polymers interacting with melt of free polymer chains, is the shift in entropy due to the reduced number of degrees of freedom. Only a small number of atomistic molecular simulations of grafted chains immersed in the matrix of homopolymers have been reported ^{13,14} and none of these studies dealt with systematic variation of P/N and σ parameters to investigate the state diagram of surface-grafted polymers in the presence of free chemically identical polymers. The aim of presented study is to explore the wetting behavior of a system composed of a solid surface being an amorphous silica which supports a layer of the end-grafted poly(ethylene oxide) (PEO) chains and is placed in a chemically identical polymer melt using fully atomistic molecular dynamics (MD) simulations.¹⁵ PEO is chosen because of its tremendous technological and biological applications and its peculiar unique characteristics such as an amphiphilic nature, perfect solubility in water and organic solvents, biocompatibility, low immunogenicity and non-toxicity. The length of tethered chains (N = 18 monomers) is kept constant while the length of the free chains (P = 3, 9, and 18monomers) is varied in order to study different regimes delineated in the theoretical (P, σ) diagram, *i.e.*, $P < N^{1/2}$, $N^{1/2} < P < N$, P = N. The grafting densities of the substrates span the range from the *mushroom* (non-overlapped regime) to the strongly-stretched brush (overlapped) regime with highly orientated PEO polymer chains in a liquidlike ordered state. The grafting density σ of grafted PEO chains, expressed as the number of chains attached to a unit area, spanned the interval 0.055 - 3.495 nm⁻². A snapshot of the simulated system composed of the PEO chains grafted at $\sigma = 0.218 \text{ nm}^{-2}$ and exposed to a matrix of the free chains of P = 3 is shown in Figure 2. All MD simulations were performed using the GROMACS package.¹⁶ The all-atom intra- and intermolecular interactions were described by the revised CHARMM force field.^{17,18} After the thermal equilibration of the systems, the production simulations were carried out in the NVT ensemble at 298 K for 50 ns



Figure 2. Snapshots of the initial conformation after the combination of the two separately equilibrated blocks (a) and final conformations after 50 ns of MD simulations at T = 298 K (b) of PEO_g chains (N = 18) grafted at $\sigma = 0.218$ nm⁻² in the presence of the matrix of free PEO_f chains (P = 3). Snapshot (c) corresponds to snapshot (b) after omitting the free PEO_f chains.

The presence of PEO_f chains induces expansion of the PEO_g chains from the silica surface which acts as an attractive support for PEO chains (Figure 2). Furthermore, the matrix of PEO_f chains behaves like a solvent in line with the theory for good and Θ solvent and the sparsely grafted PEO_g chains expand more when exposed to the matrix of shorter PEO_f trimers than to the matrix of longer PEO_f nonamers and octadecamers. Moreover, as the structural pattern of the density distribution functions suggests, PEO_g and PEO_f chains display competitive interactions with the attractive silica surface at lower grafting densities (Figure 3).



Figure 3. Density distribution of PEO_g (N = 18) and PEO_f (P = 18) chains in the composed systems as a function of the distance from the silica surface for $\sigma = 0.218 \text{ nm}^{-2}$ (a) and 3.495 nm⁻² (b). Density distributions of dry grafted PEO chains and free PEO chains above the bare silica substrate are also included for comparison.

Surprisingly, the PEO_f nonamers tend to lose their direct contact with the silica support already at lower grafting densities than the PEO_f octadecamers. This tendency might be attributed to the enhanced entanglements formed between the longer PEO_f octadecamers with PEO_g chains and locked loop-like arrangement of PEO_f octadecamers evidenced by the orientation order parameters. As anticipated, PEO_f trimers remain in the vicinity of the silica surface also at higher grafting densities.

At lower grafting densities the overlap of the PEO_f nonamers with the grafted layer is smaller than the overlap of PEO_f octadecamers, however, the overlap of PEO_f nonamers becomes larger after the PEO_f chains become detached from the silica support (Figure 4). While the overlap parameters of PEO_f nonamers and octadecamers start to be virtually the same from the grafting densities of ~ 2.2 nm⁻², the PEO_f trimers are still more significantly mixed with the grafted layer at this coverage. Although, at $\sigma = 3.495$ nm⁻², the overlap parameters still indicate little overlap between PEO_f and PEO_g chains, these parameters merge into one value for all PEO_f chain lengths.



Figure 4. Overlap parameter $P_{ov} = \frac{\int_0^{\infty} \rho_{PEOg}(z) \times \rho_{PEOf}(z) dz}{\int_0^{\infty} \rho_{PEOg}(z) dz \times \int_0^{\infty} \rho_{PEOf}(z) dz}$ between PEO_f chains of *P* monomers and PEO_g chains of *N* monomers grafted on the silica substrate as a function of the grafting density (a) and as a common area of PEO_f and PEO_g density distributions normalized by the integrated PEO_g density distribution (1 means complete wetting) (b).

The variation of the height of the grafted layer with the grafting density for the real systems qualitatively agrees with the theoretical predictions for model polymers (Figure 5).



Figure 5. Height of PEO_g chains of *N* monomers grafted on the silica surface in the presence of PEO_f chains of *P* monomers as a function of the grafting density. The solid black line serves as a guide to the eye and represents theoretically predicted scaling of the height for a dry brush layer. The solid and dashed lines, respectively, represent the characteristic scaling predicted for good-solvent (slope 1/3) and pseudo-ideal conditions (slope 1/2).

The orientation of PEO_g chains with the surface normal depends on the length of PEO_f chains more substantially at lower and moderate grafting densities, while as the PEO_f chains are getting expelled from the grafted layer at larger grafting densities the differences are diminished.

It is shown that very large grafting densities are necessary for the layer of relatively short PEO chains grafted onto the amorphous silica substrate to become dewetted from shorter or equally long free PEO chains. It turns out to be difficult even to achieve the detachment of PEO_f chains from the silica substrate. Thus, two opposing surfaces covered with irreversibly grafted PEO chains tend to repel in the presence of bulk free PEO chains of shorter or comparable molar masses.

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ANTIBACTERIAL POLYMER COMPOSITES BASED ON HYDROPHOBIC CARBON QUANTUM DOTS FOR PUBLIC TRANSPORT APPLICATIONS

Mária KOVÁČOVÁ, Mohamed SHAALAN, and Zdenko ŠPITALSKÝ*

Polymer Institute, Slovak Academy of Sciences, Dúbravská cesta 9, Bratislava 845 41, Slovakia <u>zdeno.spitalsky@savba.sk</u>

Carbon quantum dots (CQDs) are a relatively new carbon allotrope. CQDs are quasispherical carbon particles with a size of less than 10 nm with crystalline sp² cores of graphite and quantum effects. A subclass of CQDs are graphene quantum dots (GQDs), and they have a structure of one or several graphene layers with a diameter < 10 nm with higher crystallinity than CQDs. In both cases, however, CQDs are functionalized by functional groups on their surface, which can improve optical properties, solubility, and chemical stability and generally increase thesurface variability and complexity of CQDs.

CQDs have many hydrophilic functional groups at the edges or on the basal plane. Specific hydrophilic functional groups in the CQDs include epoxy and hydroxyl groups. Hydrophilic CQDs are very well soluble in water and other polar solvents due to their chemical composition; therefore, they differ from other carbon-based nanomaterials. Additional advantages of CQDs include their nontoxicity and biocompatibility. The second types of CQDs are hydrophobic CQDs containing carboxyl and carbonyl functional groups. In comparison to hydrophilic CQDs, hydrophobic CQDs are more effective in producing reactive oxygen species (ROS) responsible for the antibacterial activity of CQDs.

CQDs have extensive application usage from sensors through photoelectrochemical water splitting, chemiluminescence, LEDs, and photovoltaic solar cells up to photocatalysis and readers can find several reviews about it. CQDs also play an important role in medicine. CQDs are used in intracellular ion detection, toxin detection, pathogen, vitamin, enzyme, protein, nucleic acid, and biological pH value determination. QDs also have great utility in bioimaging, biosensing (forexample, QD modification with metal ions or biomolecules), fluorescence labelling of cellular proteins (biolabeling), genetic technologies, and cell motion tracking.

Despite the broad range of biomedical applications, we would like to focus on antibacterial properties of pure CQDs and their polymer composites. The antibacterial effect of CQDs is based on noninvasive photodynamic therapy (PDT). PDT can cause a specific biological response on the cellular or subcellular level, such as apoptosis, programmed death, or necrosis, a nonprogrammed pathway. During this process, CQDs absorb light (photons). One electron absorbs this energy and moves into a higher excited single state. This state is in nanoseconds, and it can emit light and lose its energy or dissipate as heat. The excited photosensitizer in the singlet state may also undergo the process known as an intersystem crossing. The spin of the excited electron inverts to form the relatively long-lived (microseconds) excited triplet-state that has electron spins parallel. The long lifetime of the CQD triplet state is explained by the fact that the loss of energy by the emission of light (phosphorescence) is a spin-forbidden process as the CQDs would move directly from a triplet to a singlet state. In the presence of molecular oxygen, part of the energy can be transformed into an oxygen molecule which changes to ROS. One of the most important type of ROS is singlet oxygen (¹O₂). Singlet oxygen and other ROS react with a wide range of biological targets and are known to be involved incellular signalling and cell damage. Therefore, CQDs act as indirect antibacterial materials after illumination with light generates singlet oxygen.^{1,2}



Scheme Schematic view of light-triggered polymer nanocomposite with CQDs

In our work, we focused on the preparation of polymer composites with hydrophobic carbon quantum dots for PDT in public transport applications. In our presentation, we will focus on two ways how to use CQDs polymer composites. One of them is plastic parts prepared by 3D printing. The second one is surface coating with thin polymer films.

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LOW-TEMPERATURE SULFUR VULCANIZATION OF NBR

Jakub WRĘCZYCKI and Dariusz M. BIELIŃSKI*

Institute of Polymer & Dye Technology, Faculty of Chemistry, Lodz University of Technology, Stefanowskiego 12/16, 90-924 Lodz, Poland dariusz.bielinski@p.lodz.pl

Introduction

In the presence of components of the crosslinking system, namely organic accelerators, and inorganic activators, the process of sulfur vulcanization of rubber occurs much faster and allows effective chemical bonding of rubber macromolecules with sulfide bridges even in a time of few minutes¹. Regardless of their presence, the process of sulfur vulcanization is customarily carried out at a temperature of at least 160 °C, which is due, among other things, to the intense increase of the concentration of reactive linear sulfur diradicals formed by the elemental sulfur ring opening (S8) via thermolysis of the S-S bonds (homolytic cleavage)². Activation of the S8 ring in addition to homolytic cleavage of sulfur-sulfur bonds can also occur through heterolytic cleavage. Various electrophilic or nucleophilic chemical agents can cause the cleavage of S-S bonds and the S8 ring opening even at room temperatures leading to active sulfurization forms³. However, in the context of sulfur vulcanization of unsaturated elastomers, to our knowledge, there are no direct literature and patent reports on the addition or co-addition of chemical species that cause heterolytic dissociation of the S-S bonds that could activate elemental sulfur and allow sulfur vulcanization at significantly lower temperatures.

Experimental

The rubber samples were prepared using a David Bridge laboratory two-rolls mill equipped with two watercooled rollers (30 cm long and 15 cm in diameter) rotating with 18 and 20 rpm (friction 1.1). The amount of modifier⁴ was calculated as mol % equivalent on elemental sulfur (S8) used to prepare the rubber mixture. The rubber mixtures were conditioned at room temperature for 24 h before rheometric testing. The composition of the prepared mixtures is summarized in Table 1.

| Curing system | | Curing system | Conventional (CV) | Semi-efficient (SEF) | Efficient (EF) | | |
|-------------------------------------|---------------------|---------------|----------------------|-------------------------|-------------------|--|--|
| Compound | | | [phr] | | | | |
| Acrylonitrile-bu | ıtadiene | rubber (NBR) | 100 | | | | |
| Zinc oxide (ZnC |)) | | | 3.0 | | | |
| Stearic acid (ST) | | | 1.0 | | | | |
| Tetramethylthiuram disulfide (TMTD) | | 0.56 | 1.80 | 2.25 | | | |
| 2-Mercaptobenzothiazole (MBT) | | 0.44 | 1.40 | 1.75 | | | |
| Elemental sulfu | r (S ₈) | | 1.5 | 1.0 | 0.6 | | |
| | Sample symbol | M60% | 0.919 | 0.613 | 0.368 | | |
| Nualaanhilia | | M40% | 0.613 | 0.409 | 0.245 | | |
| modifier (M)* | | M20% | 0.306 | 0.204 | 0.123 | | |
| | | M10% | 0.153 | 0.102 | 0.061 | | |
| | | REF | 0 | 0 | 0 | | |

 Table 1. Composition of rubber mixes.

The kinetics of vulcanization was determined using a MDR 2000 rheometer. The bottom rotor was working with the standard oscillation frequency of 1.667 Hz at an oscillation angle of 3° . The optimum of vulcanization was determined from changes in torque as the time required to reach 80% of the modulus increase possible under the given conditions. The tests were carried out at 120 °C for 60 minutes. The vulcanization parameters of the rubbers were determined following ISO 3417. The prepared rubber mixtures were vulcanized using a hydraulic press at a given temperature under a pressure of ca. 20 MPa for a period of t_{80} , determined rheometrically.

The total crosslink density of the NBR vulcanizates was determined by equilibrium swelling in toluene and calculated on the basis of the Flory–Rehner equation⁵. Five samples (0.03-0.05 g) were cut out from each analyzed vulcanizate. After weighing, the samples were placed into closed weighing bottles with toluene and left for 72 h at room temperature $(25 \pm 1 \text{ °C})$, to reach swelling equilibrium. Afterward, the swollen samples were immersed one by one for a few seconds in diethyl ether, which was followed by drying their surfaces carefully with a blotting paper. The swollen samples were weighed. After drying the samples to constant mass in a vacuum oven (at 60 °C for 72 h), they were weighed again. Based on the obtained values of the samples' masses, the necessary parameters

were determined to calculate the Flory-Rehner equation. Flory–Huggins coefficient for sulfur crosslinked NBR–toluene pair used in the equation was 0.435. The determined NBR density was 0.97 g/cm³.

The crosslinked structure of the NBR-rubber vulcanizates was studied by thiol-amine analysis according to the procedure developed and described by Saville and Watson⁶. Two sets of reagents were prepared that selectively cleave particular types of sulfide crosslinks. The "soft" thiol-amine reagent was prepared as a mixture of 2-propanethiol (0.4 M) and piperidine (0.4 M) in toluene, which cleaves strictly polysulfide crosslinks and remains after treatment disulfide (C–S₂–C), monosulfide (C–S–C) and carbon-carbon (C–C) crosslinks in the rubber structure. The analysis based on a "soft" reagent was conducted for 2 h on pre-swollen vulcanizates (12 h in toluene) in a closed glass vial under a nitrogen atmosphere. The "hard" thiol-amine reagent was prepared as a mixture of 1-dodecanethiol (1.0 M) and piperidine⁷, which cleaves polysulfidic (C–S–C) and carbon-carbon (C–C) crosslinks. The analysis based on the "hard" reagent was conducted for 24 h on NBR vulcanizates in a closed glass vial under a nitrogen atmosphere. After both analyses, the samples were removed instantly from the probes and washed at least a few times in order to get rid of reagent residues using toluene (15 min of extraction). Afterward, the samples were swollen to equilibrium mass in toluene, according to the crosslink density analysis procedure by equilibrium swelling. The remaining crosslink density was calculated from the Flory–Rehner equation.

Mechanical properties of the vulcanizates under static conditions (tensile strength (TS), elongation at break (Eb), and modulus at 200% of elongation (SE200)) were investigated with the use of a Zwick Roell type 1435 universal mechanical testing machine. The measurements were carried out on dumbbells type 3 (ISO 37) specimens (four for each sample) at a temperature of approx. 23 ± 1 °C with the constant crosshead speed of 500 mm/min.

Results & Discussion

Three types of curing systems (conventional - CV, semi-efficient - SEF, efficient - EF) and four different amounts of additive (M) were applied in order to investigate their impact on the curing characteristic, crosslink density and structure, and mechanical properties of vulcanizates under static conditions. The values of curing parameters of corresponding vulcanizates: CV, SEF, and EF, can be found in Table 2.

| Sample | Curing system | t80 [min] | M _L [dNm] | M _H [dNm] | ΔM [dNm] |
|----------|---------------|-----------|----------------------|----------------------|----------|
| CV_REF | | 27.00 | 0.84 | 5.93 | 5.09 |
| CV_M10% | CL | 5.50 | 0.75 | 6.37 | 5.62 |
| CV_M20% | CV | 5.50 | 0.75 | 7.00 | 6.25 |
| CV_M40% | | 10.00 | 0.71 | 6.82 | 6.11 |
| CV_M60% | | 11.50 | 0.69 | 9.20 | 8.51 |
| SEF_REF | | 15.17 | 0.67 | 7.81 | 7.14 |
| SEF_M10% | OFF | 5.22 | 0.77 | 9.02 | 8.25 |
| SEF_M20% | SEF | 5.40 | 0.76 | 9.32 | 8.56 |
| SEF_M40% | | 7.60 | 0.75 | 9.41 | 8.66 |
| SEF_M60% | | 10.00 | 0.69 | 9.44 | 8.75 |
| EF_REF | | 20.00 | 0.76 | 6.91 | 6.15 |
| EF_M10% | F F | 20.00 | 0.76 | 6.35 | 5.59 |
| EF_M20% | EF | 11.24 | 0.69 | 7.60 | 6.91 |
| EF_M40% | | 5.90 | 0.76 | 7.58 | 6.82 |
| EF_M60% | | 12.28 | 0.76 | 8.36 | 7.60 |

Table 2. Curing characteristic parameters of rubber mixes studied.

 t_{90} optimum vulcanization time; M_L minimum torque; M_{H-} maximum torque; ΔM - torque increase

Each time, the addition of the modifier to the curing system, regardless of its type (CV, SEF, EF), results in significant changes in the dynamics of the vulcanization process at 120 °C. An increase in the maximum torque (rheometric modulus) and a significant reduction in the vulcanization time are observed. The only sample deviating from the general trend is the sample with the designation $EF_M10\%$, which contains the smallest, 10% molar addition of modifier in the effective system. Due to the rapid course of the first stage of vulcanization, resulting from the chemical activation of elemental sulfur by the incorporated nucleophilic modifier and the subsequent stepwise nature of the course of vulcanization, t_{80} was taken as the optimal curing time, which, depending on the

amount of modifier introduced, ranges from 6 to 12 minutes, relative to mixtures without its addition, 27 minutes (CV system), 15 minutes (SEF system), 20 minutes (EF system), respectively.

Analysis of the total crosslink density of studied samples by the equilibrium swelling and crosslink structure of vulcanizates analyzed by means of thiol-amine analysis led to the results summarized in Table 3. In the case of a conventional curing system, the vulcanizates exhibit the lowest total crosslink density of all the systems used. Despite the significant acceleration of the vulcanization process and the increase in the achieved maximum torque, for the addition of modifier in the molar amount of 10-40% calculated on S8, its introduction affects the reduction of the total crosslink density of vulcanizates. For a 60% molar addition (CV_M60%), the crosslink density reaches a peak value about 34% higher than the reference sample (CV_REF). Due to the low ratio of accelerators to curing agent (ratio equal to 0.67), the network structure is dominated by polysulfide crosslinks (90-97%) and small participation of shorter crosslinks. The vulcanizate with the highest amount of modifier (60%) shows a much higher diversity of individual sulfide crosslinks (66.6% polysulfidic, 14.7% disulfidic and 18.7% C-C + monosulfidic).

| Sample | Total crosslink density | Polysulfidic crosslinks | | Disulfidic crosslinks | | C-C and monosulfidic crosslinks | |
|----------|----------------------------|----------------------------|------|--------------------------|------|------------------------------------|------|
| | [mol/cm ³] | [mol/cm ³] | [%] | [mol/cm ³] | [%] | [mol/cm ³] | [%] |
| CV_REF | 2.07E-04 | 1.81E-04 | 87.4 | 1.54E-05 | 7.4 | 1.08E-05 | 5.2 |
| CV_M10% | 1.27E-04 | 1.22E-04 | 96.4 | -8.61E-07 | -0.7 | 5.39E-06 | 4.3 |
| CV_M20% | 1.19E-04 | 1.16E-04 | 97.2 | -1.17E-06 | -1.0 | 4.47E-06 | 3.7 |
| CV_M40% | 1.68E-04 | 1.53E-04 | 90.8 | 4.23E-06 | 2.5 | 1.13E-05 | 6.7 |
| CV_M60% | 2.79E-04 | 1.86E-04 | 66.6 | 4.11E-05 | 14.7 | 5.22E-05 | 18.7 |
| SEF_REF | 3.06E-04 | 1.05E-04 | 34.2 | 5.30E-05 | 17.3 | 1.48E-04 | 48.5 |
| SEF_M10% | 3.08E-04 | 1.87E-04 | 60.8 | 5.46E-05 | 17.8 | 6.61E-05 | 21.5 |
| SEF_M20% | 3.13E-04 | 1.86E-04 | 59.3 | 5.49E-05 | 17.5 | 7.25E-05 | 23.2 |
| SEF_M40% | 3.07E-04 | 1.66E-04 | 53.9 | 5.04E-05 | 16.4 | 9.14E-05 | 29.7 |
| SEF_M60% | 3.40E-04 | 1.22E-04 | 35.9 | 5.48E-05 | 16.1 | 1.63E-04 | 48.0 |
| EF_REF | 2.56E-04 | 6.24E-05 | 24.3 | 4.60E-05 | 18.0 | 1.48E-04 | 57.7 |
| EF_M10% | 2.38E-04 | 3.59E-05 | 15.1 | 3.26E-05 | 13.7 | 1.70E-04 | 71.2 |
| EF_M20% | 2.75E-04 | 7.80E-05 | 28.3 | 5.94E-05 | 21.6 | 1.38E-04 | 50.1 |
| EF_M40% | 2.17E-04 | 1.04E-04 | 47.9 | 6.74E-05 | 31.1 | 4.56E-05 | 21.1 |
| EF_M60% | 3.19E-04 | 2.62E-05 | 8.2 | 5.74E-05 | 18.0 | 2.36E-04 | 73.8 |

Table 3. Participation of various types of crosslinks in the studied vulcanizates structure.

In the extension of the studies, samples cured with semi-efficient system containing nucleophilic modifier were studied. In that case, the crosslink density of all vulcanizates oscillates in a similar range, just as in the course of rheometric curves. This means, that SEF system cured samples are the least sensitive to the changes in the concentration of modifier. Significant differences in vulcanization time and achieved maximum torque values occur, however, in comparison to the reference sample. The vulcanizate with the highest modifier addition (SEF_M60%) has by far the highest crosslink density.

In contrast to previously discussed curing systems, no clear relationship can be established between the crosslink density and the content of the modifier additive in the case of an efficient system. However, vulcanizates cured with an effective crosslinking system have a predominance of short crosslinks (monosulfidic and C-C) due to a high content of accelerators and a low content of elemental sulfur (ratio equal to 6.67). The vulcanizate with the highest additive of modifier (EF_M60%) possesses a definite advantage of these sulfidic sequences (74%) over longer sulfidic bridges (8%).

The influence of crosslink density and structure is reflected by the mechanical properties of the rubber vulcanizates as shown in Figure 1. Taking into consideration the impact of nucleophilic modifier addition on the mechanical properties of vulcanizates, in the CV cured system, 10% and 20% molar addition, due to lower crosslink density of vulcanizates, slightly increases their elasticity (higher elongation at break) and their performance (increase of tensile strength). In contrast, samples cured with the additive of 40% and especially 60%, are less stretchy and possess similar values of tensile strength but higher modulus at 200% of elongation compared to the reference sample. In the semi-efficient cured system, the addition of modifier in any concentration clearly increases the endurance of samples either at 200% of elongation or at the point of elongation at break, which,

besides the extremely positive impact on curing characteristic, constitutes a good additive value of its incorporation to rubber mixes. In the efficient cured system just a slight impact on the vulcanizate's durability is observed while samples are exposed to mechanical forces aiming to improve the overall performance characteristic.



Figure 1. Mechanical properties of the vulcanizates cured with a conventional (CV), semi-efficient (SEF) and efficient (EF) curing system.

Conclusions

Incorporation of nucleophilic modifier to rubber mixes based on NBR that contain elemental sulfur as a curing agent lead to the chemical activation of S8 and allow the successful vulcanization process at a significantly lower temperature or provide highly acceleration effect at a traditional temperature (160 °C). Such an effect can be noticed in the vulcanization curves of modified curing systems in comparison to the reference samples. The achieved torque (rheometric modulus), at each stage of the vulcanization process at 120 °C, is significantly higher, and the time required to optimum torque is distinctly shorter.

A very promising from the technical application point of view seems to be the modified semi-effective (SEF) curing system, which provides very good curing characteristics (high rheometric modulus achieved in a short time), high crosslink density and balanced participation of selected types of sulfide crosslinks. This effect is achieved even with the addition of 10% of the modifier and due to semi-efficient curing system being the least sensitive to the changes in the modifier concentration.

Generally, the addition of a modifier highly improves the curing characteristics of the NBR-based rubber mixes without deterioration of the mechanical properties of the vulcanizates. In some cases, the endurance and elasticity of the sample were even improved.

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ELECTROMAGNETIC INTERFERENCE SHIELDING OF RUBBER COMPOSITES

<u>Ján KRUŽELÁK^{1*}</u>, Andrea KVASNIČÁKOVÁ¹, Michaela Džuganová¹, Rastislav DOSOUDIL², Ivan HUDEC¹

¹Faculty of Chemical and Food Technology, Slovak University of Technology, Radlinského 9, Bratislava, 812 37 ²Faculty of Electrical Engineering and Information Technology, Slovak University of Technology, Il'kovičová 3, Bratislava 812 19 jan.kruzelak@stuba.sk

Abstract

Manganese-zinc ferrite, nickel-zinc ferrite and the combinations of both fillers were used for fabrication of composites based on acrylonitrile-butadiene rubber. The main goal was to investigate the influence of magnetic fillers on absorption shielding efficiency and physical-mechanical properties of composites. It was revealed that incorporation of ferrites into rubber matrix leads to fabrication of composites that can shield electromagnetic radiation. The higher was the amount of nickel-zinc ferrite in fillers combinations, the higher was the shielding performance of composites. The results showed that nickel-zinc ferrite demonstrated better shielding potential. The biggest preference of ferrites filled rubber composites is their ability to shield electromagnetic radiation by absorption mechanisms.

Introduction

The electromagnetic interference (EMI) shielding effectiveness can be understood as the sum of reflection, absorption and multiply reflection of EMI [1, 2]. The basic condition for reflection shielding is the materials electric conductivity, while materials possessing magnetic or electric dipoles are suitable candidates for absorption shielding. The multiply reflection operates via the internal reflections of electromagnetic radiation waves from various in-homogeneities and phase interfaces within the shield. From the practical point of view, the shielding by absorption has become the most demanding, as the electromagnetic radiation waves are efficiently absorbed by the shield and not emitted back to the surrounding. The absorbed energy is usually transformed into another form of harmless energy, as for instance into heat.

Polymer composites used as efficient EMI shields have been much more preferred in practical applications over traditional metal based solid plates due to their advantages such as flexibility, lightweight, stability, corrosion resistance, ease processing, or low cost. They can be easily shaped, processed, diffracted, or coiled without the loss of their electromagnetic characteristics. As polymers are typical electrical insulators, EMI shielding properties to the polymer composites can be imparted by incorporation of different fillers. These fillers include metallic powders, metal oxides, ferrites, MXenes, or various carbon-based fillers (as carbon black, graphite, graphene, graphene oxide, carbon fibers, carbon nanotubes, etc.) [3-5]. The application of filler can not only modify electromagnetic characteristics, viscosity, or thermo-oxidative stability. Polymer composites as efficient EMI shields have already been used in practical applications in the sphere of automobiles, aerospace, aircraft, power electronics, and communication systems.

Experimental

Manganese-zinc ferrite MnZn and nickel-zinc ferrite NiZn in powder form were provided by Epcos s.r.o., Czech Republic. Both fillers represent magnetic soft ferrites with spinel structure and similar particle size distribution. Although the total particle size distribution is relatively wide, most particles for both fillers ranged from 10 to 30 μ m. Acrylonitrile-butadiene rubber NBR provided by Sibur International, Russia (SKN 3345, content of acrylonitrile 31-35 %) served as rubber matrix. Cross-linking of rubber composites was performed by application of sulfur curing system con-sisting of stearic acid, zinc oxide, N-cyclohexyl-2-benzothiazole sulfenamide CBS and sulfur (Table 1).

| NBR | 100 | 100 | 100 | 100 | 100 |
|--------------|-------|-------|-------|-------|-------|
| ZnO | 3 | 3 | 3 | 3 | 3 |
| stearic acid | 2 | 2 | 2 | 2 | 2 |
| CBS | 1.5 | 1.5 | 1.5 | 1.5 | 1.5 |
| sulfur | 1.5 | 1.5 | 1.5 | 1.5 | 1.5 |
| MnZn ferrite | 300 | 200 | 150 | 100 | 0 |
| NiZn ferrite | 0 | 100 | 150 | 200 | 300 |
| designation | Mn300 | Mn200 | Mn150 | Mn100 | Ni300 |
| | | Ni100 | Ni150 | Ni200 | |

Table 1. Composition of composites in phr and their designation

The rubber compounds were fabricated in two-step mixing process in a laboratory mixer Brabender. In the first step (9 min, 90°C), the rubber and the filler were compounded. In the second step (4 min, 90°C), the curing system was introduced.

The curing characteristics of rubber compounds were investigated from the corresponding curing isotherms measured by MDR2000 at 160 °C. The curing process was performed at 160 °C for the optimum curing time under a pressure of 15 MPa by using a hydraulic press Fontijne.

The tensile properties of tested composites were evaluated by using Zwick Roell/Z 2.5 appliance.

High frequency single-layer electromagnetic wave absorption properties (return loss *RL*, matching thickness d_m , matching frequency f_m , bandwidth Δf for *RL* at -10 dB and *RL* at -20 dB, and the minimum of return loss RL_{min}) of composite materials were obtained by calculations of return loss: $RL = 20 \log |(Z_{in} - 1)/(Z_{in} + 1)|$, where $Z_{in} = (\mu/\varepsilon)^{1/2} tanh[(j\omega d/c)(\mu \varepsilon)]$ is the normalized value of input complex impedance of the absorber, *d* is the thickness of the single-layer absorber (backed by a metal sheet), *c* is the velocity of light in vacuum.

Results and discussion

Manganese-zinc ferrite, nickel-zinc ferrite and their combinations were incorporated into matrix based on NBR. The total content of fillers was kept on constant level -300 phr. The main aim was to investigate the influence of magnetic soft ferrites on absorption shielding performance of rubber magnetic composites, which was characterized trough determination of return loss *RL*. Return loss provide information about the amount of incident EMI that can be efficiently absorbed by the shield. It has been demonstrated in scientific studies that materials reaching return loss at -10 dB can absorb roughly 90-95 % of incident electromagnetic plane wave. Return loss at -20 dB have been reported to be equivalent with absorption of about 99 % EMI [6, 7]. EMI absorption shielding performance of rubber composites was investigated within frequency range from 1 MHz to 6 GHz.

The frequency dependences of return loss for composites filled with magnetic soft ferrites are graphically illustrated in Fig. 1. The computed values of electromagnetic absorption characteristics, i.e. minimum value of return loss RL_{min} at a matching frequency f_m , matching frequency f_m and effective absorption bandwidth Δf for RLat -10 dB and -20 dB are summarized in Table 2. As shown in Fig. 1 and Table 2, with increasing content of nickelzinc ferrite in fillers combinations, the absorption maxima and absorption shielding effectiveness of composites shift to higher frequencies of EMI. The matching frequency for the composite filled with manganese-zinc ferrite (Mn300) was 2660 MHz with the absorption maximum -58 dB, while matching frequency for the composite filled nickel-zinc ferrite (Ni300) was 5260 MHz with absorption maximum reaching -62 dB. It also becomes apparent that the composite filled with 300 phr of MnZn ferrite exhibited the lowest effective frequency bandwidth at -10and - 20 dB (RL at -10 dB within 1700 - 4200 MHz frequency range and RL at -20 dB within 2320 - 3060 MHz frequency range), which means that this composite is the least effective for EMI absorption shielding. On the other hand, as the best absorption shielding material can be considered the composite loaded with 300 phr of nickel-zinc ferrite (Ni300) as it demonstrated return loss at -10 dB and -20 dB within the widest frequency range, i.e. from 2250 MHz to 6 GHz at -10 dB and from 3910 MHz to 6 GHz at -20 dB. It must be noted that due to the limitation of the used equipment and possibility to measure only up to 6 GHz, the effective absorption bandwidth for this composite would be much wider. In the case of composites filled with combinations of both fillers one can see that effective frequency ranges for absorption shielding at -10 dB and -20 dB become broader with increasing ratio of nickel-zinc ferrite. As the absorption shielding ability of composites increased with increasing content of nickelzinc ferrite, it becomes clearly apparent that NiZn filler demonstrates better absorption shielding potential. Though, based upon the achieved results it can be stated that all composites show satisfactory absorption shielding potential as they reached return loss at - 10 dB and - 20 dB within broad frequency ranges.

| sample | $RL_{min}(dB)$ | $f_m(MHz)$ | Δf (MHz) -10 dB | $\Delta f(MHz)$ -20 dB |
|------------|----------------|------------|-------------------------|------------------------|
| Mn300 | -58 | 2660 | 2500 | 740 |
| Mn200Ni100 | -49 | 3980 | 3600 | 1160 |
| Mn150Ni150 | -63 | 3250 | 3800 | 1130 |
| Mn100Ni200 | -69 | 4140 | 3800 | 1530 |
| Ni300 | -62 | 5260 | 3750 | 2090 |
| | | | | |

Table 2. Electromagnetic absorption parameters of composites



Fig. 1. Frequency dependences of return loss for composites

The results obtained from determination of physical-mechanical characteristics revealed that moduli and tensile strength of composites filled with ferrites or ferrites combinations were low. As ferrites are stiff metalbased powdery materials with relatively wide particle size distribution, they do not reinforce the rubber matrix and thus low tensile characteristics were expected. There was recorded almost no change in physical-mechanical properties of composites in dependence on the type of ferrite or ferrites combinations.

Conclusion

The results of the study revealed that composites filled with magnetic soft ferrites exhibited absorption shielding performance as they demonstrated return loss in specific frequency ranges. With increasing proportion of nickel-zinc ferrite in ferrites combinations, the absorption maxima and absorption shielding efficiency of composites shift to higher frequencies. Simultaneously, the effective absorption frequency bandwidth became broader, which means that absorption shielding efficiency of composites increased with increasing ratio of nickel-zinc ferrite. The influence of the of ferrite or ferrites combinations on physical-mechanical properties of composites was negligible.

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THE EFFECT OF ZINC COMPOUNDS ON VULCANIZATION OF NATURAL RUBBER

Drahomír ČADEK*, Eliška MANLIGOVÁ and Antonín KUTA

The University of Chemistry and Technology, Prague, Department of Polymers, Technická 5, Prague 6 – Dejvice, 166 28, Czech Republic drahomir.cadek@yscht.cz

Vulcanisation is a process in which the linear chains of rubber are formed into a spatial network by the action of a vulcanising agent. It is a key process of the rubber industry carried out under elevated temperature and pressure. The resulting products have a fixed shape and good mechanical properties. A vulcanizing system consists of a vulcanizing agent, an accelerator and a vulcanization activator. Activators increase the crosslinking efficiency of the curing system so that less curing agent is required to achieve a certain degree of crosslinking than without the use of an activator. Zinc oxide is most commonly used in sulfur curing.^{1,2}

Zinc oxide is a widely used chemical due to its chemical and physical properties. It plays an important role, for example, in tyres, ceramics, paints and textiles. About 105 tonnes are produced annually and most of it is consumed in the rubber industry.³ ZnO can be divided into classes that differ in their purity and specific surface. While some grades are in international standards, many companies use their own designations. With decreasing purity, these include gold seal (99.99%), pharma grade (99.8 - 99.9%), white seal (99.8%), green seal (99.6 - 99.7%), red seal (99.5%), and American grade (98.5 - 99.5%).⁴ Zinc oxide as activator require the presence of coactivator. These are fatty acids that convert them to a rubber soluble form. In the rubber industry, 12-18 carbonic acids are used, but in most cases it is stearic acid or lauric acid, which is more expensive but more soluble and does not flourish.¹ Their effectiveness in activating vulcanization is related to their solubility in rubber, which depends on molecular weight and melting temperature. Chain length affects reactivity with zinc oxide. The rate of vulcanization decreases with increasing length.^{5, 6}

The industry also uses other zinc-containing compounds such as zinc stearate, zinc 2-ethylhexanoate or zinc borate for activation. Zinc salts of fatty acids are the oldest additives. They improve the processing properties of NR and synthetic rubbers. The most widely used of these is zinc stearate. Zinc 2-ethylhexanoate is also used for natural rubber, which reduces stress relaxation and primary creep of vulcanizates compared to stearate. Zinc borate is a white, non-toxic powder that can be processed at higher temperatures. It is mainly used as a flame retardant and for radial tyres.⁷

The exact course of the accelerated sulphur vulcanisation reaction in the presence of an activator is not known; there are several ideas and theories, but only a rough basic description is generally accepted. Initially, the activator reacts with the accelerator. The resulting complex of activator and accelerator interacts with sulfur molecules. The product reacts with the carbon chain of the rubber. The resulting bridge precursors react with another precursor or polymer chain. Polysulphidic cross-links between the chains are formed, which are then converted by desulphurisation into shorter bridges or by degradation to form cycles or other modifications of the main chain.⁷⁻¹¹ The effects of the activator can be shown by the example of ZnO used with stearic acid, which converts it into a soluble form, zinc stearate. Zinc oxide has a greater effect on the amount of crosslinks formed, while stearic acid rather affects the rate of reaction at which bridges are formed.¹² Stearic acid surrounds ZnO, causes it to disperse better in rubber and also helps to dissolve zinc cations, thereby accelerating their access to the accelerator and sulfur.⁵

The presence of zinc compounds affects the by-products formed and the desulfuration of the bridges formed. It contributes to the shortening of the bridges and the formation of additional crosslinks from the sulfur atoms obtained. The compounds differ in their activity, which may be related to their different accessibility of the zinc cation and the stability of the resulting complex with the accelerator. A stable complex will not be very prone to further reactions. For example, in a system with ZnO, stearic acid is needed as a coactivator, which reacts with the oxide to form a salt. Not only is the salt in question soluble in the rubber, but it also makes more accessible the zinc cations that would otherwise be rendered inaccessible in the oxide by their location in the crystal lattice.⁷

As the ZnO concentration increases, the efficiency and rate of vulcanization increases to an optimum concentration of 1 dsk. ZnO prevents reversion even at low concentrations. Stearic acid accelerates the vulcanization only slightly. The greatest acid-induced acceleration is achieved at the optimum concentration, which depends on the type of rubber and the composition of the system. The dependence of the speed on the acid concentration above the optimum value is influenced by the curing temperature and the composition of the system. In any case, dilution of the system will cause a decrease in the network density of the resulting rubber. The use of nanoparticles reduces the amount of activator required and also significantly improves the physical properties of the rubber, especially its abrasion resistance and tensile strength. This happens due to the dependence of its activity on the particle surface size. Reducing the particle size will increase the surface area, thereby achieving easier

dispersion and higher oxide activity. This is probably due to the improved accessibility of zinc ions to the surface.^{8, 10}



Figure 1. Vulcanization curves of natural rubber mixtures with different zinc activators (160 °C)

Although the reaction of zinc oxide with stearic acid produces zinc stearate, which then forms complexes, it makes a difference whether the system uses a combination of oxide and acid or a straight salt. The system with ZnO and stearic acid has a higher vulcanization optimum value (T_{90}) and a slower vulcanization process. This is probably due to the poorer ability to release the zinc cation from the crystalline lattice than with salts. It has a higher degree of vulcanization. The higher cross-link density is due to the presence of ZnO.¹¹

The work focused on the activation of sulfur vulcanization by zinc compounds. In addition to the commonly used zinc oxide and zinc stearate, other zinc compounds were tested with different ratios of coactivator. The vulcanization behaviour (Fig. 1) – course and kinetics was studied on the prepared mixtures, followed by the determination of the crosslinking density of the vulcanizates.

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DIGITAL RUBBER PROCESSING –EXTRUSION AND DIGITAL TWIN OF THE EXTRUDATE

Alexander ASCHEMANN, Benjamin KLIE and Ulrich GIESE

Deutsches Institut für Kautschuktechnologie e. V., Eupener Straße 33, 30519 Hannover – Germany <u>Alexander.Aschemann@DIKautschuk.de</u>

In the context of Industry 4.0, the plastics and rubber industry are undergoing a transformation in which the application and use of automation technologies as well as the digitalization of process workflows are inevitable from an economic and technical point of view. However, the implementation of the required technologies in rubber processing industry encounters considerable challenges based on the complexity of the material, the multitude of elaborate process steps, the lack of suitable data interfaces, characteristic data and evaluation criteria for the control as well as the prediction of the efficiency of processing operations.

The combination of machine learning, classical modelling and new measurement approaches for the online characterization of rubber compounds is being developed and applied using the example of the extrusion process. The aim of this study is to develop a computer-aided linking of the "mixing-rolling-extrusion" production chain which, by means of material databases and a digital model of the process (digital twin), as well as the use of "online" measurement methods, makes it possible to automatically detect batch-related fluctuations in the material and to regulate the process accordingly with the aid of artificial intelligence (AI). In this way, production can be carried out more consistently at the optimum level of efficiency and quality. For this purpose, available measurement methods as well as those to be developed are combined in the online measurement of quality characteristics in order to enable an automatic quality assessment of raw materials and their final products. In addition, the implementation of "machine learning" algorithms ("data mining") will make material-immanent correlations predictable, which have an influence on the quality of the extruded product. By developing an AI that monitors the entire production chain and automatically identifies and adjusts process and material parameter deviations, a constant quality of the end product can be achieved.

For characterization and quality assessment of the extrudate, the thermal homogeneity was determined via a temperature measurement blade. In addition, the extrudate contour and surface defects were measured using an inline measuring system. The required data interfaces were programmed and integrated into the laboratory network.

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CAE SIMULATION VS. PART AND MOLD DESIGN

Miroslav Kollár

SimulPlast s.r.o., Na letisko2129/28, 058 01 Poprad, simulplast@simulplast.sk

The demands of the automotive industry on the quality of plastic products are at a high level. The aim of the work was to debug the product quality with the CAE software Moldex3D and to optimize the economics of the product production.

The original design of the closing knob proposed for the plastic door in the trunk of the car shows obvious appearance defects: a large sink mark in the middle of the product, white (silvery) smudges on the surface. When the product is cut and metallographically grinded and polished, a porous structure appears in the central part.

A digital model of the part, mould and simulated injection moulding process was created in Moldex3D software according to the product manufacturer's data. By analysing the simulation results, weaknesses in the design of both the part and the mould were identified. The small diameter of the gate causes a high shear rate of 225,000s-1 (Fig.:2), which exceeds the maximum value for this material by 5 times, resulting in degradation at the gate edge, white smudges on the moulding. At the same time, the small diameter of the gate induces a jetting effect (Fig.:1).



Fig.1. Free jetting into the cavity

The material solidifies prematurely and does not allow long enough to compensate the shrinkage of the material in the packing phase (Fig.: 3).





Fig.3. Sink mark

On the basis of the analysis, 2 main objectives were defined:

1. Eliminate melt accumulation due to the large wall thickness of the product

To optimize the runner system in terms of product quality and process economics 2.

Optimisation of the product geometry based on the first analysis, areas with melt accumulation were defined. One is the central part of the part with a thickness of 9 mm, the other is the central rotary pin with a thickness of 6 mm. Models with progressive wall reduction were developed (Fig.: 4).



Fig. 4 New models

A volume shrinkage minimization method was selected to evaluate the quality of the product model



Fig.: 6. Volumetric shrinkage of new parts design in cut view

Conclusion

| | Volume | $e(cm^3)$ | Cyclus time (s) | The |
|------------|--------|-----------|-----------------|---------------|
| | Runner | Part | Cyclus time (s) | result is the |
| Old design | 4,44 | 8,60 | 65 | final part, |
| New design | 3,15 | 7,25 | 26 | which was |
| Saving % | 29 | 16 | 60 | then |

optimised

with the position of a new gate with an optimised size. The aim was to extend the action of the packing pressure to approximately 5 - 6 seconds. The resulting model was subjected to a comprehensive manufacturability analysis. Due to the modification, the volume shrinkage was below 5%, so that the possibility of voids (porosity) formation was eliminated. Uniform thickness walls prevented the formation of sink marks. The new position of the gate and its size supported the process in terms of elimination of sink marks, reduced shear rate, thus preventing material degradation and completely eliminating the possibility of jetting.

The resulting model was subjected to an economic balance. By reducing the wall thickness of the moulding and optimising the runner system, a material saving of 1.7 g per part was achieved on average, which represents a saving of 2,000 kg for an annual volume of 1,200,000 pieces. Even more significant is the reduction in cycle time by modifying both the part and the runner system, which is on the order of 60%. CAE optimization with Moldex3D software not only eliminated the appearance and strength problems of the product but also brought significant economic savings, which exceeded the cost of additional mould modification several times over.

SUSTAINABLE SBR/BR COMPOUNDING THROUGH ECO-DESIGN AND RECYCLING

Lorenzo Alesi, Federico S. Grasso and Fabio Bacchelli

Versalis SpA (Eni), Via Baiona, 107 – 48123 (Ravenna, Italy) lorenzo.alesi@versalis.eni.com

The Circular Economy approach includes the diversification of feedstock for products and/or packaging through renewable sources and secondary raw materials, the integration of recycled materials into the production chain and the development of mechanical, physical and chemical recycling technologies for plastics and rubbers through internal research and partnerships with associations and consortia.

Alongside the traditional development of innovative products aimed at reducing emissions in the tire sector, a range of "Bio Attributed (BA)", "Bio-Circular Attributed (BCA)" and "Circular attributed (CA)" polymers with reduced GHG is introduced. Circularity is obtained through pyrolysis oil from chemically recycled plastic waste, while bio-attribution comes from bio-naphtha feedstock at the refinery stage.

As a further, important, contribution, product design is applied to rubber recycling. Emulsion SBR containing a dispersion of rubber powder from end-of-life tyres (ELTs) are introduced to increase compound sustainability. This technical solution was developed for increasing the powder mixing efficiency and for reducing powder handling problems. Dry and oil extended SBR/ELT powder masterbatches are addressed, pointing out dynamic response, rubber reinforcement and aging behavior through linear and nonlinear rheology. Compound properties are then tested and discussed in various formulations.

SUSTAINABLE PROCESSING PROMOTERS FOR TREAD COMPOUNDS BASED ON FUNCTIONALIZED POLYMERS

Antonia ALBERS*

LANXESS Deutschland GmbH, BU Rhein Chemie, BL SRP, Application Development EMEA ISC, Kennedeyplatz 1, 50569 Köln, Germany <u>antonia.albers(@]anxess.com</u>

Today's use of functionalized SSBRs and BRs combined with silica loading above 100 phr are state of the art for tire treads of passenger cars targeting low rolling resistance combined with outstanding grip and improved abrasion. This combination of ingredients and concentrations also brings features such as very high Mooney values in the initial mixing stages, low green strength and stickiness.

It is the scope of this contribution to investigate the use of specially designed processing promoters, with an increased content of sustainable ingredients, in tackling the aforementioned challenges and even improving the rolling resistance and wet grip properties of tread compounds.

ELECTRICAL AND MECHANICAL PROPERTIES OF CARBON-BASED ELASTOMERIC COMPOSITES

Tuba EVGİN^{1,2,3*}, Jozef PREŤO⁴, Ivan CHODÁK¹, Maria OMASTOVÁ¹

¹Polymer Institute SAS, Dúbravská cesta 9, 845 41 Bratislava, Slovakia

²Centre for Advanced Materials Application, Dubravska cesta 9, 845 11 Bratislava, Slovakia ³Dokuz Eylul University, Engineering Faculty, Mechanical Engineering Department, Tinaztepe Campus, 35397, Buca, Izmir, Turkey

⁴Vipo, a.s., Generála Svobodu 1069/4, 958 01 Partizánske, Slovakia

e-mail address: tuba.evgin@deu.edu.tr

One aim of the materials science is to enhance the composites with better electrical and thermal properties and higher mechanical strength while decreasing the weight and ensuring high resistance against external factors¹. The reason is the rapid improvements in technological applications demands to better performance in material properties². The filler materials are commonly used in the polymers for different purposes, e. g for enhancement of various mechanical and physical properties, cost reduction, thermal stability and flammability³. The elastomer composites are excellent candidates for application in high-performance structural materials, such as those in production for automotive, sports facility, aircraft, marina, and spacecraft application⁴. Numerous studies have been reported that the properties of composites are affected by several variables with various characters of filler such as dimensions, shape, size, content, degree of dispersion and orientation, and the interaction between the matrix and nanofillers, type, intrinsic properties of the matrix and fillers, processing method and conditions¹.

In recent years, carbon-based materials, carbon black (CB), graphene nanoplatelets (GnPs), multiwall carbon nanotubes (MWCNTs), etc. are commonly used as filler materials to improve the properties of matrix². The allotropes of carbon exist in different shapes, from 0D to 2D and in different sizes from micro sizes to nano sizes⁵. Each carbon allotrope has a diverse range and distinct of physical properties⁶. Among carbon nanofiller materials, multiwalled carbon nanotubes (MWCNTs) have attracted increasing interest both in basic research and industry due to their excellent thermal (thermal conductivity of 3000 W/mK), mechanical (Young's modulus of ~1TPa, yield strength of 20-100 GPa), and electrical properties (electrical conductivity of 10³-10⁷ S/m), low density, low melt flow viscosity, and high aspect ratio³. Graphene nano platelets, formed by several graphene layers bonded together by Van der Waals forces, are a potential alternative to graphene which exhibit approximately the same properties at low-cost⁷. Carbon black is the most frequently used nanofiller for rubber matrix because of low-cost and providing good reinforcement to rubber⁸. The dimensions of filler material play a circular role in the properties of elastomer composites. The aim of this study is to compare the electrical conductivity enhancement of natural rubber (NR)-based nanocomposites prepared using following fillers: 0D carbon black (CB), 1D multiwalled carbon nanotubes (MWCNTs) and 2D graphene nanoplatelets (GnPs) to understand influence of these carbon-based filler materials on composite properties.

The ethylene–propylene–diene monomer (EPDM) has been gaining increasing attention especially due to its high thermal and thermo-oxidative stability, compared to other high-volume rubbers. Further attractive features are the high resistance to ultraviolet (UV) light, oxygen, fatigue, weather, and moisture resistance⁹⁻¹⁰. Moreover, EPDM is widely used in many applications due to its ability to be reinforced with high nanofiller loading¹¹. In this study, nanocomposites with three different types of carbon fillers, CB, GnPs and MWCNTs were prepared, using the same parameters (production process, mixing conditions, filler concentration, matrix materials). The dimensional effect of carbon-based materials on the electrical conductivity and mechanical properties of EPDM-based composites was investigated.

EPDM, Keltan 4450S, including 52 wt.% ethylene monomers with the viscosity of 42 MU (ML (4 + 1), 125 °C) and a specific density of 0.86 kg/cm³ was supplied by SpecialChem (New York, NY, USA). GnPs with 1.5 μ m of diameter and 3 nm of thickness were provided by Nanogarafi (Ankara, Turkey). MWCNTs (NC7000) were bought from Nanocyl (Sambreville, Belguim). According to data sheet provided from the manufacturer, the average diameter and length are 9.5 nm and 1.5 μ m, respectively. Other ingredients using for composite preparation was paraffin oil, 2,2,4-trimethyl-1,2-dihydroquinolin (AOX-TMQ), zinc oxide (ZnO), stearic acid, tetra-methyl thiuram disulphide (TMTD), and sulphur. All ingredients were used as supplied without any further functionalization or purification process.

The nanocomposites were fabricated by melt mixing in Brabender Plasticorder PLE 331 internal mixer (Brabender GmbH, Germany) with a 30 ml mixing chamber at 100 °C for 7 min of total mixing time at 30 rpm of mixing speed. The samples for the measurements were vulcanized by compression molding, using a hot press (Fontijne 200, Fontijne, The Netherlands) at 160 °C without pressure for 30 sec and under pressure (5 MPa) for 10 min. Broadband dielectric spectroscopy (BDS) measurements were conducted using a Novocontrol Concept 40 instrument with an Alpha dielectric spectrometer supplied by Novocontrol Technologies GmbH (Germany) in the

frequency range 10^{-1} - 10^7 at room temperature. The tensile measurements of samples were carried out by using an Instron 3365 (Instron, High Wycombe, UK) universal testing machine with a cross-heat speed of 50 mm/min at room temperature. The mean values and standard deviations of six tests were reported for each sample.

| Samples | Filler | σ | Tensile | Elongation | M100 | M100 |
|--------------|---------|-------------------------|---------------|------------|---------------|---------------|
| | loading | (S/cm) | Strength | at Break | (MPa) | (MPa) |
| | (phr) | | (MPa) | (%) | | |
| EPDM | | 8.7×10 ⁻¹⁶ | 1.5 ± 0.2 | 362±67 | $1.0{\pm}0.1$ | 1.4±0.1 |
| EPDM/CB | 10 | 31.6×10 ⁻¹⁶ | 3.5±0.4 | 497±49 | $1.0{\pm}0.0$ | 2.0±0.1 |
| | 20 | 44.0 ×10 ⁻¹⁶ | 7.2±1.4 | 531±80 | 1.6 ± 0.1 | 3.8±0.3 |
| | 10 | 28.7×10 ⁻¹⁶ | 6.1±0.7 | 757±41 | $0.9{\pm}0.1$ | 1.7±0.1 |
| EPDIVI/GIIPS | 20 | 40.4 ×10 ⁻¹⁶ | 6.4±0.3 | 897±47 | $1.0{\pm}0.0$ | $1.7{\pm}0.0$ |
| EPDM/MWCNTs | 10 | 1.4×10 ⁻³ | 4.7±0.2 | 314±17 | 2.3±0.1 | 4.6±0.2 |
| | 20 | 2.1×10 ⁻² | 9.0±0.1 | 291±13 | 4.6±0.2 | 9.1±0.0 |

Table 1. Electrical and mechanical properties of EPDM-based composites.

The results of electrical and mechanical properties for EPDM-based composites are summarized in Table 1. As known, the neat EPDM is electrical insulating material $(8.7 \times 10^{-16} \text{ S/cm})$. The electrical conductivity of composites increases with increasing filler loading. The addition of CB and GnPs up to 20 phr does not change electrical conductivity value significantly. As shown, the composites including CB and GnPs exhibits poor conductivity and can be classified as an insulating-materials. The electrical conductivity of the corresponding composite exhibits significant enhancement, attaining a maximum of ~0.02 S/cm when 20 phr MWCNTs is added. At the same loading, the relative enhancement effectiveness in the electrical conductivity of EPDM/carbon-composites is as follows: CB~GnPs<MWCNTs. 1D MWCNTs have greater efficiency than that of CB and GnPs in improving the electrical properties. The morphology of filler materials can significantly influence on the electrical properties of the nanocomposites. It is clear that 1D MWCNTs can create effective and more stable conductive network because of their structure¹². On the other words, in terms of forming conductive pathways, MWCNTs are the most effective carbon-based fillers, because MWCNTs can easily entangle and produce conductive networks due to their one-dimensional structure¹². CB agglomerate in branched clusters and the relatively poor improvement with high aspect ratio GnP particles may be attributed to the absence of significant graphene layers' exfoliation and difficulty in obtaining particles' interlacing to form a conductive pathway¹³.

Tensile strength, elongation, M100 and M300 for three types of EPDM-based composites are presented in Table 1. It is observed that after addition of carbon-based filler materials, mechanical properties of EPDM-based composites are significantly altered. With progressive inclusion of filler materials, there is an important improvement in tensile strength, elongation at break, M100 and M300 up to 20 phr of filler loading, expecting for elongation at break for the systems including MWCNTs. A significant drop in elongation at break up to the maximum MWCNTs loading is observed. At certain filler concentration, the tensile test exhibits a significant enhancement of mechanical properties for composites including MWCNTs followed by CB and GnPs. It is known that the distribution of filler materials in matrix and the interfacial properties play a key role in determining the composite characteristics. 1D MWCNTs exhibit better dispersion in the matrix and interactions between the matrix and filler, hence which provide better load transfer from the EPDM matrix to filler materials. The most promising results are obtained for EPDM/MWCNTs systems, produced final composites with higher conductivity and good mechanical performance.

In next stage composites will be prepared with hybrid carbon-based fillers for achieving the best performance in terms of electrical, thermal and mechanical properties.

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EFFECT OF ISOLATION CONDITIONS ON LIGNIN PROPERTIES TOWARDS LIGNIN-BASED POLYMER MATERIALS

Richard Nadányi*, Aleš Ház, Dominika Smatanová, Matúš Majerčiak

Slovak University of Technology in Bratislava, Faculty of Chemical and Food Technology, Institute of Natural and Synthetic Polymers, Department of Wood, Pulp and Paper, Radlinského 9, 812 37 Bratislava <u>richard.nadanyi@stuba.sk</u>

Introduction

Lignin is the second most abundant biopolymer on the planet. It is the main component of plant biomass. Its primary role in plant corps is to bind polysaccharides and protect carbohydrates from external risks, such as bacteria, fungi, and water^{1,2}. Lignin has a very complex structure that makes it difficult to characterize and identify properly. Therefore, the complete isolation of the lignin polymer in its natural form without any changes in the structure has proved to be impossible now³. The repeating unit that forms its structure is called the phenylpropane unit. From its structure, three lignin precursors (alcohols) are derived, sinapyl alcohol, coniferyl alcohol, and p-coumaryl alcohol, which form three main building units, namely syringyl (S) with two methoxyl groups, guaiacyl (G) with one methoxyl group, and p-hydroxyphenyl (H) without methoxyl groups^{3,4}. In addition, all three building units have one phenolic hydroxyl group. There are multiple different linkages that are presented between the lignin building units. Generally, they can be divided into two main categories: ether bonds (C–O–C), and carbon-carbon bonds (C–C)^{5,6}. Furthermore, lignin is bonded to carbohydrates, mostly hemicelluloses (xylene), forming a lignin-carbohydrate complex (LCC)^{6,7}. The complexity and differences in the lignin structure make it a very promising material for different applications, but at the same time it is very difficult to understand its isolation processes and hard to implement it in an industrial scale application.

As mentioned above, lignin has different functional groups at different concentrations. Characteristic ending groups in the lignin structure can be simplified into hydroxyl, methoxyl, and carboxyl groups⁸. Hydroxyl groups are the most interesting because they are the most reactive functional groups in lignin structure for certain applications⁹. Hydroxyl groups in lignin are divided into two main categories, aliphatic (R–OH) and phenolic (Ph–OH) hydroxyl groups. There is also a carboxyl (R–COOH) hydroxyl group, but they are not as abundant¹⁰. There are many other ending groups among the three main mentioned earlier that can be "added" to the lignin structure is to increase the reactivity of the lignin toward its final application and to add ending groups that are not naturally present in the lignin, thus increase the possible applications of lignin.

Isolation of the lignin is mostly done in the pulp industry where the wood chips undergo the lignin dissolution process in various chemicals to obtain polysaccharides (cellulose) for further application in paper production. Among all different pulping processes, the kraft process is the most abundant, making it the best candidate to implement lignin recovery units¹¹. Nowadays, lignin is used in pulping plants as a source of energy. Dissolved lignin is in the form of a highly alkaline liquid, called black liquor, burnt in recovery boilers to produce energy, heat, and regenerate chemicals. There are several well-known processes for the isolation of lignin from black liquor, the most common being LignoBoost and LignoForce¹². Both are based on lignin recovery after the acidification of black liquor from the pulping process. Lignin is highly soluble under alkaline conditions, but it can be recovered if the pH of the solution is decreased to an acidic area. The isolation processes are performed under different precipitation conditions. Several studies show that pulping conditions can influence the properties of lignin. Especially pH and temperature vary from place to place and can affect the final quality of lignin^{13–16}. Therefore, it is important to investigate the influence of pH and temperature during the precipitation of lignin from alkaline to acidic conditions on its final properties, such as molecular weight, functional group concentration, yield, and others. According to these results, it is possible to find potential applications of lignin in different fields. Furthermore, the estimated annual production of lignin from chemical pulping in 2025 is 44 to 66 million tons, which shows great potential for lignin to become a valuable source of phenols and to participate in the polymer industry as a bio-polymer¹⁷. The presented study shows the influence of precipitation conditions, namely pH and temperature, on the lignin structure and its properties. In addition, possible applications of prepared lignin are summarized.

Materials and methods

Lignin was precipitated from alkali lignin originating from Mondi SCP. The preparation conditions were determined using statistical analysis – design of the experiment (see Table 1). The observed parameters ranged from 25 to 80 °C for temperature and from 2,0 to 4,5 for pH. Determination of the molecular weight and concentration of methoxyl, carboxyl, and hydroxyl functional groups (both phenolic and aliphatic) was determined using NIR. The conjugated and non-conjugated hydroxyl groups were determined by ultraviolet-visible (UV-vis)

analysis. All results were evaluated with a statistical program implemented in MS Excel, and the dependences of the measured parameters from both factors were determined.

Results and Discussion

Preparation conditions and results are presented in Table 1. The analysis also showed that the concentration of carboxyl groups varies between 0,32 and 0,36 mmol/g and the results do not show any significant dependence on temperature or pH. In addition, the polydisperse index (PDI) and the mean molecular weight (M_n) were also determined with NIR. The results did not show any dependence on two factors and ranged from 1,6 to 2,4 for PDI and from 2700 to 4000 for M_n , respectively.

| # | T [°C] | рН | Ph-OH [mmol/g] | R-OH [mmol/g] | OCH3 [mmol/g] | Mw [g/mol] | Non- conj. OH [mmol/g] | Conj. OH [mmol/g] | Total OH [mmol/g] |
|----|-----------|-----|-------------------|------------------|------------------|---------------|------------------------------|----------------------|----------------------|
| 1 | 33 | 2,4 | 3,60 | 1,44 | 5,53 | 6250 | 1,91 | 0,28 | 2,19 |
| 2 | 72 | 2,4 | 3,92 | 1,45 | 5,93 | 5850 | 1,06 | 0,20 | 1,26 |
| 3 | 33 | 4,1 | 3,67 | 1,47 | 5,62 | 6650 | 1,73 | 0,24 | 1,97 |
| 4 | 72 | 4,1 | 3,96 | 1,54 | 6,05 | 6100 | 2,21 | 0,33 | 2,54 |
| 5 | 25 | 3,3 | 3,82 | 1,47 | 5,83 | 6100 | 1,92 | 0,27 | 2,19 |
| 6 | 80 | 3,3 | 3,82 | 1,43 | 5,72 | 6400 | 2,89 | 0,35 | 3,24 |
| 7 | 53 | 2,0 | 3,60 | 1,26 | 5,22 | 5650 | 2,58 | 0,33 | 2,91 |
| 8 | 53 | 4,5 | 3,55 | 1,46 | 5,47 | 6850 | 1,43 | 0,24 | 1,67 |
| 9 | 53 | 3,3 | 3,39 | 1,36 | 5,17 | 6000 | 1,81 | 0,26 | 2,07 |
| 10 | 53 | 3,3 | 3,41 | 1,46 | 5,30 | 6900 | 1,94 | 0,30 | 2,24 |
| 11 | 53 | 3,3 | 3,46 | 1,45 | 5,32 | 6500 | 1,16 | 0,27 | 1,43 |
| 12 | 53 | 3,3 | 3,60 | 1,46 | 5,54 | 6550 | 1,57 | 0,29 | 1,86 |
| 13 | 53 | 3,3 | 3,48 | 1,44 | 5,37 | 6550 | 1,36 | 0,22 | 1,59 |

Table 1 Measured characteristics of precipitated lignins under the conditions of the design of the experiment.

Evaluation showed that there is significant quadratic dependence of the phenolic hydroxyl groups from temperature passing through its local minimum and linear dependence of the aliphatic hydroxyl groups from pH. The highest concentration of Ph-OH should be at 80 °C and the local minimum at 48,7 °C. The highest concentration of R-OH should be at a less acidic pH, specifically at 4,5 and the lowest value should be under the most acidic conditions (pH = 2,0). Methoxyl groups are similar to phenolic hydroxyl groups that depend quadratically on the temperature of the precipitation. The highest concentration is at 80 °C and the lowest should be at 49,7 °C. For conjugated and non-conjugated hydroxyl groups the confidence interval α was changed to the value 0,10 because the interval 0,05 does not show any reliable dependence. The concentration of non-conjugated hydroxyl groups shows a slight quadratic dependence from the temperature passing through a local minimum, with a maximum value at 25 °C and a minimum at 33,0 °C. Conjugated hydroxyl groups showed a slight dependence on both factors. In this case, the synergic effect of temperature and pH during precipitation is observed. The highest concentration of conjugated hydroxyl groups is at 80 °C and pH 4,5 and the lowest value should be at 25,0 °C and pH 4,5. The predicted values for the parameters that showed dependence on at least one factor are summarized in Table 2. Prediction was calculated using the MS Excel add-in program Solver.

| Table 2 Predicted highest and lower | t values of measured | parameters of lignins. |
|-------------------------------------|----------------------|------------------------|
|-------------------------------------|----------------------|------------------------|

| Ending group | Max. value | Min. value | | | | | | | |
|----------------------------|------------------|------------------|--|--|--|--|--|--|--|
| $\alpha = 0.05$ | | | | | | | | | |
| Ph-OH [mmol/g] | $4,13 \pm 0,231$ | 3,46 ± 0,231 | | | | | | | |
| R-OH [mmol/g] | $1,55 \pm 0,114$ | $1,32 \pm 0,114$ | | | | | | | |
| OCH ₃ [mmol/g] | $6,24 \pm 0,407$ | $5,31 \pm 0,407$ | | | | | | | |
| $\alpha = 0,10$ | | | | | | | | | |
| Non-conjugated OH [mmol/g] | $3,09 \pm 1,068$ | $1,35 \pm 1,068$ | | | | | | | |
| Conjugated OH [mmol/g] | $0,18 \pm 0,086$ | $0,39 \pm 0,086$ | | | | | | | |

The results obtained from the lignin preparation and further calculations show that it is possible to affect the structure, i.e., the ending groups, only by changing the precipitation conditions. The following are described potential applications of lignin in different lignin-based materials according to its structure.

Lignin can be used as a filler in natural rubber preparation. More important than functional groups is the elemental composition of the lignin, especially the carbon and oxygen content. In the study of Intapun et al., Klason lignin is used as a filer in natural rubber with a carbon and oxygen composition of 45,54 % and 54,46 %, respectively. The results showed that lignin increased the scorch time, improved processability and also increased the delta torque, modulus levels of 100 % and 300 %, and tensile strength of the vulcanized rubber¹⁸. Lignin prepared according to DoE showed that the carbon content is a higher percentage than referred to in the previously mentioned publication (58,1 – 60,7 %). The calculated oxygen values in lignins range from 31,6 - 34,5 %. These values do not show any dependence on the preparation conditions, so it can be assumed that all lignins prepared in the selected condition are according to carbon suitable as a filler for natural rubber composites and are slightly lower for oxygen.

| Application | Ph-OH [mmol/g] | R-OH [mmol/g] | OCH3 [mmol/g] | M _W [g/mol] | Ref. |
|----------------|-------------------|------------------|----------------|------------------------|------|
| Natural rubber | 4,08 - 4,83 | 1,46 - 2,23 | Not identified | 7 800 - 27 500 | 19 |
| Polyurethane | 2,39-4,30 | 1,22 - 3,13 | Not identified | 1 322 - 65 521 | 20 |
| Bioplastics | 2,1-4,3 | 0,9-2,9 | Not identified | $1\ 320-6\ 470$ | 21 |
| Biocomposites | 2,81 - 5,18 | 0,92 - 1,60 | 0,90 - 1,31 | $1\ 750 - 2\ 750$ | 22 |

Table 3 Selected lignin applications with its important parameters.

It is proved that aliphatic hydroxyl groups from lignin, in combination with hydroxymethylation of lignin, improve mechanical properties, such as tensile strength. The thermal stability and the increase in density of PU adhesives are also observed²³. It means that the content of aliphatic hydroxyl groups plays an important role in the application of lignin as an adhesive additive. In addition, it can be assumed that increasing the molecular weight of lignin will improve the mechanical durability of the material, that is, the stiffness or resistance to deformation of lignin-based polyurethanes²⁰. Lignin in adhesives and resins can replace 31 % of total PU and the final properties are at least the same as for phenol formaldehyde resin²⁴.

Table 4 Illustrative example of predicted characteristics of lignin prepared under specific conditions.

| T [°C] | рН | Ph-OH [mmol/g] | R-OH [mmol/g] | OCH3 [mmol/g] | Mw [g/mol] | Non-conj. OH [mmol/g] | Conj. OH [mmol/g] |
|--------|-----|-------------------|------------------|------------------|--|-----------------------------|----------------------|
| 80,0 | 2,0 | 4,13 ± 0,23 | 1,35 ± 0,11 | 6,01 ± 0,41 | $\begin{array}{ccc} 5530 & \pm \\ 680 \end{array}$ | 1,98 ± 1,07 | 0,24 ± 0,09 |

Lignin used in bioplastics can also improve its properties. For example, the UV stability of PE is improved with lignin in a concentration similar to that used for HALS widely²⁴. Bio-composites based on lignin blended with PBAT have glass transition temperatures lower than those of pure lignins. Furthermore, these products have higher tensile strength and elongation at break as raw lignin equivalents²². Comparing the chemical characteristics of lignins from the literature presented in Table 3 with our results from Table 1 and Table 2 respectively, one can conclude that lignins prepared under specific conditions are suitable for selected applications. An illustration is shown in Table 4. According to the results, the specific lignin presented in Table 4 should be suitable for the applications in Table 3. However, for natural rubbers, it is better to have a higher molar mass than lignins prepared with DoE, but other parameters show great potential for lignin applications in different lignin-based materials.

Conclusion

The presented work showed that lignin has great potential to become a renewable material in the polymer industry. Moreover, it is possible to affect the properties of lignin not only through modification reactions but also by different precipitation conditions, temperature, and pH. It means that for companies that isolate lignin and produce lignin-based materials, it is possible to change preparation conditions according to the final applications of lignin. This knowledge could help to expand the lignin market and make it even more interesting for lignin-producing companies and also bio-based materials. Today, it is still a long journey to implement lignin completely in industrial scale applications, and it is necessary to carry out deep research in this field, but as shown in this paper, there are many potential applications of lignin.

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APPLICATION OF CALCIUM LIGNOSULFONATE AS A COMPONENT OF RUBBER COMPOSITES

Klaudia JESZEOVÁ*, Ján KRUŽELÁK, Ivan HUDEC

Slovak University of Technology in Bratislava, Faculty of Chemical and Food Technology, Institute of Polymer Materials, Department of Plastics and Rubber, Radlinského 9, 812 37 Bratislava, Slovakia klaudia.jeszeova@stuba.sk

Abstract

The aim of the work was to investigate the influence of biopolymer filler calcium lignosulfonate on the properties of composites based on acrylonitrile-butadiene rubber (NBR). Three different vulcanization systems were used for crosslinking of rubber composites (sulfur vulcanization system, organic peroxide, and organic peroxide with co-agent). The work is focused on the evaluation of the influence of lignosulfonate and the vulcanization system on vulcanization characteristics, crosslink density, rheological and physical-mechanical properties. Calcium lignosulfonate was incorporated into rubber formulations in concentration scale ranging from 0 to 60 phr. From the results it is evident that calcium lignosulfonate has an influence on the vulcanization characteristics, physical-mechanical and rheological properties of NBR based composites. By application of different vulcanization system, it is possible to modify all important properties of rubber compounds filled with calcium lignosulfonate.

Introduction

The most widespread renewable resource in the world is biomass (both wood and non-wood). In woody biomass, lignin is the second most abundant biopolymer in amount around 15–40% of the wood weight (1). Lignin is the general name for a group of polyphenolic, organic polymers present in plants with a three-dimensional structure typical for individual types of plants (2). It is an amorphous polymer composed of phenylpropane units connected by ether and carbon-carbon bonds (3).

Lignin is considered an underutilized material because only 1-2% of the 50-70 million tons of lignin produced annually is used for production of value-added products. Today, lignin is used to generate energy by combustion in the pulping process, and therefore it is highly advantageous to develop lignin-based value-added products and methods for their production (1, 4).

To produce value-added lignin products, lignin should be first separated from biomass, and several methods have been developed. Lignins from sulfite pulping processes are referred to as lignosulfonates and are produced using sulfuric acid and/or sulfite salts (magnesium, calcium, sodium or ammonia) at various pH levels (1, 5). Lignosulfonates are commercially available as calcium or sodium salts and have been used in industry in many applications (6). Calcium lignosulfonate is an amorphous material that is soluble in water (6). The structure of the polymeric fraction of calcium lignosulfonate is presented in Scheme 1 (6).



Scheme 1 Structure of calcium lignosulfonate (6)

Experimental

According to the results obtained in our previous work (7) there was decided to examine the influence of calcium lignosulfonate as a filler on selected properties of rubber compositions. Properties of the calcium lignosulfonate (Borrement CA 120; Borregaard Deutschland GmbH, Germany) are listed in Table 1.

| Table 1 | Pro | perties | of | calcium | lignosulfonate |
|---------|-----|---------|----|---------|----------------|
| | - | | - | | |

| Product | Calcium content | Sulfur content | pH (10% | $M_w (g \cdot mol^{-1})$ |
|-------------|-----------------|----------------|-----------|--------------------------|
| | (%) | (%) | solution) | |
| Borrement 5 | 5 | 7 | 4,5 | 24000 |
| CA 120 | | | | |

Calcium lignosulfonate was added into rubber blends in the amount ranging from 0 to 60 phr. Acrylonitrilebutadiene rubber NBR, SKN 3345 (Sibur International, Russia) was used as rubber matrix. Semi-EV vulcanization system composed of ZnO (Slovzink a.s., Slovakia), Stearin III (mixture of stearic and palmitic acid; Setuza Ústí nad Labem, Czech Republic), sulfenamide accelerator CBS (N-cyclohexyl2-benzothiazyl sulphenamide; Duslo a. s., Slovakia) and sulphur (Siarkopol Tarnobrzeg, Poland) was used as sulfur vulcanization system. Peroxide vulcanization systems consisted of dicumyl peroxide DCP (Sigma Aldrich, USA) or a combination of dicumyl peroxide DCP and a co-agent trimethylolpropane trimethacrylate TMPTMA (Sigma-Aldrich, USA).

Rubber blends were mixed in two steps in a Plasticorder Brabender chamber at 90 °C and with a 55 rpm rotor speed. In the first step, rubber and fillers were compounded together, and the curing ingredients were added in the second step. The entire mixing time was 10 min and the rubber blends were calendered in two roll mill after each mixing step. The prepared rubber blends were vulcanized at 170 °C and 15 MPa in a hydraulic press for the optimum cure time t_{e90}. Crosslink density was determined by swelling kinetic of tested samples in xylene and calculated according to Flory-Rehner equation. Tensile properties were measured by using Zwick/Roell Z2.5 device with a displacement speed of 500 mm·min⁻¹. Rheological and vulcanization properties were carried out in rheometers RPA 2000 and MDR 2000.

Results and Discussion

The scorch time of rubber compounds (Fig. 1) crosslinked by a sulfur system is higher than the scorch time of rubber compounds with applied peroxide vulcanization systems, while this difference is the biggest for the samples without lignosulfonate and for the compounds with a low lignosulfonate content. Due to the influence of a sulfur vulcanization system, a decrease in scorch time was achieved with increasing of calcium lignosulfonate loading. The scorch time is not changed depending on the degree of lignosulfonate loading in the case of blends vulcanized with DCP and the combination of DCP + TMPTMA. The optimum vulcanization time (Fig. 2) of rubber compounds with a sulfur system was significantly shorter compared to compounds with applied organic peroxide, or its combination with a co-agent TMPTMA. Incorporation of calcium lignosulfonate led to a decrease in the optimum vulcanization time.

Composites with a sulfur vulcanization system exhibited the lowest degree of crosslinking (Fig. 3). The crosslink density of composites cured with DCP varied between the crosslink density of equivalent vulcanizates cured with sulfur system, or organic peroxide in combination with a co-agent, respectively. The influence of calcium lignosulfonate on the crosslink density of DCP cured composites was not observed. The lowest crosslink density of DCP crosslinked vulcanizates in combination with a co-agent caused the highest restriction of elasticity and mobility of the rubber chains and the lowest elongation at break of the equivalent composites was observed. The application of lignosulfonate into the rubber matrix with sulfur vulcanization system led to an increase in elongation at break. The elongation at break of rubber composites cured with peroxide vulcanization systems does not depend on the lignosulfonate loading.

The highest tensile strength was achieved by composites cured with DCP in combination with co-agent (Fig. 5). However, these vulcanizates exhibited the most significant decrease in tensile strength depending on the increasing lignosulfonate loading. The tensile strength for vulcanizates cured with sulfur system as well as with organic peroxide were very similar and had a similar dependence with increasing amount of lignosulfonate.

Fig. 6 shows the complex viscosity of NBR rubber composites filled with calcium lignosulfonate and cured with sulfur vulcanization system. It has been found that the complex viscosity increases with increasing amount of calcium lignosulfonate in rubber blends.



Figure 1. Dependence of scorch time t_{S1} of rubber compounds on calcium lignosulfonate loading



Figure 2. Dependence of optimum vulcanization time t_{c90} of rubber compounds on calcium lignosulfonate loading



Figure 3. Dependence of crosslink density v of rubber composites on calcium lignosulfonate loading



Figure 4. Dependence of elongation at break of rubber composites on calcium lignosulfonate loading



Figure 5. Dependence of tensile strength of rubber composites on calcium lignosulfonate loading



Figure 6. Dependence of complex viscosity on shear rate of rubber compounds cured with sulfur system

Conclusion

It is evident from the results that calcium lignosulfonate has an influence on the vulcanization, physicalmechanical and rheological properties of NBR based rubber composites. The choice of vulcanization system is important because rubber composites showed different behavior when applying different vulcanization systems. A common feature is a decrease in crosslink density with increasing loading of calcium lignosulfonate. It was found out by incorporation of calcium lignosulfonate into NBR rubber compounds that calcium lignosulfonate behaves as an inactive filler.

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CRITICAL TESTS OF TUBE THEORY THROUGH EXPERI-MENTAL VERIFICATION OF POLYMER MOLECULAR ARCHITECTURE RESPONSE IN THE LINEAR AND NON-LINEAR RHEOLOGICAL DOMAINS

<u>Rex P. Hjelm</u>*, Leslie A Sasa, Erik J. Yearley, Luke T. Andriano, Nino Roucco, Daniel P. Olds, L. Gary Leal

<u>New Mexico Consortium, 4200 W Jemez Rd #200</u>, Los Alamos, NM 87544 USA <u>rexhjelm@mac.com</u>

Background and Scientific Importance

Understanding the relationship between the bulk rheological properties of entangled polymeric liquids and the polymer molecular architecture is one of the most interesting and important problems of polymer science. Polymers, as non-Newtonian fluids, exhibit a number of critical rheological properties from a practical and industrial perspective^{1, 2}, as under high strain rates, $\dot{\gamma}$ (Hz), polymers show non-linear viscoelastic properties, the structural fundamentals of which are not well understood. Furthermore, there is interest the addition of polymers of more complex architectures, such as stars, in producing blends with optimal properties³.

The relationships among rheological behavior and the molecular structural responses of entangled polymers is based largely on the theoretical framework of tube models, in which a mean field tube, formed by a polymer chain's neighbors, represents the conformational constraints on the chain from entanglements with its neighbors. The tube restricts the lateral but not the curvilinear chain motion. Chain rearrangements within the tube occur very fast over the Rouse entanglement segment relaxation time, τ_e . Movement over the entire chain length, the Rouse time, in the tube is considerably longer, as $\tau_R = Z^2 \tau_e$, where Z is the number of entanglements. The chain must escape the tube in order to relax stress. There is a hierarchy of ways that the polymer deforms and then relaxes toward equilibrium, due to topological constrains imposed by the tube and its motion relative to the test polymer. Multiple first order relaxation processes are involved, in which the polymer and confining tube move relative to each other. These occur over time scales, $\tau_I \sim \dot{\gamma}^{-1}$. The GLaMM model⁴, of tube theory provides a means to calculate polymer structural response in the linear and non-linear rheological domains. over several orders of magnitude,⁵⁻⁷ included in the fundamental theory⁸. The slowest of these is reptation, $\tau_{d} = 3Z^{3}\tau_{e}$, which is the time required for a linear chain to escape the tube. This mechanism cannot occur with a star polymer due to the constraints imposed on an arm by the other arms.⁹ The others in decreasing characteristic times, thus active at increasing $\dot{\gamma}$, are contour length fluctuation (CLF), convective constraint release (CCR) and constraint Rouse relaxation (CRR). CLF allows that the end of the test chain can retract from the confining tube then extend into the new tube region. In the linear rheological regime with a linear polymer reptation and CLF relaxation processes result from chain diffusion. This problem is even more complex in the nonlinear regime where the test chains must move relative to the confining tube as a consequence of the viscous flow. This results in an alteration of the chain entanglements and the confining tube geometry described by CCR¹⁰. In CCR the perturbation time scale is much

faster than the time scale of the tube to reform. Polymer stretching, CRR, is predicted over higher $\dot{\gamma}$, as, $\tau_{s}\dot{\gamma} \geq 1$

Direct evidence on polymer architecture, structural response in linear and non-linear rheology in melts comes from rheo-optical techniques,¹¹ neutron spin-echo scattering,¹² dielectric relaxation,¹³ and small-angle neutron scattering (SANS).¹⁴ Regardless there is still a lack of information on these interrelationships under steady flow at high strain rates in the non-linear regime and with polymers with complex architectures all of which are of importance to polymer physics, industrial processing and reinforced durable rubber products. ¹⁻⁴, ¹⁵

Objective and approach

We address the problem of understanding the relationship between the bulk rheological properties of entangled polymeric fluids and molecular architecture in a flow field over the non-linear rheological domain, defined by the criterion that the Weissenberg number, $Wi = \dot{\gamma}\tau_{,i} > 1$.

Previously, we considered the source of the non-linear rheological property characteristic of the CCR domain,

shear thinning, where the viscosity of the melt decreases as $\eta \sim \dot{\gamma}^{-16}$. We looked at three plausible theories to explain the role of shear thinning as a result of interactions of surface bound polymers with the bulk: slip-shear, or wall-slip,^{17, 18} exchanges of surface polymer with the bulk, or disentanglement of surface-bound polymer from the

bulk, using rheo-NR depth profiles to determine the structural response of surface-bound protonated polystyrene (h-PS) against a perdeuterated (d-PS) melt. While the tethered polymer reversibly retracted 15-20% in the CCR domain, it remained entangled with the bulk polymer¹⁹. This result was confirmed in a subsequent study²⁰. Thus, the mechanism for shear thinning is likely to be from the polymer response to stress in the bulk.

As a consequence of this finding we address the behavior in the bulk through measurements of polymer structural responses to shear in viscous flow in Couette geometry using, rheo-SANS²¹ in high molecular weight linear polymer melts and in a star polymer-linear polymer melt²² to provide critical tests of tube theory in the CCR domain for linear polymers and polymers with more complex architecture. The melts are mixtures of perdeuterated and protonated polymers under continuous shear stress. The difference in neutron scatter from the hpolymer verses d-polymer highlighted the former, such that we can observe the conformation response of the entangled polymers. The rhometry of the melts with $\dot{\gamma}$ was measured simultaneously with SANS

Experimental

We designed a neutron rheometer in Couette geometry for rheo-SANS,²¹. The cell was designed to meet the optical requirements of the SANS measurements, to mitigate surface slip effects and curvilinear instabilities in elastic flow.

SANS data was placed in absolute units, $\frac{d\Sigma(Q)}{d\Omega}$ (cm⁻¹), of

differential cross-section per unit volume. Here Q is the modulus of vector \mathbf{Q} in the scattering plane, which is defined as

 $\mathbf{Q} = \frac{4\pi}{\lambda} \sin \theta$, where θ is half the scattering angle and λ is the

wavelength. SANS was done with the incident neutron beam normal to the shear-velocity plane, along the shear gradient. This geometry probed the polymer conformation along the flow plane. As shear stress leads to anisotropy in the scattering plane,

vector, \mathbf{Q} is expressed as its components along, $\mathcal{Q}_{x}\left(\mathbf{Q}\right)$ and

perpendicular, $Q_y(\mathbf{Q})$ to the flow axis.

D-PS and h-PS were synthesized using anionic polymerization. The PS samples for rheo-SANS reported here had molecular weights of 114, 167 and 192 kDa with polydispersity index (PI) of 1.3. The volume fraction of h-PS, ϕ , in the rheo-SANS measurements was 0.1.



Figure 1: Anisotropy ratio observed in rheoSANS data for samples with different Mw as a function of $\dot{\gamma}$.

The star polymer blend melt consisted of a protonated polybutyldiene (h-PBD) symmetric four-arm star 176 kDa at $\phi = 0.1$ in a perdeuterated linear chain, d-PBD 89 kDa with PI of 1.08 for both the star and linear polymer, again using anionic polymerization. The star arms are roughly half the length of the linear d-PDB chain.

Results and Discussion

Linear Chain Melts

A frequency sweep measurement of the loss, $G\square(\omega)$, and elastic, $G\square(\omega)$, moduli of the 114 kDa sample at 150 C showed a cross over from fluid to solid like behavior between $G\square(\omega)$ and $G\square(\omega)$ at $\omega \cong 6 \text{ s}^{-1}$, giving an estimate for the slowest characteristic relaxation time, $\tau_d \cong 0.17$ s. Using the scaling relationship that $\tau_{\alpha} \square M^{34}$, and applying a time-temperature shift to account for the temperature difference of the measurements, gives $\tau_d \cong 0.14$ s and 0.23 s for the 167 and 192 M_W samples, respectively, at 200 C. Thus, from the range of $\dot{\gamma}$, Wi spans 0.85 to 8.5 for the 114 kDa sample, 0.3 to 7 for the 167 kDa sample and 0.5 to 14 for the 192 kDa sample.

We have shown that the 114 KDa sample in the absence of shear is modeled by the Random Phase Approximation,

$$\frac{d\Sigma(\mathbf{Q})}{d\Omega} = \left(\boldsymbol{b}_{\boldsymbol{\mu}-\boldsymbol{\mu}\boldsymbol{s}} - \boldsymbol{b}_{\boldsymbol{\mu}-\boldsymbol{\mu}\boldsymbol{s}}\right) \frac{n}{\nu_{m}} \frac{\Phi(1-\Phi)D(R_{g},\mathbf{Q})}{1-2\chi n\Phi(1-\Phi)D(R_{g},\mathbf{Q})} + B \ (\mathrm{cm}^{-1}),$$

where *n* is the average number of monomers in a single h-PS and d-PS chain and Φ is the volume faction of one of the phases. Here, b_d. PS and b_{h-PS} are the scattering lengths of d-PS and h-PS monomers, v_m is the monomer excluded volume in the melt, χ is the Flory-Huggins interaction parameter between monomers of d-PS and h-PS and *B* is a background contribution. If the chains are in a random coil conformation (RCC), the form factor, D, is given by the Debye

function,
$$D(R_g, Q) = 2 \frac{\exp(-Q^2 R_g^2) - 1 + Q^2 R_g^2}{(Q^2 R_g^2)^2}$$
, where R_g is the

weight-average radius of gyration of the random coil. The same is true of the higher molecular weight, 167 and 192 kDa, polymers included here.



Figure 2: SANS data and the tube theory interpretation. Upper figure: data at $\dot{\gamma} =$ 0 Hz; the polymer is relaxed. Lower figure at $\dot{\gamma} = 10$ Hz; the polymer is stretched. At $\dot{\gamma} > 10$ Hz the polymer partially returns to its relaxed state due to loss of entanglements.

The rheo-SANS measurements "see" only the anisotropic SANS response of the protonated polymer with $\dot{\gamma}$, indicative of chain alignment. Frequency and flow sweep

measurements for the linear chain mixture show that stress, $\sigma = \eta \dot{\gamma}$, is constant above $\dot{\gamma} = 1$ Hz where viscosity,

 $\eta \sim \dot{\gamma}^{-1}$, or shear thinning is observed, as Wi > 1. This is characteristic of convective constraint release (CCR) of

tube theory. Linear chain anisotropy computed as,
$$A = \frac{\int_{-\infty}^{\infty} \frac{d\Sigma}{d\Omega} (Q_{\perp}) dQ}{\int_{-\infty}^{\infty} \frac{d\Sigma}{d\Omega} (Q_{\perp}) dQ}$$
, (Fig. 1) is observed as $\dot{\gamma}$ increases to 10

Hz. This is illustrated schematically with examples of the two-dimensional rheoSANS data in Figure 2. Lower molecular weight chains loose anisotropy for $\dot{\gamma} > 10$ Hz, returning to their equilibrium Gaussian chain conformation. Longer chains retain the anisotropy at for $\dot{\gamma} > 10$ Hz. Thus, CCR is progressive with $\dot{\gamma}$, leading to complete loss of constraint, for shorter chains, but not for longer chains, even though all mixtures showed the same $\eta \sim \dot{\gamma}$ behavior.

Detailed analysis of the polymer responses to $\dot{\gamma}$ on polymer extension with molecular weight showed that when viewed along the line of flow (**Q**) the polymers retain the RCC (Eq. 2) characteristic, but R_g declines roughly

in proportion to the asymmetry, A. However, when viewed perpendicular to the line of flow (\mathbf{Q}_{1}) the 114 kDa polymer shows power law scatter, indicative of alignment with the shear flow, the two larger polymers less so. These observations show alignment with flow, with the perturbation from RCC stretching in inverse proportion to the molecular weight.

In tube theory the $\dot{\gamma}^{-1}$ dependence of the viscosity is characteristic of the CCR mechanism¹⁶. The shear rates where CCR is the likely dominant mechanism for non-linear rheological response is $\tau_a \ge \dot{\gamma} \ge \tau_R$. At higher shear rates, $\tau_R \dot{\gamma} > 1$, chain stretching is predicted. This mechanism has also been invoked to explain polymer non-linear polymer rheology, However, our measurements where at shear rates well below τ_R , as we estimate τ_R from Z and

our estimates of τ_d , as $\tau_R = \frac{\tau_d}{3Z}$ to be 0.011, 0.006 and 0.009 s for the 114, 167 and 192 kDa samples, respectively,

the reciprocal of which is well above the highest shear rates used here. Thus, our measurements were within CCR domain.

Whereas the loss of constraints through the CCR mechanism should inhibit chain extension, this implies that the chain extension should saturate as some value of $\dot{\gamma}$, then level off. It has been posited that chain retraction back toward the equilibrium state can occur from loss of entanglement in the CCR at sufficiently high flow rates. Estimates of the time constant for chain retraction, τ_s , gives $\tau_s = 2\tau_R$, well above the point where we observe chain contraction. In support of the view that CCR inhibits chain orientation, Milner *et al.* showed that CCR suppression

of extension is required to explain the relatively small orientation and extension observed in the SANS measurements of PS sheared in the parallel plate geometry, even at the lower shear rates used in that study. *Star-linear polymer Melt*

The star polymer response with $\dot{\gamma}$ in the non-linear domain provides additional critical tests of tube theory²². Both the length of the star arms and the d-PDB linear matrix are entangled. However, the star while semi-dilute is below the entanglement volume fraction, estimated to be 0.15. Furthermore, the blend composition is such that the star arms do not self-entangle.

Frequency sweep measurements of the loss, $GI(\omega)$, and elastic, $G(\omega)$, moduli of the star, linear and starlinear melts at 25° C gave cross overs from fluid to solid like behavior between $GI(\omega)$ and $G(\omega)$ corresponding to estimates for τ_d of 16.6, 0.045 and 0.065 s, respectively. The rheoSANS measurements were done at 25°C at $\dot{\gamma}$ = 0, 8.1, 16.1 and 24.2 s⁻¹. Thus, the corresponding values for Wi for the rheoSANS measurements were 0.36, 0.72 and 1.09, for the linear chain interactions, largely within the linear domain of reptation and CLF relaxations, as these mechanisms remain largely unchanged in the presence of a small amount of star polymers. This is consistent with a comparison of frequency sweep measurements of star and linear polymers, which show that the rheology is dominated by the linear component; thus, it does not provide information on the source of the observed star rheoSANS anisotropy.

On the other hand, the rheoSANS signature shows the distortion of the star arms as aligned with the flow due to entangled interactions. To obtain Wi for the star entanglements we need an estimate for the slowest relaxation time of the start arms, replacing that for reptation

relaxation, which is not possible for a star, as, $\tau \simeq \frac{2}{3\pi^2} \tau_d Z_{sm}^2$, with τ_d

being the reptation relaxation time for the linear polymer and $Z_{arm} = 20$ the number of entanglements of a star arm. From Eq. 4. $\tau \Box \approx 1.2s$; Thus, Wi values are estimated to be 9.8, 19.6 and 29.4 at the respective $\dot{\gamma}$, well into the CCR domain.

Figure 3 shows the q (= Q) dependent chain structure factor anisotropy ratios, $S(Q_{\perp})/S(Q_{\parallel})$, from the rheoSANS of the star-linear chain melt at $\dot{\gamma} = 0$ Hz and at Wi ≈ 9.8 , 19.6, 29.4. The anisotropy shows that the orientation of the star polymer along the flow axis increases with Wi and increases with lower Q.



Figure 3: Anisotropy radios for the rheoSANS data. Data is from ref.

A model for the conformation of the star arms with $\dot{\gamma}$ a tube theory model for linear polymers in the nonlinear rheological domain GLaMM was modified for star polymers by the removal of relaxation by reptation, GLaMM-R¹¹. GLaMM calculates the tube contour **R**(s,t), where s and continuous variables for distance along the tube and time. The stochastic evolution of **R** is calculated through solutions for the tangential correlation function,

 $\left\langle \frac{\partial R_{a}((\mathbf{s},t))}{\partial \mathbf{s}} \frac{\partial R_{b}((\mathbf{s},t))}{\partial \mathbf{s}^{\Box}} \right\rangle$, the terms for which account for flow and the different relaxation mechanisms in tube

theory.

GLaMM-R captures the star behavior over larger Q-values. However, there are deviations of the modeled anisotropy from the data at lower Q, at the largest Wi values.

The rheoSANS results for the linear-linear and star-linear polymer mixtures indicate that a more detailed theory may be required.

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NEW TRENDS IN TIRE DEVELOPMENTAT CONTINENTAL

Mária Podobová

Inštitút odoborného vzdelávania, s. r. o., Streženická cesta 45, Púchov 020 01 maria.podobova@conti.sk

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A COMPREHENSIVE VIEW OF TYRE RUBBER DEGRADATION IN SERVICE

Radek STOČEK^{1,2*}, Reinhold KIPSCHOLL³

¹Centre of Polymer Systems, Tomas Bata University in Zlín, tř, Tomáše Bati 5678, 76001 Zlín, Czech Republic ²Polymer Research Lab., s.r.o., Nad Ovčírnou 3685, 76001 Zlín, Czech Republic ²Coesfeld GmbH & Co. KG, Tronjestraße 8, 44319 Dortmund, Germany e-mail address: <u>stocek@utb.cz</u>

Abstract

Within the work three measuring appliances Tear and Fatigue Analyzer (TFA[©]), Instrumented Cut and Chip Analyzer (ICCA[©]) and Intrinsic Strength Analyzer (ISA[©]) will be introduced for a complete characterisation of rubber used for tire application with respect to their wear behaviour under cyclical load. The systematic use of these test devices in the comprehensive characterisation of the fracture behaviour of rubber will ensure the prediction of the resistance of rubber in tires to degradation mechanisms caused by cyclic loading in service. Such characterisation at the design and development stage of the rubber compound will ensure a significant reduction in development time and cost. Last but not least, early prediction and selection of a degradation-resistant material will reduce the environmental burden by reducing the emission of rubber particles resulting from degradation processes and tread abrasion. This comprehensive methodology and equipment has a multidisciplinary overlap and constitutes an effective tool for the development of rubber compounds resistant to degradation processes in service. Validation of the comprehensive methodology will be presented and discussed on relevant rubber materials.

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RECYCLED PLASTICS FOR MARINE AND AUTOMOTIVE APPLICATIONS

Christian W. KARL^{1,*}, Fredrik K. MÜRER², Henrik Brynthe LUND³

SINTEF AS, Department of Polymer and Composite Materials, Forskningsveien 1, 0373 Oslo, Norway <u>christian.karl@sintef.no</u> ²SINTEF Helgeland AS, Halvor Heyerdahls vei 33, 8626 Mo i Rana, Norway ³SINTEF AS, Department of Technology Management, Strindvegen 4, 7030 Trondheim, Norway

Widespread inefficiencies in the value chain in a linear economy, from resource extraction and product design to end-of-life disposal, link the operational process of take, produce, and dispose.

Here, the focus is on the profitability which increases pressure on finite resources and carries two twin problems: limited scope for resource recovery due to unfortunate product design, and non-regenerative activities within the natural ecosystem that damage the health of the land. The circular economy, on the other hand represents a system that maximizes the efficient use of resources and wastes through closed-loop, regenerative, and collaborative approaches, while simultaneously optimizes the unnecessary consumption of natural resources (e.g energy, water and materials) and the generation of waste through the optimization of processes and the exchange of technologies, thus contributing to the reduction of costs [1].

In January 2018, the European Union (EU) implemented the European Strategy for Plastics in a Circular Economy [2]. As a result, the EU enacted the Directive on the Reduction of the Impact of Certain Plastic Products on the Environment (EU 2019/904, [3], which targets single-use plastics and plastic-containing equipment from fisheries and aquaculture. This selection of products was based on a survey of beach cleanups conducted in Europe. One of the main measures of this directive is the implementation of extended producer responsibility (EPR) for plastic-containing equipment used in fisheries and aquaculture, which must be established by January 1, 2025 [3]. In 2018, the Norwegian Environment Agency conducted a background study on EPR for fisheries and aquaculture [4], but it was not followed up by the Ministry of Climate and Environment at the time, as they were waiting for the EU directive. In 2022, the Norwegian Environment Agency has proposed a sketch for the EPR policy for fisheries and aquaculture. With EPR policies in place, the producers of the equipment will be responsible for the equipment even when it becomes waste, in accordance with the polluter pays principle [5-10]. The Norwegian Environment Agency recommends implementing minimum requirements (in percentages) for both the collection and recycling of plastics from fisheries and aquaculture, to ensure material recycling of plastic waste from the industries. The report suggests that a minimum recycling requirement could incentivize innovation and increase material recycling. Waste collection will draw on existing schemes, such as the EU Directive (2019/883) on port reception facilities for the delivery of waste from ships for waste from fisheries, and existing, well-functioning schemes that are already in operation within aquaculture. Moreover, establishing new recycling companies capable of collecting and recycling waste is essential [10].

A major challenge concerning the recycling of plastics from fisheries and aquaculture (F&A) is to find application areas, i.e. products and value chains, that could ensure large volume offtake of recyclates from F&A. There are some examples of utilization of recyclates from F&A. These include furniture production, walkways used on net pens, interior design products, and serving trays for fast-food restaurants [11-12]. There are several barriers that hinder reuse of recyclates. Within the value chain for plastic components in the aquaculture industry Damman et al. identified a lack of knowledge among plastic manufacturers, both in terms of utilization of recyclates vs. virgin material in production and requirements to put forward to recycling companies concerning material properties as two important barriers [13]. The authors argue that there is a need for collaboration and knowledge sharing within the value chain to promote learning and overcome this barrier. Drawing on these lines of thought, we argue that cross-value chain collaboration is necessary to succeed with increasing the degree of recycled plastic waste from F&A. In this regard, we find that the automotive industry could be a potential user of recyclates from F&A plastics, as the automotive industry is pushed by EU legislation to increase the degree of recycled materials in new cars [14]. The revision of the so-called End-of-Life Vehicles Directive offers an important opportunity to further develop circular solutions for plastics used in the automotive sector [15]. If this is to be successful, we believe that providers of recyclates, i.e. recycling companies, and potential automotive manufacturers (users), need to engage in strategic partnerships to develop the capabilities of both users and producers. Arguably, with the automotive industry in Europe building producing approx. 13 million cars per year [16], of which much of the interior and exterior components are made from plastics, there is potential for a large offtake of recyclates originating from the Norwegian F&A industries [17]

As far as the design and the development of automotive parts are concerned, plastics are a favoured material choice due to their moldability, flexibility and light weight to meet the requirements for CO₂ emission reductions. Consequently, they are also well suited for recycling. Possible barriers are still the shortage of recyclates, the lack of cost-efficient recovery infrastructures, the lack of markets for recyclates as well as a lack of infrastructure and

heterogeneous mix of plastics. Furthermore, there are knowledge gaps between producers, consumers and facility operators. Used plastics often end up as downcycled materials or even as landfill products [18-19].

Plastic materials are used in exterior parts (e.g. body panels, seals, wheel covers, bumpers, fender, air dams, trims) and interior parts (e.g. instrument panel, dashboard, door panels, steering wheels, seat and associated parts, instrument panel skin as well as decorative parts and design elements), [20]. Scheme 1 exhibits an overview about components and the types of polymers used in automotive. The so-called engineering plastics include PA, ABS, PC, PPS, PMMA and PBT [20-21]. They belong to the high-performance segments of non-renewable resources showing better properties in contrast to commodity plastics (e.g. PE, PP, PVC and PS). These commodity plastics are well-suited for many automotive applications due to excellent strength, good temperature resistance, toughness, and stiffness as well as chemical resistance and abrasion resistance behaviour. Engineering plastics are used as single plastics or for specific applications (e.g. sunroof systems with glass fiber reinforced copolymer), [22]. The most used polymers in the automotive industry are PA, ABS, PC, PET and PS [20]

| Component | Types of Polymers |
|--|----------------------------------|
| Bumpers and fascia systems | PS, ABS, PC/PBT, PP, PA, PU, TPO |
| Seating | ABS, PA, PP |
| Instrument panels | ABS, PC, ABS/PC, PP |
| Fuel systems | POM, PA, PBT |
| Under hood components | PA, PBT |
| Interior trim | ABS, PET, POM |
| Electrical components | PBT, PA |
| Exterior trim | PS, PVC, ABS, PA, PBT, POM, ASA |
| Lighting systems | PC, PBT, ABS, PMMA |
| Upholstery | ABS, PU |
| Liquid reservoirs, cooling, battery carriers | PA |
| Wheel covers | ABS |
| Body parts | ABS |
| Tires | PA |
| Parts of engine | PA, phenolic resins |

ABS (acryl butadiene styrene), ASA (acrylonitrile styrene acrylate), PA (polyamide), PBT (polybutylene terephthalate), PC (polycarbonate), PET (polyethylene terephthalate), PMMA (polymethyl methacrylate), POM (polyoxymethylene), PP (polypropylene), PS (polystyrene), PU (polyurethane), TPO (thermoplastic polyolefins).

Scheme 1: Common plastics used in a typical car [20].

Cost is an important factor in the use of engineering plastics. In addition, the extensive use of and rapid growth rates in engineering plastics have led to large amounts of plastic waste. The use of recycled engineering plastics offsets the higher price of new engineering plastics which have better properties than new standard/commodity plastics at a similar cost. Engineering plastics exhibit good properties after use and can be recycled. Recycled plastics with reinforced fillers might be used for automotive parts having good mechanical properties [23-24]. Furthermore, recycled fiber-reinforced composites with recyclable fibers are promising and used as exterior components in the automotive sector [25] despite the fact that the quality of the recyclates and the recycling techniques as well as the process parameters still need to be improved [26-27]. Estimated costs, the efficiencies and in addition the environmental impact are regarded as critical as far as the recycling of plastics in the automotive industry is concerned. PA, PP and PET are among the polymers currently recycled in the automotive sector [28-34]. For example, some recycling processes for PA 6.6 used in fishing nets having excellent mechanical properties as well as abrasion resistance, are described, such as chemical recycling [35-36] thermal pyrolysis [37], and mechanical recycling processes [29]. Furthermore, it has been demonstrated that modified pellets consisting of recycled PA 6,6 originating from fishing nets could be further processed into gearwheels using chain extenders [38]. Polyamide from fishing nets could be blended with virgin PA to improve the mechanical properties and would be a possible alternative polymer material for numerous technical applications also in the automotive sector without using additional additives [39]. Plastic parts (e.g. fuel tanks, decorative wheel trims, grilles) which are not used any longer are turned into pyrolysis oil by chemical recycling. It would be the aim to create new products from this pyrolysis oil [40].

Floating aquaculture installations consist of multiple pens, supported by a system of ropes, chains and anchors. Each pen consists of a floating collar, mainly composed of HDPE pipes, which then support a net, which is typically made from HDPE or PA. Ropes used for aquaculture installations vary in composition, however a commonly used ropes are mix of 75% PP and 25% PE [41]. Both mechanical and chemical recycling methods have been proposed for handling of EOL aquaculture installation plastics. Mechanical recycling comprises multiple steps of sorting, shredding, washing and melt filtrated regranulation to make pellets which can then be manufactured into new products [42-43]. This process does not alter the chemical structure of the plastics, however

additives, e.g., antioxidants can be added to the recycled plastics, to some extent alleviate the degraded mechanical properties of the recycled plastics as compared to virgin plastics [43-44]. Mechanical recycling of aquaculture plastics has in the recent years been implemented by several European companies, and the recycled plastics has been used to create e.g. furniture, carpets and food trays [13]. A recent research project aims to reuse mechanically recycled aquaculture floating collars to produce new floating collars [45].

Chemical recycling allows for depolymerization of EoL aquaculture plastics to create a raw material with the exact same properties as virgin raw material, hence it is also referred to as feedstock recycling. Chemical recycling is well-established for PA nets, e.g. through the Norwegian actor Nofir [46]. The advantage of chemical recycling is that more combinations of mixed plastics and contaminants can be handled as opposed to in mechanical recycling. Thermoplastics such as PE and PP can also be chemically recycled, however due to the excessed energy consumption, higher investment costs and increased CO₂ emissions compared to mechanical recycling, it has previously been reported that mechanical recycling is more suitable for HDPE and PP aquaculture plastics, if the fractions are sorted and clean [17,47].

While recycling pathways for larger fractions of aquaculture plastics are readily being implemented in industry, there is still a knowledge gap in handling of mixed plastics, e.g. ropes with metal cores used in fisheries. In the SHIFT-PLASTICS project (Research Council of Norway, grant no. 326857, leading industry companies within the handling of aquaculture plastics waste are studied and LCA case studies are built to propose new designs and pathways for fishery and aquaculture components and to identify the best solutions for handling plastics in the fisheries and aquaculture sector in terms of material quality, analysis of suitable environmental impacts, residual value and cost [48-49]. In the project Plasticene (Research Council of Norway, grant no. 318730) tools for increased resource utilization, circularity, and regulatory support of plastic use in Norway are developed. A multidisciplinary approach is adopted to adequately address material flow analysis and characterization, circular economy model development, policy implementation, and stakeholder interaction [50].

The use of plastics from renewable sources would be a step further in meeting the environmental goals of the automotive industry. Bioplastics (bio-based, biodegradable materials or both) being biodegradable or compostable [51], composites containing natural fibers and fiber-reinforced polymers would be good alternatives to fossil-based plastics. Bioplastics and bio-based plastics, which also include natural fiber composites and engineering plastics reinforced with natural fibers such as flax, hemp, jute and sisal as well as other sustainable-based materials [52], are currently being used by many automotive manufacturers [20]. Lignin has been successfully incorporated in HDPE and PP as it was shown previously [53]. It is also being discussed that single-use plastics should not be used from 2030 [54].

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ADDITIVE MANUFACTURING OF CONTINUOUS FIBER MULTI-DIRECTIONAL REINFORCED COMPOSITES

Petr RESL*

University of Pardubice, Faculty of Chemical Technology, Institute of Chemistry and Technology of Macromolecular Materials, Studentska 95, 53210 Times, italics 10 pt flush left <u>petr.resl@student.upce.cz</u>

This abstract describes the concept of a technological solution for additive manufacturing of composites with continuous fiber reinforcement. Technology will process the continual glass, carbon, or polymer fiber combined with UV-cured resin. The intended technology allows the production of products independent of their shape, including an unmachinable shape or one that cannot be cast. In addition, the products can be reinforced in all directions. Thus the technology manages the production of a solid part with reinforcement tailored to the deformation within the application.

A composite (composite material) is a material composed of several materials, matrices, and fillers. In our case, a matrix is a resin, and filler is fiber in the role of reinforcement. The result is a generally strong, light, corrosion-resistant, and chemical-resistant material.

The main advantages of the technology:

- Controlled reinforcement to the degree of deformation during application
- Reinforcement in multiple directions
- Non-planar reinforcement
- Reinforcement of holes
- Printing new hollow structures that reduce weight with less impact on strength

Uniqueness

- Processing of thermoset liquid resins.
- Combination of innovative additive technology with industrial standard-grade material.
- Controlled reinforcement tailored to the deformation within the application.

What problems does it solve?

- Guide the reinforcement in the product in the optimal directions where it has the greatest importance.
- Produce a complex composite part in one production process (simplifying and speeding up the production).
- To produce a strong, light, durable, corrosion-resistant, chemical-resistant, and magnetic-resistant.
- Thanks to topological optimization, the weight can be reduced even more without sacrificing the strength of the final part.
- Production of reinforced holes.
- It brings solutions where low-cost, efficient production is needed.

The first tests for the suitable matrix were performed on an industrial-grade isophthalic unsaturated polyester resin with styrene as a reactive diluent. A photoinitiator was used for UV curing. In the printing head, the fiber is saturated by the resin and deposited on the platform through the nozzle. The saturated fiber is irradiated by UV radiation, and the resin is cured, resulting in a layer of composite. The main strength of the composite is in the longitudinal direction of the fiber.

Technology is at the beginning of development. The whole technology is divided into 3 segments: Material, Hardware (HW), and Software (SW). The material is the key segment, and the entry for the HW and SW will be set up according to the Material properties. Material is at the TRL 3 level (laboratory-tested matrix with glass rowing), HW at the TRL 2 level (basic desktop three-axis construction ready for implementing print head and dosing device), and SW at the TRL 1 level (open-source slicer for FFF 3D printing that needs to be modified).

The development is divided into several phases. Firstly, the proof of concept will take place on a three-axis system, on which the printing process will be optimized, and the next step will be the deployment of a multi-axis system, either a multi-axis portal or a robotic arm. In this phase, the printing potential of the composites will be verified. In the development process, we also count on material development. As the concept is verified on the three-axis system, it is possible to move on to the development of materials to get the resulting composite even stronger, more chemically resistant, non-flammable, resistant to radiation, and other properties required in composite applications.

EXTRUSION BIOPRINTING AS AN EMERGING STRATEGY FOR TISSUE ENGINEERING

Pavla HÁJOVSKÁ^{*1,2,3}, Abolfazl HEYDARI^{2,3}, Igor LACÍK^{2,3}

¹Institute of natural and synthetic polymers, Faculty of chemical and food technology, Slovak University of Technology in Bratislava, Radlinského 9, 812 37, Bratislava, Slovakia ²Polymer Institute SAS, Dúbravská cesta 9, 845 41 Bratislava, Slovakia ³National Institute of Rheumatic Diseases, Nábrežie. I. Krasku 4782/4, 921 12 Piešťany, Slovakia

*pavla.hajovska@stuba.sk

Tissue engineering (TE) has emerged as a multidisciplinary scientific field combining engineering principles with life sciences with a goal of *in vitro* fabrication of functional TE constructs capable of replacing damaged tissues or restoring malfunctioning organs [1]. Different traditional fabrication techniques have been used for preparation of scaffolds, such as phase separation, membrane lamination, melt molding, fiber bonding, gas foaming, solvent casting, freeze drying, etc. However, most of these techniques are limited in terms of manufacturing reproducibility and flexibility [1,2]. Bioprinting, using additive layer-by-layer fabrication manner, has shown the potential to overcome the above limitations of traditional scaffold-based TE approach [2].

During last decades, various bioprinting modalities have been developed, such as acoustic bioprinting, microvalve bioprinting, laser-induced forward transfer, and others, however the majority of the research is employing extrusion-based bioprinting (EBB) technique. During EBB, bioink consisting of cells, transferring biomaterial and eventually other additives is deposited onto the substrate in the form of a continuous filament [3].

Although various biomaterials are currently used for different applications in TE, the majority of these materials is not directly suitable for the use as a bioink in 3D bioprinting [1]. The development of a bioink therefore represents a crucial part of the bioprinting process. There are several criteria a bioink needs to fulfill (Figure 1). These vary based on the selected bioprinting modality and target application; therefore, both these aspects must be kept in mind during bioink design.



Figure 3: Schematic representation of essential bioink properties [4]

The printability of the bioink depends on the parameters such as viscosity of the solution, surface tension, and the crosslinking ability. At best, the viscosity of the bioink should be tunable, to facilitate the usage of the same bioink in different printing machines. The other important aspects of bioinks include crosslinking mechanism, biomimicking the tissue structures, mechanical integrity, short post printing time for maturation, and immunological compatibility, when implanted *in vivo*. Cost and industrial scalability have to be also considered. Due to their high water content similar to native extracellular matrix, hydrogels have drawn significant attention as bioinks for 3D extrusion bioprinting. The main components are usually either natural or synthetic polymers, or their combination. Some examples are schematically presented in Figure 2 [5-7].



Figure 4: Schematic representation of some target bioprinting applications with an example of bioink composition previously reported for the use in particular application [5-7]

Although great progress has been done in the last years, there are still challenges that have to be addressed prior to translation into clinical practice. These include mostly vascularization, bioactivity or mechanical strength of TE constructs. Systematic development of advanced multicomponent bioinks as a major component of the bioprinting systems therefore represents one of the first steps on the way to successful clinical translation.

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BIODEGRADABLE BLENDS PLA/PHA FOR EXTRUSION BLOW MOLDING

<u>Andrej Baco*</u>, Katarína Tomanová, Pavel Alexy, Zuzana Vanovčanová, Vojtech Horvath, Jozef Feranc, Lucia Danišová, Ema Mojžišová, Slávka Hlaváčiková, Ján Bočkaj, Roderik Plavec, Leona Omaníková, Ivana Galisová, Mária Fogašová, Mária Mikolajová.

Institute of Natural and Synthetic Polymers, Faculty of Chemical and Food Technology, Slovak University of Technology, Radlinského 9, 812 37 Bratislava, Slovak Republic e-mail address: <u>andrej.baco@stuba.sk</u>

Key words: biodegradable polymers; polylactic acid; polyhydroxyalkanoates, extrusion blow molding

ABSTRACT

This work is focused on the development of PLA/PHA blends based on renewable raw materials, intended for extrusion blow molding technology. The aim was to find a composition of the mixture, which is possible to process by extrusion blow molding technology. Processing stability was monitored as well as rheological properties, mechanical properties and DSC were also measured. Final blends have good processing window and good mechanical properties.

INTRODUCTION

In the recent years, the production of the plastics has increased to almost 360 million per year. Plastics have excellent properties which makes them materials that can be used in practically every industry sector. Almost 50 % of produced plastics are used in packing industry and in the same time this industry is considered as a largest producer of plastics waste. The downside is that plastics often end up thrown freely in nature, in rivers and oceans after the end of their life which causes many problems for animals. (1) In 2021 EU banned the use the use single – used plastics products (such as straws, cotton buds, cutlery, food and drink containers made from expanded polystyrene) in order the achieve carbon neutrality. (2) Based on restrictions manufacturers are trying to replace commercially used plastics with bio plastics. The prefix bio gives the impression that is something from nature but this may not be true. Therefore, is necessary to know what is hidden under the term bio-plastics. (3) There are three groups of plastics materials whir different impacts in the environment. One of the groups of bio-plastics are plastics are plastics has recently attracted more and more attention on itself. (4)

This scientific work is focused on the development of PLA/PHA blends which are suitable for extrusion blow molding. The final product of this work are bottles. The content of the individual components of the mixture can improve the mechanical properties and processability into the final product.

MATERIAL AND METHODS

Materials

Polylactide acid (PLA) - (TotalEnergy, Corbion, NL) Poly(B-hydroxybutyrate) (PHB) - (Tianan Biologic Materials Company, CN) Modifier- (Panara, a.s.) Crodamide TM BR - (CRODA, UK)

Methods

Preparation of blends

The blends were prepared on a twin screw extruder (Labtech, Thailand) with parameters L/D = 40, D = 16 mm, with intermeshing, co-rotating screws. The extruder was heated to operating temperature, the raw materials were fed to the hopper. The melt of the mixture was extruded in the form of a strand of circular cross-section. The extruded material was cooled by water and subsequently granulated on a granulator which is part of the device

Preparation of test specimens for measuring physical-mechanical properties

The test specimens were prepared using a BOY 60E hydraulic injection molding machine. The parameters of the injection process were: injection volume: 18 cm, injection pressure: 1200 bar, melt temperature: 180 °C, mold temperature: 30 °C.

Measurement of rheological properties

The testing and analysis of the rheological properties of the prepared blends was measured in an oscillating rheometer RPA 2000 from Alpha Technologies.

Measurement of thermal properties

Measurements were performed on a Mettler Toledo DSC1 (DSC with power compensation), purge gas nitrogen at a flow rate of 50 ml/min, aluminum standard dishes, samples 3-5 mg. The samples were measured with the following program:

heating 10 K/min, -20 – 200°C cooling 10 K/min, 200 – -20°C heating 10 K/min, -20 – 200°C

RESULTS AND DISCUSSION

The ratio of the basic polymer components PLA/PHB was constant for all mixtures. The differences between blends are toughness modifier and inorganic filler content. The blends have following designations NR/638 to NR/645.

Figures 1 and 2 show the curves of how the complex viscosity changes depending on the temperature and composition of the mixture without filler and with inorganic filler. A decrease in the complex viscosity can be observed depending on the increasing temperature in both cases with and without filler. A correlation between polymer blend composition and complex viscosity was noted at lower temperatures. In particular, the addition of a toughness modifier reduces viscosity at low temperatures, both for lower and higher filler content in the mixture. The inorganic filler increases the complex viscosity at low temperatures, at temperatures above 150°C the differences in the complex viscosities of individual mixtures are negligible. Figures 1 and 2 show the temperature range between 130 and 150°C. The viscosity of mixtures without filler can be considered constant within this range (Figure 1). In the case of mixtures with a filler, there is an increase in viscosity in this range. From a processing point of view, it is necessary that the complex viscosity does not grow exponentially in this temperature interval, which is important from the point of view of the processing window when producing the product by extrusion blow molding technology.



Fig. 1: Dependence of complex viscosity on modifier content (without filler).

Fig.2: Dependence of complex viscosity on modifier content (with filler).

Furthermore, the dependence of the crystallization temperature on the change in the composition of mixtures with and without inorganic filler was monitored (Figure 3).



Fig. 3: Dependence of the crystallization temperature T_c on changes in the composition of the mixture (with filler - blue columns, without filler - orange columns).

Mixtures containing inorganic filler have a higher crystallization temperature than mixtures without inorganic filler, which indicate sooner solidification of the filled material during cooling of the melt. The NR/638 mixture has the lowest crystallization temperature and the NR/645 mixture has the highest. In picture Figure 3 it is possible to see that the crystallization temperature is also affected by the modifier, as the mixture NR/638 contains the most modifier and the mixture NR/645 contains the least modifier. By comparing figure 2 and figure 3, it can be said that a higher crystallization temperature has an effect on the viscosity of mixtures at temperatures below 140°C. It is obvious that there is an increase in complex viscosity at lower temperatures due to the formation of crystal regions.





Figure 4 shows the dependence of the flexural modulus on the change in the composition of the mixture with and without inorganic filler. As the content of the modifier increases, the flexural modulus of the resulting mixtures decreases, which applies to filled and unfilled mixtures. Mixtures with inorganic filler have a higher flexural modulus, regardless of the content of the modifier.

CONCLUSION

Test specimens (bottles) of all mixtures were produced on the laboratory processing equipment for extrusion blow molding from the company Labtech. Mixtures without inorganic filler were better processable than those containing inorganic filler. In the automatic cycle was possible to produce only mixtures without inorganic filler. The results of complex viscosity measurements at different temperatures show a difference in the processing window between filled and unfilled mixtures. It was found that unfilled mixtures have a comparable viscosity in the temperature range from 130°C to 150°C, regardless of the amount of modifier in the mixture, which probably also has an impact on better processability compared to filled mixtures.

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PLA/PHB-BASED MATERIALS FULLY BIODEGRADABLE UNDER BOTH INDUSTRIAL AND HOME-COMPOSTING CONDITIONS

<u>Mária Fogašová</u>, Silvestr Figalla¹, Lucia Danišová, Elena Medlenová, Slávka Hlaváčiková, Zuzana Vanovčanová, Leona Omaníková, Andrej Baco, Vojtech Horváth, Mária Mikolajová, Jozef Feranc, Ján Bočkaj, Roderik Plavec, Pavol Alexy, Martina Repiská, Ema Mojžišová, Radek Přikryl¹, Soňa Kontárová¹, Anna Báreková², Martina Sláviková², Marek Koutný³, Štěpán Krobot¹, Ahmad Fayyazbakhsh³ and Markéta Kadlečková³

Institute of Natural and Synthetic Polymers, Faculty of Chemical and Food Technology, Slovak University of Technology, Radlinského 9, 812 37 Bratislava, Slovak Republic e-mail address: maria.fogasova@stuba.sk

¹Institute of Materials Science, Faculty of Chemistry, Brno University of Technology, Purkyňova 464/118, 612 00 Brno, Czech Republic

²Department of Landscape Engineering, Hortyculture and Landscape Engineering Faculty, Slovak University of Agriculture in Nitra, Hospodárska 7, 949 76 Nitra, Slovak Republic

³Department of Environmental Protection Engineering, Faculty of Technology, Tomas Bata University in Zlín, Nad ovčírnou III 3685, 760 01, Zlín, Czech Republic

Key words: Polylactic acid (PLA); Polyhydroxybutyrate (PHB); Blend polymeric material; Biodegradation; Industrial compost; Home-compost

INTRODUCTION

Biodegradable polymers are suitable providers of substitutes for conventional synthetic polymers due to their advantages of biological decomposition without leaving unacceptable waste and microplastics [1,2]. The goal of the development and application of these polymers and their materials is fulfillment of the necessary requirements for processing, mechanical and barrier properties associated with the possibility of their biological degradation in the conditions of not only industrial but also home compost. A combination of different biodegradable polymers together with different additives and fillers is necessary to achieve these proper characteristics. Therefore, especially the right composition of the material, which should include the selection of only biodegradable and naturaly originated components, significantly affects its biological degradability and compostability.

Based on previous studies, this work is focused on the development of PLA/PHB materials and their decomposition possibilities under the conditions of industrial and home composting. Starting of biodegradation process of pure PLA polymer, a temperature above 50 °C is required, what is related mainly to the glass transition temperature (T_g) of PLA and therefore provides its compostability only in industrial compost (industrial composting requires a temperature of around 55-60 °C) [3]. Therefore, the biodegradation of PLA even in the conditions of home compost, where the temperature is around 20-30 °C, can be achieved by preparing its blends with PHB together with additives such as plasticizers or TPS (thermoplastic starch). These components have the potential to accelerate the biodegradation of the material based on their lower T_g despite the fact that PHB can act as a nucleating agent and slow the biodegradation of the material.

As part of this study, the biodegradation of specific model products based on PLA/PHB produced by different process technologies was investigated in simulated conditions of industrial (58 °C) and home (28 °C) composting. By using other supporting methods of monitoring the biodegradability and compostability of the investigated materials, this study aims to show that biodegradable materials on a natural basis, specifically PLA/PHB blends, provide, in addition very good mechanical and processing properties, also biological degradability and compostability in a simple municipal composting plant or in a home compost.

MATERIALS AND METHODS

Materials:

Using different types of processing technology, the following PLA/PHB or PLA/PHB/TPS samples were prepared with the composition shown and basic characteristics in Table 1:

| Blend No | Blend for Technology | PLA %wt. | PHB %wt. | plasticiser %wt. | TPS %wt. | MFI | Р | TS | 3 | Tg |
|-------------|-------------------------|-------------|-------------|---------------------|-------------|-----|-----|----|-----|-----|
| IM 2 | Injection moulding | 40 | 50 | 10 | 0 | 5.8 | 1.2 | 31 | 8 | N/A |
| IM 1 | Injection moulding | 30 | 40 | 5 | 25 | 35 | 1.3 | 34 | 5 | 53 |
| TF -1 | Thermoforming | 65 | 30 | 5 | 0 | 6.2 | 1.2 | 28 | 36 | N/A |
| FB 2 | Film blowing | 70 | 15 | 15 | 0 | 18 | 1.2 | 18 | 330 | 28 |
| FB 1 | Film blowing | 50 | 10 | 15 | 25 | 33 | 1.3 | 11 | 288 | 24 |

Table 1. Basic characteristics of tested materials.

MFI, Melt flow index 180°C, 2.16 kg, g/10min; P, Density g/cm³; TS, Tensile strength at break MPa; ε , Elongation at break %; Tg, Glass transition temperature, °C.

Preparation of blends:

Thermoplastic starch TPS was prepared by blending of corn starch + glycerol in twin screw extruder at 160° C. Blends according to composition in Table 1 were prepared by blending in co-rotating twin screw extruder with the next parameters: L/D=44, D=26mm, temperature profile from hopper to head: 50-160-170-170-170-170-170-160-160°C, screw speed 150 rpm. Blends were cooled in the water bath and pelletized. All blends were used for producing of various products by technologies from Table 1, which are shown in the Table 2.

Table 2. Products for testing of biodegradability and compostability



Biodegradation Testing by respired CO2

Biodegradability tests were performed according to the adapted and miniaturized ISO 14855 method in 500 ml biometric flasks with septum equipped stoppers with mature compost from a nearby municipal composting facility (TSZ Ltd., Czech Republic). This test was done at 58 °C as industrial composting and at 28 °C to simulate home-composting conditions. The internal production of CO_2 in blank incubations was always subtracted to calculate net sample mineralization. After sampling the gas at appropriate intervals, the amount of CO_2 was determined using a gas analyzer (UAG, Stanford Instruments, USA). Biodegradation percentage (D_t) was calculated as

$$D_t = \frac{(CO_2)_t - (CO_2)_b}{ThCO_2} \times 10$$
(1)

Where $(CO_2)_t$ is the released CO_2 by each sample, $(CO_2)_b$ is CO_2 produced by the blank flasks, and $(ThCO_2)$ is the theoretical CO_2 from the sample. A Flash Elemental Analyzer 1112 (Thermo Fisher Scientific, Waltham, MA, USA) was used to measure the carbon content of the samples.

Compostability testing in the electric composter

Small electric composter GG 02 from JRK company (Slovakia) was used for testing of biodegradation testing while the samples were incubated together with kitchen waste. Operating conditions were 65°C during the whole operation time, except for one hour per day when the temperature increased to 75°C to ensure hygienisation of the content. The internal stirrer was activated for 20 minutes during each hour, providing altered mixing sequences in forward and reverse directions. Samples of PLA/PHB or PLA/PHB/TPS blends were inserted into the composter two weeks after the stabilization of the process in the composter. Each day 0.5-1.0 kg of kitchen food waste was added to the composter. Samples were weighed before inserting into the composter. Only one sample was measured for every composition because of technical reasons of the experiments. The content of the composter was removed each week and sieved through a sieve with a mesh size of 2x2 mm. Pieces larger than 2 mm (which did not pass through the sieve) were collected from the fraction above the sieve. Collected samples were washed in water, subsequently dried in the air oven for 1 hour at 90°C, and weighted with the precision of 0.0001 g. Then the samples were returned to the composter immediately after weighting. Biodegradation was evaluated as the percentage of disintegration. Microbiology inside the composter was monitored with DNA isolation and sequencing following an already established methodology [4].

SEM microscopy

Surface changes on the tested films were observed using SEM. Samples were coated by gold/platinum alloy using Balzers SCD 050 sputtering equipment. TESLA BS 300 was used for observation of samples composted in an electric composter, and JEOL F 7500 SEM (JEOL, Tokio, Japan) was used for samples from an industrial city composting plant, Phenom Pro Desktop SEM (Thermo Fisher Scientific, Waltham, MA, USA) was used for laboratory experiments under industrial and home-composting conditions.

RESULTS AND DISCUSSION

The final products from PLA/PHB or PLA/PHB/TPS (films, sheets and cups) from Tab 1 were made from materials whose development should lead to their compostability not only in the conditions of industrial but also home composting. All samples were tested in an electric composter and in laboratory conditions of industrial composting. Based on the relatively low thickness of the samples and the less aggressive conditions of home composting, especially for the PLA component, only film materials (D, E, F) were selected for laboratory biodegradability tests simulating home compost.

Biodegradability in a laboratory test under industrial and home composting conditions

All samples from Table 1 were subjected to a laboratory test at industrial composting conditions at a temperature of 58 °C. After measuring of three samples for each composition, including the reference sample (cellulose), the data (with an average standard deviation of \pm 8.6 for industrial composting conditions) were evaluated shown in Figure 1, where we see that in industrial composting conditions 100% mineralization was achieved for all samples after approximately 90 days of incubation. The sample containing the highest amount of PLA (70%) was the only one that showed a lag phase, which could be due to the confinement of the PHB phase inside the dominant PLA component. Apart from this sample, all others contained at least 30% easily biodegradable PHB and/or TPS, which smoothed out the lag phase on the biodegradation curves of industrial compost.

Thick-walled samples (cups) A (4 mm) and B (1 mm) showed the slowest mineralization. On the contrary, the mineralization of film D and F was fast, while F was faster at the beginning, which was probably due to the higher content of easily biodegradable TPS and plasticizers (40%) compared to D (5%). It was also surprisingly fast with relatively thick C (1 mm) containing a high PHB and TPS content (65%). The presence of TPS in the samples may initiate their early disintegration and thus ignore the importance of their thickness, since the thin film F showed a similar biodegradation course as the thick sample C. The composition of both samples was comparable, but in the absence of TPS, the thickness plays a more important role.



Figure 1. Mineralization of samples under industrial composting conditions 58°C.

After incubation, removed samples of compost were observed in SEM to evaluate microbial colonization and damage to the surface of the material (Figure 2). After 10 days in the compost, the morphological appearance indicated filamentous thermophilic actinobacteria with distinguishable round endospores. Surface erosion was also evident.



Figure 2. Scanning electron microscopy survey of the sample surface during the biodegradation test at 58 °C (industrial composting condition). 5000x magnification.

For biodegradation testing under home composting conditions (28 °C), samples D, E and F in the form of film were selected based on previous experience and scientific studies. Three samples were measured for each composition together with a reference sample (cellulose) and the average standard deviation for all compositions tested was \pm 3.9 for home composting conditions. All samples in this testing reached total mineralization in about 180 days with about a 15 day lag phase. The biodegradation curves of the samples from Figure 4 do not differ significantly from the cellulose curve. We can also see the predicted sequence where the PLA/PHB/TPS thin film

(F) mineralized the fastest, followed by the non-TPS sample (E) with the smallest gap. In this case, thickness and plasticizer probably played a significant role.



Figure 3. Mineralization of samples under home-composting conditions 28°C.

Observation of samples from tests of home compost conditions using the SEM method showed that the degree of colonization of the surface of the samples compared to the testing of industrial compost is much lower. This phenomenon is probably the result of the presence of a completely different microbial community at a given temperature. In addition to filamentous (most likely actinomyces), rod-shaped bacteria were also present (e.g., Figure 5, F, 30 days). Gradually cracks and cavities stood out. Probably the fungi at the given temperature were very active and secreted extracellular enzymes that degraded the material even though their attachment to the surface could not be seen.



Figure 4. Scanning electron microscopy survey of the sample surface during the biodegradation test at 28 °C (home-composting conditions). 5000x extension.

Composting in the electric composter

The samples from Table 2 were also tested in an electric composter, where they were inserted as test specimens with dimensions of 10x7 cm and with the original thickness. Biodegradation was evaluated through weight loss in percent. It can be seen in Figure 5 that the disintegration of all film samples was very fast and all of them disintegrated into pieces smaller than 2 mm after 20 days. Sample C (cup containing TPS) disintegrated into particles smaller than 2 mm after 40 days. PLA/PHB-based cup B and combined TPS-containing A disintegrated in a similar time period, while A slightly faster.



Biodegradation curves based on CO2 measurements in industrial and home compost conditions were also compared (Figure 6) for samples C as a typical example of all three cups and E as a film sample. We can see that in the case of the cup, the composting process ensured a direct microbial conversion to CO2 with a relatively short disintegration step. On the contrary, the films are quickly disintegrated into smaller particles and followed immediately by mineralization. This phenomenon was caused by the low mechanical resistance of the films compared to the cup to mixing inside the composter.



Figure 7. Comparison of biodegradation curves measured as CO2 in industrial compost conditions (58°C) for samples C and E, and in home-compost conditions (28°C) for sample E with disintegration curves obtained using an electric composter for samples C and E.

It is clear from the SEM images that all the tested samples showed visible changes in the surface morphology after only 6 days of incubation. In Figure 8, images of sample B without TPS and sample C with TPS, which were not immediately disintegrated, are shown as examples. Depending on the composition of the sample, voids were formed, which resulted in an increase in surface area and acceleration of the biodegradation process.





CONCLUSIO

This study was focused on investigating the compostability of a group of materials based on PLA/PHB with different compositions.

Evaluation of the obtained data from laboratory tests simulating the conditions of home and industrial composting and from electric composter confirmed the biodegradation of the investigated PLA/PHB materials in all tested cases. A very important result is that material with a high proportion of PLA due to blending with PHB can be fully biodegraded under home composting conditions. It has been verified that the disintegration and mineralization of all investigated materials ensure the avoidance of the production of microplastics in the environment after industrial as well as home composting processes.

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INFLUENCE OF PHB AND TPS CONTENT ON THE BIODEGRADATION OF PLA/PHB(/TPS) BLENDS

<u>Mária Mikolajová</u>, Lucia Danišová, Slávka Hlaváčiková, Vojtech Horvath, Andrej Baco, Ján Bočkaj, Roderik Plavec, Leona Omaníková, Mária Fogašová, Ema Mojžišová, Zuzana Vanovčanová, Jozef Feranc, Štěpán Krobot*, Ahmad Fayyaz Bakhsh**, Pavol Alexy

Institute of Natural and Synthetic Polymers, Faculty of Chemical and Food Technology, Slovak University of Technology, Radlinského 9, 812 37 Bratislava, Slovak Republic e-mail address: maria.mikolajova@stuba.sk

* Institute of Materials Science, Brno University of Technology, Faculty of Chemistry, Purkyňova 464/118, 612 00 Brno, Czech Republic

** Tomas Bata University in Zlín, Faculty of Technology, Vavrečkova 5669, 760 01 Zlín, Czech Republic

ABSTRACT

This work deals with the investigation of the influence of PHB and thermoplastic starch (TPS) content on the biodegradation (expressed as the degree of disintegration) of model blends of PLA/PHB(/TPS)-based blown films. Polymer blends contain varying ratios of PLA and PHB, with blends that also include the addition of TPS with variable contents. The prepared blends were processed as blown films and subsequently evaluated for biodegradation according to ISO 20200 and biodegradation testing by CO_2 production quantification under thermophilic as well as soil conditions. Based on the obtained results, it can be said that the increased content of PHB accelerates biodegradation under simulated conditions of home compost, but under simulated conditions of industrial compost, it does not significantly affect the speed of the process. A higher content of TPS under thermophilic conditions significantly increase speed of the biodegradation process, but under mesophilic conditions a higher content of TPS in the blend is required to speed up the disintegration process.

Keys words: polylactic acid (PLA), polyhydroxybutyrate (PHB), thermoplastic starch, biodegradation

INTRODUCTION

The increase in the difficulties for disposing of waste and the harmful effects on the environment and public health caused by the non-degradability of many synthetic polymers have increased concerns all over the world to find an alternative material that is environment friendly. Biodegradable polymers emerged as an alternative approach for many industrial applications to control the risk caused by non-biodegradable plastic [1]. Therefore this research is mainly focused on plastic material from renewable sources such as starch, polylactic acid (PLA) and polyhydroxyalkanoates (PHAs) [2] or PLA/PHB(/TPS) blends [3][4][5][6].

Both polymers PLA and PHB are polyesters and are used in consumer products due to their biocompatibility and biodegradability. They have comparable thermal and mechanical properties as the properties of some common polymers. PLA has better mechanical performance than PHB while PHB displays better barrier properties. But both of them are known as very brittle at the room temperature [5]. Combination of these two biopolymers allows obtaining new biomaterials with enhanced properties as compared to the single components, while maintaining their ecosustainability [3].

Starch is usually used in biodegradable polymer blends to improve biodegradability as well as to reduce the price of the final material. To improve starch dispersion in polymer matrices and physical properties of their blends, thermoplastic starch (TPS) is applied. TPS is usually prepared by mixing of native starch with plasticizer (mixture of glycerol and water) [6].

In this study, we focus on influence of PHB and TPS content on biodegradation in PLA/PHB(/TPS) model blends.

MATERIALS AND METHODS

1) Preparation of thermoplastic starch.

Natural starch was converted to thermoplastic starch (TPS) by blending and kneading of starch and glycerol in the laboratory twin-screw extruder, LabTech Thailand. Ratio Starch/Glycerol was 70/30 w/w. Technological parameters during starch plasticising were as follow:

Extruder diameter: 16 mm

L/D ratio: 40/1

Temperature profile from hopper to head (°C): 70-120-180-4x190-160-140-140 Screw speed: 150 rpm Atm degassing at 32 D.
2) Preparation of PLA/PHB and PLA/PHB/TPS blends.

Blends PLA/PHB or PLA/PHB/TPS were prepared by blending using the same twin-screw extruder as for TPS preparation. All components were fed into hopper of extruder. Technological parameters during blend preparation were as follow:

Extruder diameter: 16 mm L/D ratio: 40/1 Temperature profile from hopper to head (°C): 80-100-170-185-3x190-170-160-160 Screw speed: 150 rpm Atm degassing at 32 D. All blends were dried before next processing in the air oven at 70°C for 2 hours.

3) Preparation of samples for biodegradation testing.

For biodegradation testing the blown films were prepared using Plasticorder Brabender film blowing unit. Single screw extruder, diameter of screw 19 mm, L/D = 25/1 was used. Processing parameters were as follow:

Screw speed: 35 rpm

Temperature profile from hopper to head (°C): 190-180-170-160 Prepared films had thickness 0.060 mm.

4) Biodegradation testing according to ISO 20200.

Biodegradation test simulating composting conditions (IS/ISO 20200 (2004) standard) was performed. This test represents the determination of the degree of decomposition of plastics under simulated composting conditions in laboratory conditions. The degree of decomposition is determined by the weight loss of the polymer before and after testing. The test period is 90 days. The sample is fully biodegradable if it completely decomposes in this time. The composition of the model compost is shown in Table 1. Garden compost is used as the inoculum (seed culture), which must be homogeneous and without large objects such as stones, pieces of wood, etc.

Table 1. The composition of the compost (dry weight %)

| Sawdust | Feedforrabbits in theformofgranules | Mature compost | Corn-starch | Sucrose | Corn oil | Urea |
|---------|-------------------------------------|-------------------|-------------|---------|----------|------|
| 40 | 30 | 10 | 10 | 5 | 4 | 1 |

The composting reactor used in the test was a plastic box with dimensions: $17.5 \times 15 \times 6.5$ cm (length, depth, height). The box was closed with a sealing lid, holes measuring 0.5×6.5 cm were made in the middle of the depth of the box on the wider sides. The tested samples were prepared with dimensions of approximately 6.5×10 cm, and were inserted into the composting box two at a time. The experiment was started after mixing the compost, with which each box was gradually filled to half. A pre-weighed film was placed on top of this layer, on which the compost was again layered. The box prepared in this way was evenly filled with distilled water so that the total humidity was 55%. They were then incubated at 58°C. The reactor was weighed, evaporated water was replenished.

5) Biodegradation testing by CO₂ production quantification at thermophilic conditions.

Composting biodegradation tests were performed according to the adapted and miniaturized ISO 14855 method in 500 mL biometric flasks with septum-equipped stoppers. Mature compost from a nearby municipal composting facility (TSZ Ltd., Zlín, Czech Republic) was used in this part of the study. This test was done at 58°C for industrial composting and at 28 °C to simulate home-composting conditions. Into each flask, 2.5 g of dryweight compost, 5 g of perlite, and 1 mL of mineral salt medium were weighed, and the water content of the substrate mixture was eventually adjusted to 60% by the addition of sterile drinking water. One hundred milligrams of the samples were cut into 5×5 mm fragments that were placed in each sample flask. For each sample, three flasks plus 4 blank were used. The internal production of CO₂ in blank incubations was always subtracted to calculate the net sample mineralization. Headspace gas was sampled at appropriate intervals through the septum with a gas-tight needle and conducted through a capillary into a gas analyser (UAG, Stanford Instruments, Sunnyvale, CA, USA) to determine the amount of CO₂. Biodegradation percentage (D_t) was calculated as

$$D_t = \frac{(CO_2)_t - (CO_2)_b}{ThCO_2} \times 10$$

where $(CO_2)t$ is the released CO_2 by each sample, $(CO_2)_b$ is the CO_2 produced by the blank flasks, and (ThCO2) is the theoretical CO2 from the sample. A flash elemental analyser 1112 (Thermo Fisher Scientific, Waltham, MA, USA) was used to measure the carbon content of the samples.

6) Biodegradation testing by CO₂ production quantification at soil conditions.

The laboratory procedure used was based on ISO 17556 (2019) but was miniaturized and adapted for small laboratory samples of materials. The biodegradation tests [14] were realized in 500 mL flasks with septa mounted on the stoppers. The flasks contained polymer samples (50 mg), soil (15 g, plough layer, haplic chernozem; dry weight 88.4%; soil texture, silty loam, pH (H2O) 7.28; volatile solids 5.55%; soil organic matter 3.05%), perlite (5.0 g) and mineral medium (10.8 mL). The flasks were incubated at 25 °C or 37 °C air-tight as a closed system. Head space gas was sampled at appropriate intervals through the septum with a gas-tight needle and conducted through a capillary into the gas analyser (UAG, Stanford Instruments, USA) to determine the concentration of CO2. The percentage of net mineralization with respect to the carbon content of the initial samples was calculated. Three parallel flasks were run for each sample, along with four blank flasks [7].

RESULTS AND DISCUSSION

Influence of composition of PLA/PHB or PLA/PHB/TPS blends on biodegradation at various conditions was evaluated. For these purposes blends with composition given in table 1. were prepared.

| Recipe No. | PLA/PHB | Starch/(PLA+PHB) | PLA Ingeo 4043D | PHB Enmat Y1000 | Starch Merizet M100 | Glycerol 86% Pharma quality | ATBC Citrofol B2 |
|---------------|---------|------------------|-----------------|--------------------|---------------------------|--------------------------------|---------------------|
| 1.01 | w/w | w/w | % w | % w | % w | % w | % w |
| R1(30/70/0) | 30/70 | 0/100 | 25.50 | 59.50 | 0.00 | 0.00 | 15.00 |
| R2(80/20/0) | 80/20 | 0/100 | 68.00 | 17.00 | 0.00 | 0.00 | 15.00 |
| R3(30/70/50) | 30/70 | 50/50 | 11.79 | 27.50 | 37.64 | 16.13 | 6.93 |
| R4(80/20/50) | 80/20 | 50/50 | 31.43 | 7.86 | 37.64 | 16.13 | 6.93 |
| R7(40/60/0) | 40/60 | 0/100 | 34.00 | 51.00 | 0.00 | 0.00 | 15.00 |
| R8(80/20/10) | 80/20 | 10/90 | 60.22 | 15.05 | 8.02 | 3.44 | 13.28 |
| R9(30/70/10) | 30/70 | 10/90 | 22.58 | 52.69 | 8.31 | 3.56 | 13.28 |
| R10(0/0/100) | 0.00 | 100/0 | 0.00 | 0.00 | 70.00 | 30.00 | 0.00 |

Table 2. Blends composition

Biodegradation evaluated as disintegration according to ISO 20200 standard.

Biodegradation of prepared films R1 - R10 was evaluated as degree of disintegration according to ISO 20200 standard at two temperatures: $28^{\circ}C$ (simulated home compost conditions) as well as at $58^{\circ}C$ (simulated industrial compost conditions). Results in form of dependencies of weight loses on time are shown in Fig. 1-4.

Fig 1. and 2 represent dependencies of disintegration degree on incubation time for PLA/PHB blends with increasing of PHB concentration. Various PLA/PHB ratios were tested as follow: R2= 80/20, R7=40/60 and R1=30/70. TPS without any other additives (R10) was used as reference material. Mesophilic conditions of biodegradation (Fig. 1B, 2B) logically provide longer time to total disintegration of samples than thermophilic biodegradation (fig. 1A, 2A). The fastest disintegration was observed for blend containing highest PLA concentration with higher testing temperature (58°C) – Fig. 1A. Decreasing of PLA content from 80 to 40 % in this case causes slower biodegradation, but next decreasing of PLA content from 40 to 30% does not exhibits such significant effect. Mesophilic conditions (Fig. 1B) show opposite effect. The fastest biodegradation was observed in case of highest PHB content, and it is slowing down by elevated PLA concentration. In comparison to thermophilic conditions, biodegradation rate is differentiated with higher sensitivity to PLA/PHB ratio and significant difference is visible also between blends of 40/60 and 30/70. Higher content of PHB gives significantly higher improvement of biodegradability of PLA/PHB blends at home compost conditions.



Fig. 1 Influence of ratio PLA/PHB on biodegradation of PLA/PHB blends evaluated according to ISO 20200 as disintegrated part of original sample. A – thermophilic conditions, B – mesophilic conditions.

TPS concentrations (10% and 50%) were tested by the same method at two PLA/PHB ratios – 30/70 and 80/20 (Fig. 2 and 3 respectively). For PLA/PHB ratio 30/70 at thermophilic conditions, higher TPS content in the blends significantly speeds up the process of disintegration. Unexpected effect was observed at mesophilic conditions where small addition of TPS (10%) slows down process of biodegradation, but next addition of TPS (50%) accelerates the process. The same effect, but much weaker was observed when PLA/PHB ratio was 80/20 (Fig. 3B). Thermophilic conditions show only very small effect on TPS disintegration (Fig. 3A). Generally, for PLA/PHB(/TPS) blends in form of films, PHB brings positive effect on biodegradation process at mesophilic conditions. At higher temperatures effect of PHB is opposite, and in comparison to higher PLA content, the biodegradation speed is slower.



Fig. 2 Influence of TPS concentration on biodegradation of PLA/PHB blends with PLA/PHB ratio 30/70 evaluated according to ISO 20200 as disintegrated part of original sample. A – thermophilic conditions, B – mesophilic conditions.



Fig. 3 Influence of TPS concentration on biodegradation of PLA/PHB blends with PLA/PHB ratio 80/20 evaluated according to ISO 20200 as disintegrated part of original sample. A – thermophilic conditions, B – mesophilic conditions.

Interesting is effect of temperature on biodegradation of PLA/PHB blends at various PLA/PHB ratio. Comparison of disintegration curves for two different temperatures is shown on Fig. 4. While practically no changes are observed on disintegration curves for both testing temperatures (28 and 58° C) while PLA/PHB =

30/70 (Fig. 4A), very significant shift by temperature is visible if PLA/PHB ratio was 80/20 (Fig. 4B). Higher content of PLA makes biodegradability of PLA/PHB blends much more sensitive to temperature in comparison to blends with higher content of PHB. Higher content of PHB ensure good biodegradability in wide range of temperature and therefore such blends are ecologically safer than blends with higher PLA content.



Fig. 4 Effect of PHB content and effect of temperature on biodegradability of PLA/PHB blends evaluated according to ISO 20200 as disintegrated part of original sample. A – PLA/PHB = 30/70, B – PLA/PHB = 80/20.

Biodegradation testing by CO₂ production quantification.

Biodegradation testing by CO_2 production quantification was evaluated for selected samples with ratio PLA/PHB 80/20 and 30/70 as well as in the presence or absence of TPS. All selected samples were tested at thermophilic conditions and soil conditions. Results are shown in the Fig. 5 and 6.

The slight differences between biodegradation of blends containing higher concentration of PLA at thermophilic conditions was confirmed also by respired CO_2 evaluation while ratio of PLA/PHB 30/70 gives again slower biodegradation (Fig. 5). Addition of TPS to the blend with ratio PLA/PHB 80/20 exhibits practically no effect on biodegradation, in case of blend PLA/PHB 30/70 addition of 10% of TPS improved biodegradability at thermophilic conditions on comparable level to 80/20 alternative.

By comparison of both results (disintegration and respired CO_2 – Fig. 1 and 5) can be find out that 100% disintegration level according to ISO 20200 correlated to approx. 20-30% of mineralisation of the material. Therefore, it is very important whether after such disintegration in the compost, biodegradation continue also in the soil after compost application in agriculture. Consequently, testing of samples biodegradation in the soil conditions was realised. Results of more than one year testing are presented in Fig. 6.







Sample of the blend based on 80/20 PLA/PHB ratio with with TPS at which PLA/PHB with a term ophilic conditions, exhibit practically no degradability in soil. This type of TPS predition with produce microplastics in the soil (nature) or it will be degrading very slowly. As it was mentioned before, biodegradation of blends based on 30/70 PLA/PHB ratio is significantly less sensitive to temperature and it degrade much easier in the soil than blends of 80/20 PLA/PHB ratio. Additions of TPS improves biodegradability of both types of the blends. Addition of 10% of TPS to 80/20 PLA/PHB type of blend gives the similar biodegradation as 30/70 PLA/PHB based blends without TPS. Consequently, addition of 10% TPS to 30/70 PLA/PHB based blends also improve its biodegradation. Result obtained based on soil biodegradation test indicate that individual components does not decompose separately, but some synergetic effects can be observed. Very important result is that probably PLA is able to degrade in such 3-components composition also at low temperatures in the soil. Sample R8 (PLA/PHB/TPS = 80/20/10) exhibits degradation degree around 52%. It means that according to composition of blend (Table 1) minimum 12% of PLA was mineralised.

Similarly like in the previous results evaluated by disintegration degree, also in case of respired CO_2 measurements the sensitivity to temperature was evaluated for both 80/20 as well as 30/70 PLA/PHB ratios. Comparison of results obtained at thermophilic composting and in soil conditions is clear from Fig. 7.



Fig. 7 Comparison of biodegradability based on respired CO_2 evaluation at various temperatures for both 80/20 and 30/70 PLA/PHB ratios together with TPS addition effect.

Fig. 7 shows that again, the 30/70 PLA/PHB ratio gives lower temperature sensitivity to biodegradation than 80/20 PLA/PHB ratio. In both cases addition of 10% of TPS significantly improve biodegradability at low temperature in the soil. The bigger differences between higher and lower temperature in comparison to differences before can be given also by changes in microbial activity. While the Fig. 4 compare both temperatures as composting conditions, Fig. 7 compare compost with soil conditions.

CONCLUSION

The main aim of this work was to investigate the effect of PHB and TPS content on the biodegradation of PLA/PHB(/TPS)-based blends of blown films. Under the simulated conditions of industrial compost, the blends with the highest content of PLA were disintegrated the fastest. However, the fastest biodegradation under mesophilic conditions was observed on the blends with highest content of PHB and it slowed down due to the influence of PLA. At thermophilic conditions higher TPS content in the blends significantly accelerates the process of disintegration. These results were also confirmed by other biodegradation tests as CO₂ production quantification at thermophilic and soil conditions.

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BIOPOLYMER BASED MATERIALS FOR 3D PRINTING

<u>Vojtech HORVÁTH</u>, Roderik PLAVEC, Andrej BACO, Jozef FERANC, Lucia DANIŠOVÁ, Slávka HLAVÁČIKOVÁ, Ján BOČKAJ, Leona OMANÍKOVÁ, Ivana BÍROVÁ, Ema Mojžišová, Katarína Tomanová, Zuzana Vanovčanová, Mária Mikolajová, Mária Fogašová, Pavel ALEXY

Institute of Natural and Synthetic Polymers, Faculty of Chemical and Food Technology, Slovak University of Technology in Bratislava, Radlinského 9, 812 37 Bratislava, Slovakia <u>vojtech.horvath@stuba.sk</u>

INTRODUCTION

Fused Deposition Modeling (FDM) is the most famous 3D printing technology, which is widely applied in many fields of research as well as industry, mainly for modelling and prototyping, but also for the production of the final product.¹ Additive manufacturing is a relatively cheap and simple method, often used for the making of products with complex geometry. The primary advantage of 3D printing is the final product without producing large quantities of waste, which is also related to the saving of financial resources.²

Researchers are investigating the use of bio-derived materials in 3D printing for the sustainability of 3D printing technology with reducing plastics pollution, and the reduction of crude oil consumption. Biomaterials are considered a potential candidate for the replacement of petrol-based polymers thanks to their sustainable and versatile properties. Despite many obvious advantages of biopolymers from renewable resources, these materials still possess some properties, especially thermal and mechanical properties and processing stability, that are not as good as those of commonly used synthetic plastics. Therefore, research is focused on finding materials based on bioplastics which have comparable or even better properties, than the properties of commonly used synthetic plastic materials. ³⁻⁶

In this study, the influence of the composition of biodegradable PLA/PHB polymer blends on rheological and application properties is tested. The goal is to design a sustainable biodegradable material for use in FDM t 3D printing technology.

MATERIALS AND METHODS

Materials

Studied biodegradable polymer blends from renewable resources were based on polylactic acid (TotalEnergies Corbion) and polyhydroxybutyrate (TianAN Biopolymer) in various concentration ratios (0/100, 10/90, 25/75, 50/50, 75/25, 90/10 and 100/0). Two different types of PLA were used, extrusion type (labelled PLA1) and injection molding type (labelled PLA2).

Polymer blends were prepared using a twin screw extruder (Labtech) with the following parameters: L/D = 40, D = 16 mm. The geometric arrangement of the twin screw is overlapping and co-rotating. The polymer melt was extruded into the filament form, which was subsequently cooled and pelletized.

Filament preparation

The filaments were prepared using a single-screw extruder (Plasticorder Brabender) with the following parameters: L/D = 40, D = 19 mm, compression ratio 1:1. Head of the extruder was equipped with a circular cross-section die nozzle, with a 2 mm diameter. The diameter of the produced filament suitable for 3D printing was 1,75 mm. Ultimately the filament, when cooled down, was wounded up on a spool.

Rheology investigation

Processing stability

Processing stability was done using an oscillation rheometer (RPA 2000, Alpha Technologies), at a temperature of 190°C, 60° angle of oscillation and frequency of 50 cpm. The measuring time was 10 minutes, while the change in complex viscosity was recorded. For a correct comparison of the degradation rate of polymer blends, a relative complex viscosity was calculated using the formula (1).

$$\eta^{*}_{rel}(t) = \eta^{*}(t)/\eta^{*}_{0}$$
(1)

where $\eta^*_{rel}(t)$ is relative complex viscosity in time t, $\eta^*(t)$ is complex viscosity in time t and η^*_0 is the onset viscosity at the beginning of the measurement.

Strain sweep

A strain sweep test was done using an oscillation rheometer (RPA 2000, Alpha Technologies). The temperature of the measurement was set according to the ideal printing temperature selected by the temperature tower method described below. Complex viscosity at a shear rate of 35 s⁻¹ was evaluated.

Complex viscosity of the melt during cooling

At the beginning of the test, the temperature of the measurement was set to 190° C, in order to melt the polymeric material. Consequently, the temperature of the measurement was gradually reduced by 10° C decrement, until the temperature of the measurement reached 110° C. For each temperature, a complex viscosity at a shear rate of 15 s⁻¹ was evaluated.

Temperature tower

A temperature tower test was used for the determination of the ideal printing temperature, or nozzle temperature. For this test, the FDM Prusa 3D printer was used (Prusa MK3s 3D printer). The temperature tower consists of 10 identical levels, while the printing temperature of each level is different. One temperature tower in the temperature range of 220°C to 175°, with a temperature gradient of 5°C, was printed for each filament made from PLA/PHB based blends. For the determination of the ideal printing temperature the printing quality of several geometric elements, such as bridges between floors, overhangs, and horizontal and vertical circular openings, was evaluated.

Printing conditions of the temperature tower: Layer height: 0,2 mm Printing speed: perimeters: 40 mm/s Infill: 40 mm/s Bed temperature: laboratory temperature Nozzle diameter: 0,4 mm

Mechanical properties measurement

The samples, in the form of "dog bone", were prepared by FDM 3D printing technology, using Prusa MK3s 3D printer. The printing conditions were set based on the ideal printing temperature, determined using the method described in the previous paragraph. Mechanical properties were measured using Zwick Roell/Z 2.5 machine (Zwick GmbH&Co.KG, Ulm, Germany), according to technical standard ISO STN 527. Tensile strength and elongation at break were determined based on the tensile curve.

Results and discussion

The rheological characteristics of polymers represent essential parameters for the proper processing of the materials. Studied polymer blends based on biodegradable polymers from renewable resources easily undergo hydrolysis and thermo-mechanical degradation compared to the degradation abilities of conventional plastics. For this reason, it is essential to understand its processing stability to use biodegradable polymer blends in the following filament production as well as final 3D printing.

PLA/PHB based polymer blends were tested under thermomechanical loading for investigation of the degradation of polymer material during processing. The factors affecting viscosity (temperature, shear rate) remained constant during the testing, so the observed change in complex viscosity can be attributed to the reduction of molecular weight of the polymers in the investigated blends.

A significant decrease in viscosity caused by the degradation of the material can be seen (Fig. 1B) in the blends containing a higher amount of PHB (PLA/PHB: 0/100, 10/90, 25/75) and it can be stated that this applies to blends regardless of the PLA used. On the other hand, blends containing a higher amount of PLA2 (injection type PLA) do not show a decrease in viscosity caused by the thermomechanical strain as high as blends containing PLA1 (extrusion type PLA). Despite the different degradation process, caused by thermomechanical loading, it was possible to prepare a filament and subsequently use the filament for 3D printing testing samples for all of the studied polymer blends.



Figure 5: Processing stability of biodegradable polymer blends; A - dependency of complex viscosity on PLA content in the 4th minute of the test; B - dependency of relative complex viscosity on the content of PLA in PHB

For each tested material, the ideal printing temperature was determined for the printing of samples for testing of mechanical properties. At this temperature also the viscosity of the material was measured using an oscillation rheometer

for a strain sweep test, at a shear rate of 35 s⁻¹. The ideal printing temperature was determined by the temperature tower test.

A temperature tower is a vertical construction consisting of several identical levels containing identical geometric elements. Each level is printed at a different nozzle temperature, so an ideal printing temperature of a particular material can be determined. Correct nozzle temperature is one of the most important factors in FDM technology because it affects the shape of geometric elements of the temperature tower, but also its deformation, the adhesion between individual layers and stringing due to the low viscosity of the polymer.

Fig. 2 shows the temperature tower, according to which an ideal printing temperature was determined. The horizontal circular hole was printed in enough detail in the entire range of temperatures. The biggest difference between individual temperatures could be seen on the overhangs and the details printed in the space between vertical triangular and circular holes. Stringing could be observed at higher temperatures for all tested filaments.



Figure 6: Temperature towers

The ideal nozzle temperature and corresponding complex viscosity at the shear rate 35 s⁻¹ in the dependence of polymer blend composition are illustrated in Fig. 3A for blends containing PLA1 and in Fig. 3B for blends containing PLA2. The ideal nozzle temperature gradually increases with the increase of PLA content in the polymer blend. When comparing the results for both PLA types, a more significant increase in the ideal nozzle temperature can be seen in the blends containing PLA2. This can be caused by lower degradation of the material during the thermomechanical strain process (Fig. 1A and 1B).

The complex viscosity of the tested polymer materials, measured at optimal printing conditions determined for individual samples, shows a decreasing trend with the increase of PLA content in the polymer blend (Fig, 3A and 3B). From the determined complex viscosity of blends measured during cooling of the tested sample (Fig. 4A and 4B), it is clear that with the decrease in temperature, an increase in viscosity occurs with the increase of PLA content in the polymer blend. It can be stated, that with the increase in PLA content in the polymer blend, a faster solidification of the melt occurs, which affects the optimal printing temperature determined by the temperature tower method.



Figure 7: Dependency of optimal printing temperature and complex viscosity on the content of PLA in PHB; left A - PLA1; right B - PLA2



Figure 8: Dependency of complex viscosity of the melt during cooling on the measuring temperature for individual PLA/PHB blends; left A - PLA1; right B - PLA2

Mechanical properties are one of the most important characteristics for the perspective utilisation of any product, including products made by 3D printing technology. The tensile strength of samples increases with the increase of the content of PLA in the polymer blend. A similar trend can be seen (Fig. 5A) for both types of tested PLA. The influence of higher degradation of PLA1 (Fig. 1B) exhibits no influence on the mechanical properties of 3D-printed "dog-bone" samples. Since studied polymer blends based on PLA/PHB did not contain any type of plasticiser, the elongation at break remained low for all the blends. It is caused by both the high crystallinity of polyhydroxybutyrate and the high value of T_g of polylactic acid.



Figure 9: Mechanical characteristics of 3D-printed samples; A. dependency of tensile strength on the content of PLA in PHB; B. dependency of elongation at break on the content of PLA in

PHB

CONCLUSION

This study aimed to describe the influence of the composition of PLA/PHB polymers on their applicability in 3D printing technology. Rheological characteristics, mechanical properties, and the 3D printing process itself were investigated. Even though biodegradable polymers from renewable resources tend to degrade during processing, it is possible to prepare a filament, which is suitable for further processing by 3D printing if a proper printing temperature is estimated. Consequently, the production of testing samples, as well as the production of final 3D printed products, is possible with satisfactory quality. The tensile strength of PLA/PHB based blends reaches decent values, but elongation at break is low. This result could be improved by the addition of additives for flexibility adjustment.

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DE-VULCANIZED RUBBER ON INDUSTRIAL USE

<u>Ran Zamir</u>

Levgum Ltd. I.Z. Kanot – 70750, Israel Email: <u>ranz@levgum.com</u>

Introduction

Ever since vulcanization was invented by Mr. Goodyear, thus giving rubber its valuable position among raw materials, mankind (including Mr. Goodyear himself) has been struggling to find adequate solutions to the rubber waste. By adequate it is meant a solution that can deal with all the verity of rubber compounds, result in a high value or high-quality material, be cost effective and environmentally friendly (a demand of recent times). Considering that, the focus of this paper will be on high quality de-vulcanization process yielding high quality de-vulcanized rubber compound, utilizing a cost effective process.

The automotive industry uses substantial amounts of rubber (of various kinds) in its products, on increasing volumes every year. These products vary from low-end market products, such as mats and mud protectors, all the way to the very high-end market products, such as tyres. In between exists, various types of seals, diaphragms, caps, rings, cushions, and other parts. Most of these products are sulfur cured.

To help save the environment a de-vulcanization technology would be required. A technology that can take any type of sulfur cured rubber compound and de-vulcanize it, hence creating a **D**e-vulcanized **R**ubber Compound (**DRC**) that can be put again into use.

The main goal of this paper is to show that such a technology exists. It is performed for many years now on industrial scale. Orders for hundreds of MT can be supplied as of now. It is cost effective without any subsidies or government incentives of any kind, saving up to 50% to the end customer. Furthermore, it is environmentally friendly. Such technology can be used worldwide in all automotive industry, replacing some of the virgin compound. The level of replacement is to be determined by the product manufacturer. It can vary from over 90% replacement in items like mud protectors and mats, to 10% - 30% in a tyre application.

The formal definition of recycling in the EU is: "any recovery operation by which waste materials are reprocessed into products, materials or substances whether for the original or other purposes. It includes the reprocessing of organic material but does not include energy recovery and the reprocessing into materials that are to be used as fuels or for backfilling operations." Using such definition, one may choose to view waste rubber in one of two basic ways. Either there are not enough chemical bonds present in the waste rubber compound. Or there are too many chemical bonds. The first approach leads to processes such as glowing. The second approach would mainly be presented by various methods or reclaiming rubber and de-vulcanizing rubber. It is important to note that pyrolysis and other energy recovery processes will not come as recycling under this definition. In this paper we focus on de-vulcanization solution.

De-vulcanization main challenges

De-vulcanization technologies are faced with many challenges when embraced and implemented by the rubber industry.

The major ones are three: First, to obtain a material with properties as close to the virgin compound it originates from as possible. Second, to make the implementation of the DRC easy for the manufacturer. Third, to do that within the framework of responsible recycling. While the first two are relatively intuitive, the term "Responsible Recycling" has a deeper and broader meaning. It is responsibility towards the environment; towards the manufacturer (both for his workability and profitability) and towards market stabilization (in price and demand). Namely, "responsible recycling" is composed of the following:

- 1) The recycling process solves a problem. In this case that of rubber waste responsibility towards the environment and market stabilization. Having steady supply of RM
- 2) The outcome if serves as a raw material to the industry must have acceptably good properties responsibility towards the manufacturer and market stabilization.
- 3) The outcome must have practical workability to the manufacturer responsibility towards the manufacturer.
- 4) The process of producing the recycled material must be environmentally safe responsibility towards the environment.
- 5) The solution is not an idea or a small-scale solution. Rather, it is a large scale and industrially proven method that can support the large rubber industry responsibility towards the manufacturer and market stabilization.
- 6) The outcoming raw material must be cost effective responsibility towards the manufacturer and market stabilization.

There exists another challenge worth mentioning and that is the influence of products' complexity. Most products are composed products. Some are complex since they use various compounds in the same product. Some are composed of

separable and non-separable materials. Some products are both. In any case, separating the different materials is a must before de-vulcanization. Introducing more bonds or using incineration or pyrolysis processes usually overcomes the challenges of compound level complexity. Whereas alternative approaches, such as de-vulcanization may prove challenging for compound level complexity.

Levgum's technology

A mechanical chemical method to treat vulcanized rubber crumbs, at ambient temperature, has been developed and implemented. Mechanical work is being done by a 2-roller mill with closed nip (0.1mm) and high friction ratio (1:2 up to 1:3). The chemical part is contributed by a specified modifier, called EDV for Ecological De-Vulcanizer. The EDV is designed to generate, under the de-vulcanization conditions, a specific agent that selectively destroys the S-S bonds, which are weaker than the C-S and C-C bonds (see Fig. 1). EDV contains two chemical substances. The first chemical substance disposes towards dissociation to create an organic cation and an amine. The second chemical substance is a promoter of dissociation of the first chemical substance and contains a functional group consisting of an acceptor to the said amine.

Levgum's devulcanization process is carried out by adding EDV, about 3% by weight to vulcanized rubber crumb that is stressed in a two-roller mill for approximately 20 passes. This process breaks down the sulfur cross-links that connect the rubber polymer chains in vulcanized rubber. The existing sulfur atom sites are blocked by residue from Levgum's EDV, preventing spontaneous re-vulcanization (see Fig. 2). Hence, in the DRC the sulfur links that are crossed between rubber polymer chains (see Fig. 1), are broken. The sulfur atoms have the residues of the chemical agent used for the de-vulcanization around them, thus making it impossible to be vulcanized again in these sites (See Fig. 2). When introduced into a new compound the DRC is blended with the virgin compound and the whole mixture is then vulcanized. The DRC will stream in the mold and behave much like the virgin compound in all aspects. Another important result of having the blocking reagent shown in Fig. 2 is that it gives the DRC a very long shelf life. In fact, it was measured after 4 years on the shelf and was shown to have the same properties as fresh DRC.



Fig. 1 - Vulcanized rubber: cross-links between sulfur atoms exists (shown in blue)



Fig. 2 – **De-Vulcanized rubber:** no cross-links between sulfur atom (in blue color), blocking residue present (shown in red)

It is an automated process that does not produce or emit any hazardous waste or gases and is 100% environmentally safe. The EDV itself does not contain any harmful chemicals, and its production does not generate any hazardous waste or gases as it is at solid state phase. The two components of the EDV are materials heavily used throughout the world for various purposes and need not be produced specially for the process. Namely, the environmental issue was not swept under any carpet.

Properties

DRC having the residue shown in Fig. 2, will always have properties inferior to the virgin compound it originated from. However, the balance, from the rubber product manufacturer's point of view, should always be between quality reduction and cost saving in raw materials. An example of the reduction in properties and a way, using a change in curing group, to overcome it partially, can be seen in Fig. 3 and 4. At 10% to 15% by weight replacement level Elongation at Break (EB) has dropped by less than 2% and 3%, respectively. Whereas at 25% (Fig. 3) and 50% (Fig.4) replacement it has dropped by less than 13% and 19%, respectively. When acceleration is corrected the drop is less than 17% (Fig. 4). Somewhat similar results are shown for Tensile Strength although in that case the change in acceleration group has had a negligible effect. It is noted that the curing time is shortened when DRC is used. This effect can be mitigated using less sulfur and more sulfur donors, as can be seen in Fig. 4. Shore hardness remains almost the same (see Fig. 3). Viscosity is increased (see Fig. 3); however, no processing problems are to be expected with these values of Mooney Viscosity.

Other methods may mitigate the problem of properties reduction in using DRC. For example, using natural rubberbased DRC in compounds based on SBR, will lead to better elongation at break and tensile strength. This means sorting out the rubber waste and introducing it into the de-vulcanization process by the type of rubber upon which the compound is based, will open the possibility to even improve certain virgin compounds using DRC based on superior compounds. Other methods will be discussed in the presentation.

| | Reference | Sample A | Sample B |
|-----------------------------------|----------------|----------------|----------------|
| RRC concentration (% by weight) | 0 | 15 | 25 |
| Rheometer at 160 °C | | | |
| Min. torque (dNm) | 3,58 | 2,62 | 3,15 |
| Max. torque (dNm) | 19,91 | 18,94 | 19,15 |
| Δ torque (dNm) | 16,33 | 16,32 | 16,00 |
| TC90 (Minutes) | 4,04 | 3,03 | 2,59 |
| ML (1+4), 100 °C (MU) | 31 | 51 | 58 |
| Hardness Shore A | $65,6 \pm 0,2$ | 63,9 ± 0,2 | $65,2 \pm 0,3$ |
| Tensile strength (MPa) | 30,8 ± 1,4 | 27,3 ± 0,8 | 26,6 ± 1,3 |
| Elongation at break (%) | 548 ± 17 | 535 ±12 | 487 ± 19 |
| Modulus at 50 % elongation (MPa) | 1,5 ± 0,1 | 1,3 ± 0,0 | 1,4 ± 0,0 |
| Modulus at 100 % elongation (MPa) | 2,6 ±0,1 | 2,2 ± 0,0 | 2,4 ± 0,0 |
| Modulus at 200 % elongation (MPa) | 6,8 ± 0,1 | 5,7 ± 0,0 | 6,1 ± 0,1 |
| Modulus at 300 % elongation (MPa) | 12,7 ±0,3 | 11,0 ± 0,1 | $12,1 \pm 0,2$ |
| Rebound resilience (%) | 45,8 ±0,4 | $40,7 \pm 0,4$ | $41,8\pm0,5$ |
| Abrasion (mm ³) * | 108 ± 2 | 130 ± 5 | 132 ± 4 |

Fig. 3 – Test results from DIK Deutsches Institut für Kautschuktechnologie order no.05V0188



| M.B. M-90 | (Duram) |)+Devulcanize | d NR | compound | | | |
|------------------------|---------|---------------|------|----------|--|--|--|
| Corrected acceleration | | | | | | | |

| | | 14.00 | | | | | | | |
|------------------|---|--------|------------|----------|-----------|---------|--------|-------|--------------------|
| CODE | | M-90 | | M | -90 / Dev | ulcaniz | ed | Corre | ected acceleration |
| ingredien | ts | Duram | | 85/15 | 75/25 | 50/50 | 30/70 | Α | В |
| SMR CV60 | _ | 100.00 | | | | | | | |
| | _ | | M.B. M-90 | 85.00 | 75.00 | 50.00 | 30.00 | | 50.00 |
| Carbon Black | | 42.00 | | | | | | | |
| | 1 | | devulc. NR | 15.00 | 25.00 | 50.00 | 70.00 | | 50.00 |
| Zno | 12 | 2.40 | | | | | | | |
| | | | Zno | 0.26 | 0.43 | 0.88 | 1.20 | | 0.88 |
| Stearic acid | | 1.50 | | | | | | | |
| | 1 16 | | Stearine | 0.18 | 0.30 | 0.60 | 0.80 | | 0.60 |
| Flectol TMQ | TE. | 1.00 | | | | | | | |
| | AS | | | | | | | | |
| 6PPD | Ē | 1.00 | | | | | | | |
| | | | | | | | | | |
| Struktol A-60 | | 1 50 | | | | | | | |
| | _ | | | | | | | | |
| TOTAL | | 149.40 | | 100.44 | 100.73 | 101.48 | 102.00 | | 101.48 |
| Sulfur | z | 1.60 | Sulfur | 1.00 | 1.00 | 1.00 | 1.00 | 0.60 | 0.80 |
| тмтм | _ Ę | 0.05 | MBS | 0.50 | 0.50 | 0.50 | 0.50 | 0.60 | 0.70 |
| DTDM 80% | - 1 22 | 0.22 | DTDM | | | | | 0.80 | |
| CBC | | 0.63 | | | | | | | |
| Struktol A-60 | - V | 0.50 | PVI | | | | | | 0.10 |
| ML | | 1.95 | | 2 17 | 2.37 | 2.86 | 3.51 | 2.85 | 3.02 |
| MH | - <u>É</u> e | 14.84 | | 13.29 | 13 70 | 14 43 | 14.26 | 14 59 | 13.50 |
| TS2 | - 19 P | 2.50 | | 1.58 | 1 34 | 0.87 | 0.65 | 1 29 | 1 17 |
| T50 | | 3.17 | | 2.48 | 2.06 | 1 37 | 1.03 | 1.20 | 1.66 |
| T90 | ~ š | 4.82 | | 4.66 | 3.89 | 2.64 | 2.05 | 2.62 | 2.81 |
| 0 Hardne | | 60 | | 61 | 62 | 63 | 63 | 62.5 | 61.5 |
| + Sho | re A | | | | | | | 02.0 | 01.0 |
| 0 | 1 2 | 28 | | 22 | 22 | 25 | 29 | 25 | 22 |
| + 100 | , ci | | | | | | | | |
| 0 | , ş | 62 | | 55 | 54 | 63 | 74 | 62 | 55 |
| + 200 | l in the second s | | | | | | | | |
| 0 | odt | 120 | | 107 | 107 | 125 | 148 | 122 | 109 |
| + 300 | Σ | | | | | | | | |
| 0 Tensile s | trength | 289 | | 257 | 250 | 238 | 224 | 239 | 240 |
| + kg/c | cm ^z | | | 500 | 500 | | | | 170 |
| | tion 0/ | 548 | | 538 | 503 | 445 | 387 | 448 | 479 |
| + Elonga | | | | | | | | | |
| COMP. C | | | | <u> </u> | | | | | |
| GRAVI | Y S.G. | 1.087 | | 1.095 | 1,100 | 1.111 | 1.120 | 1.111 | 1.111 |
| | NCE III | 123 | 1 | 136 | 125 | 145 | 1/0 | | |
| ADRASION RESISTA | | 125 | | 150 | 155 | 145 | 143 | | |
| TROUSERS DI | E ka/cm | 18.8 | | 16.1 | 16.2 | 9.0 | 7.9 | | |
| | | | | | | | | | |
| | | | | | | | | | |

DURAM RUBBER PRODUCTS Uzi Frumer AB MANAGER

ST ISO 9001

KIBBUTZ RAMAT HAKOVESH 44930, ISRAEL, FAX.972-9-7474479, TEL. 972-9-7474458, 44930 קיבוץ רמת הכובש E-mail: duram@netvision.net.il

Fig. 4 – Test results

Implementation

DRC is mixed at the level of master batch by the manufacturer. Some manufacturers would prefer, mainly due to type and age of equipment used, to get the material in the form of sheets. To that end, Sundaram Industries PL. together with Levgum Ltd. have developed "Silsheet. Using flow control agents and a process (patent protected) the DRC resulting from the Levgum process was made into sheet form with improved properties. When discussing the properties of the Silsheet a distinction between Silsheet on its own and Silsheet in a compound should be made. Since neither Silsheet nor any other reclaimed or de-vulcanized material is used by itself. Rather it is always implemented in some virgin compound, Silsheet is compared to some of the highly considered recycled materials. Among those are superfine reclaim (SFR) and high tensile reclaim (HTR). Silsheet is showing to have better properties. When used in a compound, Silsheet was introduced at the same rate (36 phr) as SFR, as well as #30 and #80 powders in a control master batch; Silsheet superior properties are easily manifested. An example of which can be seen in Fig. 5; whereby using Silsheet the control compound tensile strength has been recovered in 90%.

| E | 1 | 2 | 3 |
|-----------------------|-----|-----|-----|
| CTRL | 189 | 188 | 191 |
| 3 0C | 130 | 133 | 134 |
| 80 C | 159 | 164 | 162 |
| SILSHEET | 170 | 172 | 175 |
| SUPER FINE RECLAIM | 154 | 151 | 149 |

Fig. 5 - Tensile strength comparison

To demonstrate Silsheet workability and how simple it is to implement it into virgin compounds, two case studies will be presented. One of Silsheet in treads and the other of Silsheet in mats made of recycled material only. Namely, focus will be made on the two extremes of rubber products. One being the very high end is the usage of Silsheet in compounds for high performance tyre parts. The second will be on the very low end of rubber products, i.e., products with high loading of Silsheet, such as mats made of recycled material only.

Acknowledgment

It is with great pleasure and high respect that we wish to thank M/S Sundaram Industries PL., its managers, and employees and especially to Mr. Thiru Nedumaran, Head of The Recycling Division, for his innovative and groundbreaking ideas, and for outstanding collaboration through many years of ploughing the field of de-vulcanization together. Mr. Nedumaran's devotion and excellent professionalism has played a key role in transforming Levgum's DRC to a better and easier to implement product - Silsheet.

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DE-VULCANIZATION EFFICIENCY FOR SULFUR CROSSLINKED NATURAL RUBBER AND STYRENE BUTADIENE RUBBER

Jannik LAAGES and Ulrich GIESE

Deutsches Institut für Kautschuktechnologie e. V., Eupener Str. 33, 30519 Hannover jannik.laages@dikautschuk.de

Concerning sustainability of rubber products recycling especially of tires is of high interest. Following the policy of a circular economy, feedstock recycling of rubber products is preferable to mechanical recycling or energy recovery in cement plants. Feedstock recycling can only be achieved through selective scissoring of crosslinks, which were formed during the initial vulcanization step. For sulfur cured rubber carbon-sulfur and sulfur-sulfur bonds must be broken selectively. This process is called de-vulcanization.

This work focuses on thermo-chemical de-vulcanization for model tire tread compounds. A new approach to achieve optimal dispersion of the de-vulcanization agent in the rubber matrix is presented. As polymer-matrix natural rubber as well as styrene butadiene copolymer were used. The influence of the initial vulcanization system (semi-efficient (SEV), efficient (EV) and conventional (CV)) on the de-vulcanization efficiency were studied. Devulcanization efficiency was analyzed using two step soxhlet extraction and swelling experiment to determine additional sol fraction and decrease in crosslink density after treatment.

FOAMING AS A SUITABLE TOOL FOR ACHIEVING THE DESIRED PROPERTIES OF THERMOPLASTIC CABLES.

Henrich Krump, Peter Kapitán, Miloš Matej,

Bizlink Technology (Slovakia) s. r. o. 914 01 Trenčianska Teplá 1356, Slovakia <u>milos matej@bizlinktech.com</u>

The objective of this work was to find out whether foaming could be implemented to offer new propertycombinations for sheathing in electrical thermoplastic cables. Foaming, as a introduction of gas filled cells into hot polymer matrix via usage of chemical blowing agents was controlled through different set-up variants. Viscosity of the compound, selection of blowing agents, as well as screw design were crucial by achieving good homogeneity and cells distribution in the polymeric compound.

The foamed thermoplastic sheathing of cables exhibits a desirable properties like flexibility at bending tests, light weight or resistance to impact while maintaining standard mechanical and electrical properties.

The outcome of this work was recognized by receiving patents in US, China and Germany.

STUDY OF EPOXIDES WITH IMPROVED FLAME RESISTANCE BY CONE CALORIMETRY

Anna VYKYDALOVÁ*^{a,b}, Jozef RYCHLÝ^a, Edita MATYSOVÁ^d, Zdenko ŠPITÁLSKÝ^a

^a Polymer Institute, Slovak Academy of Sciences, Dúbravská cesta 9, 845 41 Bratislava, Slovakia

^b Institute of Inorganic Chemistry, Czech Academy of Sciences, Husinec-Řež 1001, 250 68 Řež, Czech Republic

^c Center for Advanced Materials Application SAS (CEMEA), Dúbravská cesta 5807/9

845 11 Bratislava, Slovakia

^d SYNPO, a.s., S. K. Neumanna 1316, 532 07 Pardubice, Czech Republic <u>anna.vykydalova@savba.sk</u>

Flame retardants are various chemicals applied to materials such as plastics, textiles, coatings and other products and building materials to prevent burning or slow the spread of fire. Flame retardants may even have the ability to prevent the initial ignition¹. Learning how these chemicals, and in what amounts, may cause human health effects and their balanced amounts on flammability is an area of active research. Although flame retardants can offer benefits when added to certain products, increasing scientific evidence shows that many of these chemicals may harm animals and humans². As generally known epoxides are highly reactive cyclic ethers. This property is widely used to manufacture plastics, adhesives, coatings, sealers, or primers. This property also can be used in other products as in materials for building and construction applications. Therefore, the study deals with the development of new more ecological and more environmentally friendly flame retardants.

Focus on the improvement of thermal and flame retardant properties of epoxy carbon laminates and so extend the possibilities of their applications, especially in the transport industry (aviation, automotive, train production) and possibly the construction industry is the aim of this study. Under the study are the research and development of novel flame retardants. Cone calorimetry was used to study the effect of the novel type of flame retardants that are environmentally more friendly and less toxic than the current ones. The novel flame retardants are covalently bound to the matrix and contain phosphazenes and an amine group. The results have shown that these flame retardants are a promising alternative to currently used products.

Acknowledgement

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THERMAL MATERIALS, ADHESIVES, SEALANTS & FUNCTIONAL COATINGS FOR ELECTRIC VEHICLES

Eduard Oswald

Henkel Slovensko s.r.o., Záhradnícka 91, 821 08 Bratislava eduard.oswald@henkel.com

Henkel is driving e-Mobility forward

As all major automotive OEMs and new players are rapidly launching new electric vehicle (EV) models, Henkel is leveraging its broad technology base and many years of expertise and experience to drive the transformation from traditional engines to electrified powertrains. The portfolio combines existing with new technologies to enable cost-efficient large-scale assembly and lifetime protection of battery architectures.

Strict regulatory fleet consumption and CO2 emission targets are shaping the challenges of the automotive industry. With hundreds of new EV models being designed and launched at an increasing speed, the integration and protection of batteries and electronic components play a crucial role. With a comprehensive range of technologies and deep know-how tailored to solving these new challenges, Henkel is determined to be the industry's leading full-solutions partner, supporting its customers from design to integration.

For battery manufacturers in specific, Henkel has identified three major challenges. First, as the value per battery kWh continues to be a significant commercial challenge, materials and adhesives applied in the assembly process of hundreds to thousands of cells in the battery pack need to provide high-speed curing and short cycle times. Second, for operational safety, solutions must comply with thermal management requirements as well as the UL94 flammability standard. Finally, to ensure lifetime performance of EVs, the battery pack housing requires technologies that will allow it to be reopened.

"Our innovative adhesive products and engineering services are playing a major role in optimizing the cost-efficient assembly, operational safety and lifetime protection of battery cells," says Frank Kerstan, Director e-Mobility & Powertrain at Henkel. "We are determined to support our customers at the forefront of e-Mobility with a seamless portfolio of technologies as well as application and process know-how for large-scale manufacturing, all available from a single source.

This is the reason why in 2019 several OEMs are launching a significant number of EV models that have been designed and assembled with Henkel technologies."

As shown on Figure 1, Henkel's solutions and services are focused on eight integrated key technologies that combine existing with new solutions:

1. Battery Assembly Adhesives:

Henkel offers multiple adhesives that are especially suitable for large scale assemblies of hundreds

and thousands of battery cells. For example, Loctite AA 3525 cures on demand with UV light within less than 15 seconds. Teroson MS 9396 is specialized for battery cell-to-cell bonding and battery case sealing. This modified-silane, easy-to-use one-component technology is environmentally friendly, non-solvent and non-silicone based. With proven performance of high temperature resistance up to 100°C and excellent elongation rate of 200 percent it ensures a stable and safe performance of the battery cells.

2. Thermal Gapfiller:

This new and specific developed thermally conductive silicone-free material with 3 W/mK performs under the harshest environmental conditions. Its cure in-place kinetics guarantees gap stability and robustness over lifetime. The unique rheology allows extremely fast dispensing for reduced processing times, decreased assembly forces and significant stress relieve for the battery cells and modules. Furthermore, the new filler technology with very low abrasiveness characteristics results in less maintenance to the dispensing equipment.

3. Thermal Adhesives:

To ensure safe and efficient thermal management of the battery cells and modules, thermal conductive adhesives such as Loctite UK 6800 and Loctite EA 9794 allow efficient heat transfer to cooling plates. The two-component polyurethane technology of Loctite UK 6800 has a thermal conductivity of 1.9 W/mK. To overcome different coefficients of thermal expansion, it also offers excellent adhesion on different substrates with a shear strength of > 10 MPa and high elongation of 44 percent.

4. Liquid Gasketing:

Henkel also provides numerous solutions to prevent leakages and variations in temperature within the battery pack housing. In order to meet the UL94 flammability standard, Teroson MS 939 FR has proven itself to be a reliable and high-performance technology. Likewise, Loctite SI 5970 acts as a custom-fit solution when it comes to resistance against oils and other automotive fluids. For the challenge of serviceability, Loctite AA 5884 (Asia: 5883) is a fast, UV light curing polyacrylate technology that provides sealing reliability by compression while allowing the battery pack housing to be reopened for repair.

5. Battery Structural Adhesives:

The structural integrity of a battery pack is relevant for dynamic load cases and crash performance. Henkel offers highstrength adhesives for aluminum and multi-metal battery frames with two-component epoxy products like Teroson EP 5065 or Loctite EA 9466.

6. Metal Pretreatment:

In the light of commercial challenges, Henkel surface technologies reduce process and maintenance costs resulting from reduced energy and water consumption. Battery housings, typically constructed of aluminum, need to be pre-treated in a cost-efficient way before painting. Henkel offers a variety of OEM approved processes: Bonderite M-NT 400, Bonderite M-NT 160 / 161 and Bonderite M-NT 5200. For mixed-metal applications, the patented Bonderite 2-step process allows energy savings and significant reduction of process sludge.

7. Conductive Coating:

Another key challenge for market success is to improve the charging and discharging performance of lithium-ion battery cells. Henkel has developed conductive coatings to overcome the weakness of the interface at the aluminum cathode. The technologies of Bonderite L-GP EB 012 and Bonderite S-FN 15000 lower the internal electrical resistance and increase the adhesion of the active material to the cathode for Lithium Iron Phosphate (LFP) and Lithium Nickel Manganese Cobalt (NMC) battery cells.

8. Impregnation Service:

Henkel's Loctite Impregnation Solutions (LIS) service leverages the flowability of low-viscosity polymeric resins to fill micro-porosities and voids ("leakers") and permanently seal components, such as aluminum casted battery housings. The company operates 30 LIS Service Centers worldwide, which are fully certified to IATF 16949, ISO 14001 and OHSAS 18001.

Henkel's comprehensive technology portfolio for EV battery architectures anticipates the needs of OEMs and suppliers from first design and prototyping to large-scale manufacturing of cells, modules and packs. More generally, backed by strong application know-how, R&D test centers around the world and strong strategic alliances (e.g. with RLE International), Henkel is in the unique position to be a partner for its customers' engineering teams. As such, the company is driving the future of e-Mobility by enabling the industry to solve its significant electrification challenges.

Bonderite, Loctite and Teroson are registered trademarks of Henkel and/or its affiliates in Germany and elsewhere.

About Henkel Henkel operates globally with a well-balanced and diversified portfolio. The company holds leading positions with its three business units in both industrial and consumer businesses thanks to strong brands, innovations and technologies. Henkel Adhesive Technologies is the global leader in the adhesives market – across all industry segments worldwide. In its Laundry & Home Care and Beauty Care businesses, Henkel holds leading positions in many markets and categories around the world. Founded in 1876, Henkel looks back on more than 140 years of success. In 2018, Henkel reported sales of around 20 billion euros and adjusted operating profit of around 3.5 billion euros. Henkel employs more than 53,000 people globally – a passionate and highly diverse team, united by a strong company culture, a common purpose to create sustainable value, and shared values. As a recognized leader in sustainability, Henkel holds top positions in many international indices and rankings. Henkel's preferred shares are listed in the German stock index DAX. For more information, please visit <u>www.henkel.com</u>.

The following illustration material is available at www.henkel.com/press-and-media.



Figure 1

Henkel provides a comprehensive technology portfolio and application know-how for efficient assembly, operational safety and lifetime protection of battery cells, modules and pack.



Figure 2

Henkel enables e-Mobility with different matching technologies for power storage systems, power generation systems and power conversion components of electric vehicles.

Acknowledgement & References 1. Henkel presentation materials

ELASTOMER COMPOSITES USING POLYSACCHARIDE BASED FILLERS FROM RENEWABLE RESSOURCES

Ulrich Giese

Deutsches Institut für Kautschuktechnologie e. V., Eupener Str. 33, Hannover (Germany) Email: <u>ulrich.giese@Dikautschuk.de</u>

Modern elastomers must fulfill several technical requirements, especially with increasing focus on light-weight composites for application in the fields of mobility or protection closes. Nanoscale polysaccharide materials from renewable resources promise interesting properties as filler materials in rubber because of their low density in comparison to carbon black or silica, high mechanical stability, anisotropy, barrier properties, chemical resistance and for most applications and processes sufficient thermal stability. The composition of polysaccharide materials like engineered polysaccharide from selective enzymatic polymerization of sucrose in water to α -1.3-glucans¹ or especially nanofibrillated cellulose (NFC) in combination with chemical surface modifications for improvement of filler-polymer interaction lead to high reinforcement effects in different rubber matrices. In this work, glucan-derivates or commercial available nano-fibrillated cellulose (NFC) materials were (i) characterized fundamentally as raw material and (ii) incorporated into different rubber matrices like NR, NBR, BIIR or CR by means of a special latex mixing technology in combination with chemical such as transmission electron microscopy (TEM), tensile testing, swelling, permeation behavior against gases and rheometry were used to characterize the polymer-filler interaction and the compound properties. Additionally, hybrid filler systems with polysaccharide and carbon black were prepared. The prepared nanocomposites show high stiffness, good tensile properties and improved permeation resistance against gases as well reduced density.

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EFFECTS OF VARYING HUMIDITY CONDITIONS ON THE MECHANICAL PROPERTIES OF THERMOPLASTIC STARCH-MONTMORILLONITE NANOCOMPOSITE DURING AGING

Hamed Peidayesh, Ivan Chodák*

Polymer Institute of the Slovak Academy of Sciences, Dúbravská cesta 9, 845 41 Bratislava, Slovakia ivan.chodak@savba.sk

1. Introduction

Thermoplastic starch (TPS) is a plasticized nonstructured version of starch. It is usually prepared by incorporation of plasticizers into a starch matrix under heat and shear conditions. TPS-based bioplastic nanocomposites represent an exciting and promising alternative to conventional plastics since they are cost-effective, renewable, abundant in nature, and biodegradable^{1,2}. Moreover, it has been widely used as an excellent candidate for partial replacement of synthetic polymers in food packaging, automotive, medical, pharmaceutic, and agricultural industries. Addition of TPS to biodegradable compostable bioplastics is a useful application of TPS aimed to a decrease of price compromising certain deterioration of physical, especially mechanical properties. However, TPS suffers from recrystallization phenomena caused by humidity. This evolution is highly detrimental, as it leads to a drastic decrease in its mechanical properties during storage^{3,4}. The addition of a definite amount of nanofillers can significantly improve the physico-chemical properties of TPS which can also influence the biological activities of TPS-based materials.

As the main groups of nanofillers, the layered silicates are frequently used for the preparation of polymer nanocomposites. Moreover, clay-based nanocomposites have found wide use in production of environment-friendly automotive parts and packaging materials. For example, Toyota Company became the first to fabricate nanocomposites based on layered silicates for automotive applications in the 1980s. Thermoplastic olefin nanocomposite reinforced with as little as 2.5% clay particles has also been employed by General Motors⁵. The ultimate properties of TPS–MMT nanocomposites are closely related to the arrangement of starch chains, molecular dynamics, and the dispersion of the clay fillers within the TPS matrix.

In designing TPS for a given purpose, mutual correlations between the source of starch, method of its modification, processing technique, physical and material parameters, as well as performance in various conditions should be considered. It is well known that TPS-based materials are sensitive to the surrounding relative humidity and storage time, which substantially affect their mechanical properties.

This contribution is focused on investigating the influence of aging under exactly defined relative humidities on the mechanical properties of TPS-MMT nanocomposite which no study has been done yet.

2. Experimental

2.1. Materials

Native corn starch Meritena[®] 100 was provided by Brenntag (Bratislava, Slovakia). The water content was around 12 wt% as determined by drying in the oven at 100 °C for 5 h. Natrified montmorillonite (Cloisite[®] Na⁺) with a cationic exchange capacity range of 80–95 mequiv/100 g was provided by Southern Clay Products (Texas, Gonzales, USA). Glycerol was purchased from Centralchem, Ltd. (Bratislava, Slovakia).

2.2. Preparation of TPS and TPS-MMT nanocomposites

Cloisite[®] Na⁺ (MMT) particles at 0.02 part (parts based on the dry weight of starch) were dispersed in water and glycerol mixture by mechanical mixing at ambient temperature for 5 min. Then, starch powder was added to the prepared mixture. The weight ratio of starch/glycerol/water was 1.0:0.5:2.3. To obtain gelatinized starch, the mixture of starch, glycerol, and MMT was heated at 80 °C for 10 min under continuous mixing for complete gelatinization. Afterward, the suspensions were dried in an oven at 100 °C for 5 h followed by maintaining overnight at 60 °C to prevent moisture absorption. Each sample was kneaded in a laboratory mixer Plastograph Brabender PLE 331 for 10 min at 130 °C and 100 rpm. 1 mm thick slabs were prepared by compression molding (laboratory press, LabEcon 300) at 130 °C using 2 min preheating without pressure and an additional 2 min at a pressure of 2.65 MPa.

The obtained samples were stored in desiccators at different relative humidities (RH) namely 11, 55 and 85% using saturated salt solutions at 25 °C with lithium chloride (LiCl), magnesium nitrate (Mg(No₃)₂), and potassium chloride (KCl), respectively.

2.3. Mechanical properties

Dumbbell-shaped test specimens with a $3.5 \text{ mm} \times 30 \text{ mm}$ dimension of the deformed area (thickness of approximately 1 mm) were punched by pneumatic toggle press equipment. The tensile properties were measured by using an Instron 3365 (Instron, USA) universal testing machine in uniaxial deformation at a cross-head speed of 1 mm/min up to 1% deformation (to determine Young's modulus) followed by a speed of 50 mm/min at higher deformations.

Dynamic mechanical thermal analysis (DMTA) was performed using the instrument DMA Q800 (TA Instruments, Germany). The specimens (ca. 10 mm \times 7 mm \times 1 mm) were measured in tensile mode at a frequency of 10 Hz and amplitude of dynamic deformation of 20 μ m. The experiments were carried out in the temperature range from -70 °C to 140 °C at a heating rate of 2 °C/min.

2.4. Moisture content

The weight of dried TPS and TPS–MMT specimens (W_l) was measured after keeping them at 80 °C for 4 h. Then, the samples in triplicate were placed in desiccators with various relative humidities and weighed (W_2) after various time intervals. The total moisture content (MC), in percentage, was calculated according to the following equation:

$$MC (\%) = \frac{W_2 - W_1}{W_1} \times 100 \tag{1}$$

3. Results and discussion

3.1. Moisture content

The moisture content of TPS and TPS–MMT nanocomposites conditioned at 11, 55, and 85% RH during storage is shown in Figure 1. It can be seen that the most significant increase in water absorption occurred within the first week of storage for all samples. This result was expected due to drying the samples before conditioning them at various humidity levels. Moreover, as seen in Figure 1, the TPS and TPS–MMT samples reached equilibrium after one week at 11 and 55% RH, while they were absorbing moisture at 85% RH for up to five weeks to reach equilibrium.



Figure 1. Moisture content curves for (a) TPS and (b) TPS–MMT samples stored at 11, 55, and 85% RHs for different storage times.

3.2. Tensile testing

Mechanical properties are considered to be important parameters considering TPS performance. These properties depend significantly on surrounding relative humidity and storage time. The values of ultimate tensile strength, elongation at break, and Young's modulus for TPS and TPS–MMT samples conditioned at various humidities for one and seven weeks are shown in Table 1. It can be revealed that the tensile strength and Young's modulus of the dried samples and the samples stored at 11% RH increase with the incorporation of MMT due to the formation of hydrogen bonds between starch chains, water, glycerol, and hydroxyl groups of MMT layers³. Considering the relation of tensile strength changes with humidity, it is seen that the tensile strength of both TPS and TPS–MMT samples is decreasing with rising RH, while the tensile strength of the dried samples and the samples stored at 11% RH are identical. Moreover, the increase in RH results in a remarkable decrease in Young's modulus in comparison with the dried samples. The higher amount of absorbed water at higher RH led to an increase in the mobility of starch chains which was caused by additional plasticizing effect.

| Table 1. Mecha | anical properties, | , including tensile | e strength, e | longation at | t break, and | l Young's | modulus | of the | TPS and |
|----------------|--------------------|---------------------|---------------|--------------|--------------|-----------|---------|--------|---------|
| TPS-MMT sam | ples stored at var | rious humidities f | for one and s | even weeks | 5. | | | | |

| | Samula Cada | ample Code Dried | | 11% RH | | 55% RH | | 85% RH | |
|------------------|-------------|------------------|----------------|---------------|--------------|--------------|--------------|-------------|--|
| | Sample Code | Drieu | 1 week | 7 weeks | 1 week | 7 weeks | 1 week | 7 weeks | |
| Tensile Strength | TPS | 7.8 ± 2.7 | 9.3 ± 0.8 | 6.8 ± 0.5 | 1.3 ± 0.0 | 2.5 ± 0.1 | 1.3 ± 0.0 | 0.6 ± 0.1 | |
| (MPa) | TPS-MMT | 10.4 ± 1.1 | 11.5 ± 1.0 | 7.6 ± 0.2 | 1.4 ± 0.1 | 2.4 ± 0.4 | 1.3 ± 0.1 | 0.6 ± 0.1 | |
| Elongation at | TPS | 1.5 ± 0.3 | 4.3 ± 1.6 | 27.1 ± 11.5 | 66.6 ± 2.1 | 34.4 ± 2.0 | 25.3 ± 1.2 | 8.2 ± 0.4 | |
| break (%) | TPS-MMT | 1.7 ± 0.2 | 3.7 ± 0.8 | 31.4 ± 5.0 | 64.1 ± 8.9 | 27.8 ± 5.5 | 24.7 ± 1.1 | 7.6 ± 1.3 | |
| Young's Modulus | TPS | 970.2 ± 207.5 | 662.9 ± 74.7 | 297.4 ± 2.4 | 9.2 ± 0.5 | 25.2 ± 3.4 | 10.5 ± 0.4 | 9.4 ± 0.8 | |
| (MPa) | TPS-MMT | 1148.2 ± 47.4 | 703.0 ± 68.9 | 435.9 ± 4.3 | 10.0 ± 1.1 | 26.5 ± 1.3 | 10.9 ± 0.6 | 9.7 ± 0.5 | |

Regarding the aging effect, the TPS samples stored at 11% RH showed a decrease in tensile strength and Young's modulus which might be related to the physical aging of the samples. The TPS samples stored at 55% RH showed a slight increase in tensile strength and Young's modulus. This phenomenon can be explained by formation of new interactions between starch, glycerol, and water after reaching the equilibrium moisture content, resulting in the formation of hydrogen bonds. On the other hand, the TPS samples stored at 85% RH presented a decrease in all mechanical properties. 3.3. Dynamic Mechanical Thermal Analysis (DMTA)

The tan δ curve of the TPS and TPS-MMT samples stored at various humidities for different times of storage is shown in Figure 2. Tan δ as a function of temperature for TPS samples indicated two relaxation peaks. The lowtemperature relaxation peak corresponds to the glass transition of glycerol-rich domains, while the high-temperature peak is ascribed to the starch-rich domains¹. As expected, T_g values for TPS-MMT nanocomposites are higher than for TPS samples due to the restrictions in starch chain mobility caused by a certain extent of intercalation of plasticizer molecules and starch chains into the MMT platelet galleries². It is seen that the first peak, which is controlled by the plasticizer molecular motion, showed a shift to lower temperature for samples stored at higher RH, indicating that regions rich in glycerol or water might be formed during water absorption. The presence of more water may decrease the intermolecular hydrogen bond density. However, low water content could not significantly affect the starch chain mobility, leading to preventing recrystallization during storage.



Figure 2. Tan δ curves for TPS and TPS-MMT samples stored at 11, 55, and 85% RHs for one, two, and seven weeks of storage.

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EFFECT OF PLASTICIZERS ON STRUCTURE AND MOLECULAR MOBILITY OF THERMOPLASTIC STARCH-BASED NANOCOMPOSITES

<u>Leoš ONDRIŠ¹, Simona SAPAROVÁ¹</u>*, Oľga FRIČOVÁ¹, Mária KOVAĽAKOVÁ¹, Hamed PEIDAYESH², Ivan CHODÁK²

¹Department of Physics, Faculty of Electrical Engineering and Informatics, Technical University of Košice, Park Komenského 2, 042 00 Košice, Slovakia

²Polymer Institute, Slovak Academy of Science, Dúbravská cesta 9, 845 41 Bratislava 45, Slovakia <u>leos.ondris@tuke.sk</u>, <u>simona.saparova@tuke.sk</u>, olga.fricova@tuke.sk, maria.kovalakova@tuke.sk, hamed.peidayesh@savba.sk, ivan.chodak@savba.sk

The research of biodegradable polymer materials is very topical, as these materials have a great potential to replace commonly used plastics. Starch-based polymer materials are in high demand since plasticization of natural starch, which is cheap and renewable polymer, provides 100% biodegradable polymer material - thermoplastic starch (TPS). TPS properties depend on the type, amount and combination of used plasticizers as well as the method of preparation. Another possibility how to influence TPS properties is to add to its structure a small amount of nanofiller¹. Clays are the most commonly used nanofillers². TPS-based nanocomposites can be studied using various experimental methods. In this paper, the effect of plasticizers on structure and molecular mobility of TPS-based nanocomposites prepared with montmorillonite (MMT) as nanofiller studied using nuclear magnetic resonance (NMR), X-ray diffraction (XRD) and dynamic-mechanical analysis (DMA) is reported.

The studied samples were prepared by thermomechanical processing of native corn starch (PS – plasticized starch) Meritena[®]100 with glycerol (G) and/or urea (U) as plasticizers and in distilled water-dispersed montmorillonite nanoparticles Cloisite[®] Na⁺ (M). A weight ratio of dry native starch, water, plasticizer(s) and MMT was 1:2.3:0.5:0.02, the weight ratio of G:U in the GUPSM sample was 1:1. The detailed information on sample preparation was already reported³.

The ¹**H BL NMR spectra** of all studied samples consist of one broad and one narrow signals (Figure 1 a)). The broad signal is attributed to ¹H nuclei in less mobile starch chains and bound molecules of plasticizers and water, the narrow signal is attributed to ¹H nuclei in mobile molecules of plasticizers, water, and in more mobile starch chains. The spectra of samples containing only glycerol differ from the spectra for urea containing samples. The spectra were deconvoluted and the data obtained are listed in Table 1. The narrow signals in the spectra for GUPSM and UPSM samples are considerably broader. The ratio of narrow and broad signal intensity is higher for samples containing only glycerol than for urea containing samples. The smaller width of the broad signal in the spectra for GPS and GPSM samples compared to the width of the broad signal in the spectra for GUPSM and UPSM samples indicates higher starch chains mobility when the starch is plasticized only with glycerol. From this, it can be concluded that glycerol is responsible for the increase in the mobility of starch chains. A comparison of the spectra for GPS and GPSM samples shows that the presence of MMT causes broadening of the narrow signal, which is probably due to the interaction of glycerol with MMT⁴.



Figure 1. ¹H BL NMR spectra and deconvolution of GPSM spectrum (a)), central parts of ¹H MAS NMR spectra (b)) and ¹³C CP/MAS NMR spectra (c)) of studied samples

| | Narro | ow signal | Broa | Broad signal | | |
|---------|----------------|--------------------|----------------|--------------------|--|--|
| Sample* | Linewidth (Hz) | Rel. intensity (%) | Linewidth (Hz) | Rel. intensity (%) | | |
| GPS | 2000 | 37.8 | 25300 | 62.2 | | |
| GPSM | 2300 | 38.8 | 25400 | 61.2 | | |
| GUPSM | 3400 | 29.5 | 27000 | 70.5 | | |
| UPSM | 3500 | 27.4 | 27300 | 72.6 | | |

Table 1. Deconvolution of ¹H BL NMR spectra of studied samples

*G - glycerol, PS - plasticized starch, M - montmorillonite, U - urea

The ¹**H MAS NMR spectra** for GPS and GPSM samples consist of a central part with one broad signal and two well-resolved signals (Figure 1b)), and rotational signals (not shown). The signals at chemical shifts of 3.7 and 5.2 ppm originate from the ¹H nuclei in the CH, CH₂ and OH groups of glycerol, respectively, signal from ¹H nuclei in water expected at chemical shift of 4.8 ppm is too broad to be resolved. The ¹H starch nuclei produce a broad background signal. From the comparison of the ¹H MAS NMR spectra of the GPS and GPSM samples can be inferred, that MMT addition causes a slight broadening of the signals resulting from restricted mobility of glycerol molecules due to their possible interaction with MMT particles. The central parts of the ¹H MAS NMR spectra for the UPSM and GUPSM samples consists of one broad signal at chemical shifts of 5.3 and 4.3 ppm, respectively which are produced by ¹H nuclei in water and plasticizers.

The ¹³C CP/MAS NMR spectra of GPS and GPSM samples consists of 5 signals (Figure 1 c)). Signals with chemical shift values of 103.1 ppm, 82.6 ppm, 73.1 ppm, 63.9 ppm and 62.0 ppm are attributed to carbon C1, carbon C4, ¹³C nuclei in CH and in CH₂ groups of glycerol and carbon C6, respectively. The signal marked as C4 comes only from C4 carbons in the amorphous regions of the sample, while the signal from the C4 carbons in the crystalline regions overlaps with the signals from the C2, C3, and C5 carbons⁵. Addition of MMT (GPSM sample) did not significantly change the ¹³C CP/MAS NMR spectrum. In the ¹³C CP/MAS NMR spectra of samples containing urea, the signal at chemical shift of 162.7 ppm (UPSM), or 163.1 ppm (GUPSM) is attributed to the ¹³C nuclei in urea. The resonances of the C1 carbons in the spectra for UPSM and GUPSM samples show only one broad signal with an amplitude at chemical shift of 103.1 ppm. The shape of this signal indicates that the starch chains are disordered in these samples. However, in the spectra for GPS and GPSM samples a broad signal in the chemical shift range of 92-108 ppm is a superposition of the signals of the C1 carbon nuclei in ordered and disordered starch chains with different conformations. The spectra for glycerol containing samples display in C6 signal range a signal at chemical shift of 63.7 ppm produced by CH₂ groups in glycerol. The small width of these signals in the spectra for GPS and GPSM samples points to the high mobility of glycerol molecules. The intensity of this signal increases with the increasing amount of glycerol and its width is larger for GUSPM sample. In the ¹³C CP/MAS NMR spectrum for UPSM sample, a relatively broad signal from the C6 carbons is observed, which points to a wide distribution of conformations, which is typical for amorphous polymers. This signal has a chemical shift value of approximately 1 ppm lower, which may be due to the higher urea content in the sample. If the urea content in the sample is higher than 10%, some urea molecules do not form hydrogen bonds with the starch molecules due to the lack of active sites on the starch molecules⁶.

The X-ray diffraction patterns of the studied samples are shown in Figure. 2a). Neat MMT nanofiller gives diffraction maximum at $2\theta \approx 7.6^{\circ}$ corresponding to the distance $d_{001} = 1.17$ nm of inter-layers space. In all diffractograms (except for the GPS sample), this maximum shifts to lower $2\theta \approx 4.8^{\circ}$ values due to the increase in d_{001} indicating intercalated MMT⁷. Small intensity maxima observed at $2\theta \approx 20.7^{\circ}$ and in the case of the GPSM sample also at $2\theta \approx 13.4^{\circ}$ are attributed to the V_A-type TPS crystalline regions which are associated with recrystallization of amylose chains. Another low intensity maximum at $2\theta \approx 19.7^{\circ}$ corresponds to the V_H-type TPS crystalline regions⁸. In the diffractogram for UPSM sample distinct diffraction maxima at $2\theta \approx 22.1^{\circ}$, $2\theta \approx 24.5^{\circ}$ and $2\theta \approx 29.1^{\circ}$ are observed, which correspond to the crystalline urea⁹. This indicates that urea crystallization occurred in the urea-rich domains. These diffraction maxima were not observed for the GUPSM sample, which may be explained by lower urea content compared to the UPSM sample, and by the interaction between the urea and glycerol molecules. From comparison of diffractograms for GPS and GPSM samples, it can be inferred that the addition of MMT to TPS matrix led to slightly more pronounced V_H-and V_A-type crystalline structure. This could indicate that the MMT particles in the nanocomposite may act as nucleation centres for the crystallization of amylose chains.



Figure 2. XRD diffractograms (a)) and temperature dependences of loss factor tan δ (b)) of all studied samples

DMA measurements in the temperature dependence of the loss factor tan δ for all sample are shown in Figure. 2b). For GPS, GPSM and GUPSM samples two maxima in tan δ temperature dependences were observed. The first relaxation transition between -40°C and -24°C correspond to the glass transitions in plasticizers-rich domains^{10,11}. The larger width of the maximum for the plasticizer-rich domains of the GUPSM sample can be explained by overlapping of the temperature intervals of relaxation processes in urea and glycerol-rich domains, as well as by the interaction between glycerol and urea causing the shift of the relaxation transition to higher temperatures¹⁰. The second maximum on the tan δ temperature dependences (observed at 55°C) corresponds to the glass transition of starch-rich domains. The processes associated with the segmental motion of the amylopectin and amylose chains in GPS, GPSM and GUPSM samples occur in approximately the same temperature interval (one broad maximum)¹¹. In the case of UPSM sample tan δ temperature dependence displays three maxima. The first maximum (at -20°C) corresponds to the glass transition in urea-rich domains. The second maximum (at 38°C) is attributed to the segmental motion of amylopectin chains is observed^{10,11}. Urea makes starch chains less flexible, it prevents formation V_A- and V_H-type of crystalline structures and for this reason relaxation transitions of linear amylose and branched amylopectin can be distinguished and occur at different temperatures⁹.

From the NMR measurements, it can be concluded that glycerol is responsible for the increase in the mobility of starch chains. The ordered structures in the only urea containing samples were not detected. Addition of MMT did not significantly change NMR spectra of studied samples. XRD measurements confirmed formation of intercalated MMT structure, formation of V_A - and V_H -type crystalline structure in glycerol containing nanocomposites. DMA measurements of all samples shows that the plasticizers are not homogeneously distributed in the samples and the type of plasticizer influences mobility of starch chains.

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CHEMICAL MODIFICATION OF POLY(ETHYLENE-PROPYLENE) COPOLYMER USED IN HOT-MELT ADHESIVES

<u>Zuzana NÓGELLOVÁ</u>¹, Juraj PAVLINEC¹, Jozef RYCHLÝ¹, Igor NOVÁK¹, Angela KLEINOVÁ¹, Jozef PREŤO², Vladimír VANKO² and Ivan CHODÁK¹

¹ Polymer Institute, Slovak Academy of Sciences, Dúbravská cesta 9, 845 41 Bratislava, Slovakia ² VIPO, a.s., ul. Gen. Svobodu 1069/4, 958 01 Partizánske, Slovakia <u>zuzana.nogellova@savba.sk</u>

<u>1. Introduction</u>

The aim of this work was to improve adhesive properties of hot-melt adhesives based on metallocene polyolefins for bonding polar materials, as paper, cardboard or wood.

Metallocene polyolefins (MePO) are often used as the main component of hot-melt adhesives (HMA)¹⁻². Polyolefins are basically nonpolar, with low surface energy. For bonding polar materials, it is important to increase the polarity of the adhesive. It can be achieved either by adding a polar additive into the adhesive composition or by chemical modification of the nonpolar chains of one of the polymers used in HMA by polar functional groups of selected polar monomer³. The latter way may be preferred since the introduction of an additional additive might affect the processing and/or application properties of HMA¹. The grafting of the selected monomer in form of side branches onto the MePO polymer chain takes place by a free-radical mechanism. The activation of grafting reaction onto polymer chains may be initiated either by thermal decomposition of organic peroxides⁴ or by radiation⁵. In some case also ozonation using a mixture of ozone and oxygen was applied⁶.

The presented contribution describes the procedure of the grafting of acrylic acid (AA) as polar monomer onto metalocene poly(ethylene-co-propylene) activated by using ozone-oxygen mixture. The grafted MePO was consequently applied as a component of HMA to increase the adhesion properties. The efficiency of grafting, as well as surface and adhesion properties were evaluated.

2. Experimental

2.1. Materials

The random metallocene ethylene-propylene copolymer Licocene PP 2602 (Clariant, Muttenz, Switzerland), with Tm = 95,1 °C, Tg = 57 °C and density = 0.874 g/cm³ was used as the main component of the HMA, as well as for the preparation of the component grafted with acrylic acid. Other polymers included in HMA composition were Licocene PP 3602 and PP 1302 (both metallocene propylene–ethylene copolymer, Clariant). Licowax PE 520 - a medium-molecular weight polyethylene (Clariant) with dropping temperature T = 120 °C was used for viscosity adjustment, and Escorez 5600 - an aromatic modified, cycloaliphatic hydrocarbon resin (Exxon Mobil Chemical, Houston, TX, USA) was applied as a tackifier. Kinox-10 - pentaerythrityl tetrakis [3-(3,5-di-tert.butyl-4-hydroxyphenyl) propionate] (HPL Additives, Haryana, India) was used as an antioxidant. Regalite R 1100 - a low-molecular weight fully hydrogenated hydrocarbon (Eastman, Kingsport, TN, USA) was used as a tackifying resin.

Acrylic acid (AA) (99% monomer purity, Sigma-Aldrich, St. Louis, MO, USA) was used for grafting. Sodium laurylsulfate (NaLS) (purity \geq 98%, Aldrich) was added as a wetting agent in the grafting process.

2.2. Grafting of acrylic acid on Licocene PP 2602

The grafting of Licocene PP 2602 (LC) with acrylic acid was initiated by activation of the polymer molecules with a mixture of $O_2 + O_3$. Ozone was generated by passing oxygen through a Profizon X ozone generator (UVC Servis, Prague, Czech Republic). The ozone concentration in the mixture with oxygen was 17.8 mg/L. Polymer was in form of powder.

Grafting of ozonated Licocene PP 2602 with acrylic acid proceeded in a 50 mL chamber of a Brabender Plasticorder PLE 331 laboratory mixer (Brabender, GmbH, Duisburg, Germany). The grafting temperature was set to 120 °C and the intensity of mixing was 30 rpm. The optimized composition of the reaction mixture consisted of basic LC polymer mixed with 18.5 wt.% of acrylic acid, and 0.5 wt.% of NaLS was added to increase the homogeneity of polar acrylic acid in nonpolar polyolefin. After completing the grafting reaction, the content of acrylic acid in the final product was 11.4 wt.% according to FTIR analysis.

2.3. The efficiency of grafting

The concentration of HPx and Px groups bonded to LC was determined by modified iodine analytical procedure⁷. The presence of peroxides, their thermal stability and kinetics of decomposition were monitored by chemiluminescence

(CL) using a LUMIPOL 3 photon-counting instrument (commercial product of Polymer Institute SAS, Bratislava, Slovakia)⁸. The measurements were performed in a temperature range between 50 and 250 °C, with a heating rate of 5 °C per minute. The instrument dark count rate was 2–3 counts/second, and the resolution level at 40 °C was 2 photons/second.

2.4. Experimental HMA preparation and characterization

The grafted Licocene copolymer was used in varying amounts as the additive for the experimental HMA. The samples were used for evaluation of surface and adhesive properties.

The samples for analytical procedures were prepared by compression molding to disks 1 mm thick with a 20 mm diameter at a temperature of 180 °C. The molding time was 3 minutes.

2.5. Surface properties

A Professional Surface Energy Evaluation (SEE) system with a CCD camera (Advex Instruments, Brno, Czech Republic) was used for experiments and the sessile drop technique was applied. The hydrophilicity of LC-g-AA surfaces was evaluated by measuring the contact angles using three testing liquids, namely redistilled water, glycerol and dimethyl sulfoxide. The volume of a drop of the testing liquid was 3 μ L. From obtained data the surface free energy (SFE) and its polar (γ s^p) and dispersive (γ s^d) component were determined.

2.6. Adhesive properties

To assess the strength of adhesion of paper to the HMA based on the modified MePO, a specific method was developed. The adhesive joints were prepared by applying a 500 μ m thick film of adhesive on a medium-density fiber board (MDF) and consequently anchoring 50 sheets of 135 g/m² paper with an area of 90mm x 90mm on the glued side of the board. Individual sheets of paper were subsequently ripped off in the specified order using an Instron 4301 universal testing machine (Instron, Norwood, MA, USA). The adhesion value was determined as the tensile strength, calculated in N per 90 mm, of the adhesive joint of HMA to paper to pull out one paper sheet. Measurements of the strength of adhesive joints were tested at 9 places of the testing paper binding and the final extent of adhesion was expressed as average values of adhesive strengths and statistical deviations.

3. Results and discussion

3.1. The efficiency of grafting

The concentration of hydroperoxide groups attached on chains of Licocene was determined by iodine titration. As seen in Table 1, the dependence of HPx concentration on the time of ozonation is nearly linear.

Thermal stabilities and decomposition of hydroperoxides presented in the activated polymer were evaluated by chemiluminescence. The dependence shown in Figure 1 confirms that several types of HPx groups with different thermal stability are formed on the macromolecule backbones of LC copolymer during ozonation.

Table 1. Time dependence of hydroperoxide (HPx) concentration on Licocene PP 2602 molecules formed during ozonation.

| Time (min) | HPx (10 ² mol/kg) |
|------------|------------------------------|
| 30 | 1.14 |
| 60 | 2.75 |
| 120 | 3.40 |
| 180 | 6.90 |

Figure 1. Chemiluminescence intensity of Licocene PP 2602 activated by ozone at various ozonation times.

The FTIR analysis of pristine LC (plot a) and AA-grafted LC (plot b) is illustrated in Figure 2. The presence of grafted PAA in LC-g-AA was proven by FTIR analysis. The bands of functional groups C-O and COC (1715 cm⁻¹ and 1170 cm⁻¹, respectively) indicate the presence of PAA chains. The ratio of the FTIR absorbance intensities of acid carbonyl compounds at 1715 cm⁻¹ and the reference band at 1464 cm⁻¹ was used to determine the PAA concentration in the grafted copolymer.



Figure 2. FTIR spectra of Licocene PP 2602: virgin (a) and grafted with 11.4 wt.% of acrylic acid (b).

3.2. Properties of grafted Licocene 2602

The results of the surface property measurements of PAA-grafted LC are summarized in Table 2. A decrease of the



water contact angles was observed with an increase of the concentration of LC grafted with 11.4 wt.% of PAA from 95.9° (for reference nongrafted LC) to 67.4° (for 27.3 wt.% of LC grafted with 11.4 wt.% of PAA), and the polar component of the SFE increased four times from 1.2 to 4.8 mJ.m⁻². On the other hand, grafting AA onto LC did not lead to any changes in the dispersive components of SFE.

The polarity of the polymers as well as the HMA is expressed by a polar fraction, which is represented by the ratio of the polar component of the free surface energy to the total surface energy. The polar fraction (xs^p) of LC after grafting significantly increased from 0.04 (pristine sample) to 0.14 (sample with 27.3 wt.% of PAA).

Table 2. Contact angles measured for water (WCA), glycerol (GCA) and dimethyl sulfoxide (DCA), surface free energy (SFE) and its polar (PC SFE) and dispersion (DC SFE) components and polarity (xs^p) of Licocene PP 2602 grafted with 11.4 wt.% acrylic acid.

| PAA Grafted in LC (wt.%) | WCA (°) | GCA (°) | DCA (°) | SFE (mJ.m ⁻²) | PC SFE (mJ.m ⁻²) | DC SFE (mJ.m ⁻²) | xs ^p |
|--------------------------------|------------------------|------------------------|------------------------|------------------------------|---------------------------------|---------------------------------|-----------------|
| 0 | $95.9\pm2.8^\circ$ | $74.7 \pm 2.4^{\circ}$ | $47.0 \pm 2.2^{\circ}$ | 31.8 | 1.2 | 30.6 | 0.04 |
| 4.5 | $88.4 \pm 2.6^{\circ}$ | $72.4 \pm 2.6^{\circ}$ | $48.2 \pm 1.9^{\circ}$ | 32.8 | 2.8 | 30.0 | 0.09 |
| 9.1 | $84.8 \pm 2.2^{\circ}$ | $69.2 \pm 2.8^{\circ}$ | $49.8\pm2.4^\circ$ | 33.4 | 3.6 | 29.8 | 0.11 |
| 11.4 | $74.8\pm2.6^\circ$ | $65.2 \pm 3.2^{\circ}$ | $51.2 \pm 2.1^{\circ}$ | 33.6 | 4.0 | 30.0 | 0.12 |
| 14.0 | $71.8 \pm 2.8^{\circ}$ | $62.8\pm2.4^\circ$ | $54.8 \pm 2.2^{\circ}$ | 34.8 | 4.4 | 30.4 | 0.13 |
| 27.3 | $67.4 \pm 2.2^{\circ}$ | $60.2 \pm 2.1^{\circ}$ | $55.6\pm2.6^\circ$ | 35.2 | 4.8 | 30.4 | 0.14 |

3.3. Properties of the hot-melt adhesives

The surface properties of prepared materials are shown in Table 3. The water contact angle (WCA) decreased with increasing polar component in the HMA (from 96.8 to 72.8°), and the polar component of the free surface energy increased from 1.8 to 3.3 mJ.m⁻².

Figure 3 summarizes the effect of concentration of the polar additive on the strength of the adhesive joint HMA/paper. The effect of polar content on the HMA adhesion strength is statistically significant and technologically interesting for the sample with the highest content, i.e. 0.544 wt.% of the polar additive, which reached a strength value of the adhesive joint of 142.3 N/90 mm compared with an adhesion of 117.9 N/90 mm for the pristine sample. This justifies the application of the AA-grafted polar modifier in HMA.

Table 3. Contact angles for various testing liquids (redistilled water WCA, glycerol GCA, and dimethyl sulfoxide DCA), surface free energy (SFE), and its polar (PC) and dispersion (DC) components of the HMA modified with AA-grafted Licocene PP 2602.

| Polar Component (wt.%) | WCA (°) | GCA (°) | DCA (°) | SFE (mJ.m ⁻²) | PC SFE (mJ.m ⁻²) | DC SFE (mJ.m ⁻²) |
|------------------------------|------------------------|------------------------|------------------------|------------------------------|---------------------------------|---------------------------------|
| 0 | $96.8\pm3.4^\circ$ | $69.1 \pm 2.4^{\circ}$ | $60.4 \pm 1.9^{\circ}$ | 31.2 | 1.8 | 29.4 |
| 0.068 | $84.2 \pm 3.2^{\circ}$ | $58.5 \pm 1.9^{\circ}$ | $63.2\pm2.4^\circ$ | 31.6 | 2.3 | 29.3 |
| 0.136 | $88.7\pm3.0^\circ$ | $61.5 \pm 2.2^{\circ}$ | $62.8 \pm 1.9^{\circ}$ | 31.9 | 2.2 | 29.7 |
| 0.272 | $76.2 \pm 2.2^{\circ}$ | $54.5\pm2.1^\circ$ | $52.3\pm2.3^\circ$ | 32.2 | 2.9 | 29.3 |
| 0.544 | $72.8 \pm 3.0^{\circ}$ | $51.6 \pm 3.5^{\circ}$ | $49.3\pm2.4^\circ$ | 32.7 | 3.3 | 29.4 |



Figure 3. Effect of the polar additive content on the tensile strength of the adhesive joint HMA/paper: A - 0 wt.%, B - 0.068 wt.%, C - 0.136 wt.%, D - 0.272 wt.%, E - 0.544 wt.% of polar component.

4. Conclusions

Ozonation of one of the main polymeric components of the hot-melt adhesive, namely poly(ethylene–co-propylene) Licocene PP 2602, leads to the formation of peroxides attached to the polymer chain, which initiate the grafting of highly polar acrylic acid on it. The addition of a small amount (0.544 wt.%) of such polymeric additive grafted with highly polar functional groups results in a significant increase in the adhesion of HMA to polar surfaces via an increased surface free energy of the HMA.

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SPECTROSCOPIC STUDY OF ELEMENTAL AND MOLECULAR EMISSIONS FROM POLYMER MATRIXES BY LASER INDUCED BREAKDOWN SPECTROSCOPY (LIBS).

Kristína VIROSTKOVÁ^a, <u>Alena MATELOVÁ^b</u>, <u>David GREBENÍČEK^b</u> and Franky PUYPE^{b*}

^aAtomtrace, a.s. Kolejní 3094/9, 612 00 Brno - Královo Pole, Czech Republic ^bInstitute for Testing and Certification, Inc., tř. Tomáše Bati 299, Louky, 763 02 Zlín, Czech Republic, fpuype@itczlin.cz

Introduction

Laser Induced Breakdown Spectroscopy (LIBS) is a promising optical emission tool for quick characterization of elements in a broad range of materials ranging from biological matrixes to geological materials and as well polymer matrixes ¹. LIBS uses a high energetic laser pulse on a target sample, creating at impact an expanding microplasma with the emission of luminous species based on the material composition and the environment as a consequence. As shown in Figure 1, the LIBS set-up consists of a laser source (Nd³⁺ doped with $Y_3Al_5O_{12}$ / ND:YAG), a moveable sample stage, and optical system (fiber) transferring the emissions to a detector. The laser is focused onto small surface (µm range) of the sample where it ablates a very small amount of material and break chemical bonds among the elements creating microplasma around the hit area. Then, the emission spectrum is focused and collected through an optical fiber connected to the optical system and detector. The emitted emission pattern is specific for each element and it gives us important information about the elemental composition of the sample ².





The difference between the LIBS evaluation of geological samples and polymers is the behavior of the matrix when ablating. The geological matrix heats up very local in the microplasma emitting the elements presented (atomic and ionic emissions), while polymeric materials transfer the heat from the microplasma on a wider scale emitting additionally molecular emissions. The evaluation of molecular emissions coupled to the LIBS technique is relatively new and therefore need extra evaluation and a carefully interpretation of specific molecular emissions. The interpretation issue is complex as each matrix might give slightly different molecular emissions and these data need to be weeded out from the additional appearing atomic/ionic emissions. However, when the measurements are done in ambient air, it can lead to recombination reactions with nitrogen and oxygen, therefore it is preferred to perform measurement under the argon atmosphere. Both approaches have a different interpretation criterium bearing in mind that the ambient air conditions are rather oxidative with the participation of free carbon atoms in chemical reactions to form new diatomic species such as CN, CH, CO, and C2, and larger carbon clusters, mostly in-flight, gas-phase, two-atom recombination. While the argon atmosphere gives rather pyrolytic/reductive products and typical argon emission lines additionally the absorption of UV emission lines can be suppressed. Mostly reported LIBS applications are focusing on inorganic matter while polymeric matrixes have been on the edge of interest. Within this short paper, the authors wanted to present optimized LIBS parameters (despite the huge number of potential variables) and identification of detected elemental (atomic/ionic) and molecular emission lines under certain conditions from polymeric materials.

Materials and methods

Optimization of LIBS parameters

Within the scope of our work the LIBS Sci-Trace (Atomtrace, Brno) has been used equipped with the LIBS interaction chamber, a ND:YAG laser source coupled optical canals to 4 simultaneous detectors each detecting a fourth of the emission spectrum ranging from 186-1050 nm. The samples were pre-cleaned in isopropanol and complementary pre-screened/identified by XRF (fillers) and FTIR (matrix) spectroscopy. For optimization a Ca/Ti filled flat surfaced

HDPE sample has been selected containing approximately 1912 mg/kg Ca and 18187 mg/kg Ti (XRF data). In order to compare the obtained absolute data from the emission spectra from Ca-atomic (I 422.6 nm) and Ti-ionic (II 334.9 nm), the intensities were normalized to the intensities from C-atomic (I 247.8 nm) and H-atomic (I 656.3 nm) as a proxy for the amount of ablated matrix. All these experiments were done under ambient conditions and peak area (not peak intensity) has been taken for evaluation. The selected parameters for optimization within this work are:

- The measurement protocol: mapping raster, overlap, and distance between the impact craters.
- The laser-energy (from 33 to 170 mJ)
- The spectrometer delay (from 0.2 to $1.4 \,\mu$ s)
- Detector integration time (from 10 till 40 µs)
- Defocus above the sample for data collection (from 0.050 to 0.250 mm)
- Data collection spectra as sum or average
- Spectral background subtraction operation methodology

Evaluation of selected elemental (atomic/ionic) and molecular emission lines from polymer matrixes.

Several polymeric materials were selected for identification of elemental (atomic and ionic) and molecular emission lines:

- PET (polyethyleneterephthalate) transparent/not filled
- PP (polypropylene) transparent/not filled
- PS (polystyrene) transparent/not filled
- PC (polycarbonate) transparent/not filled
- HDPE (high density polyethylene) $CaCO_3 + TiO_2$ filled

For these experiments flat transparent matrixes were preferred as the influence of fillers is reduced to minimum and the surface is considered to be homogenous and an ideal shape. All experiments were done in ambient air and/or under subsequential argon washed conditions – up to 3 (or 5) washes.

Results and discussion

Optimization of LIBS parameters

Firstly, measuring parameters have been optimized to find out the best conditions. From the range of possibilities, the optimized parameters within this work are shown (**in bold**):

- The measurement protocol: mapping raster area 5 (width) × 5 (length) and 5 (depth) shots per each location have been used. Distance 0,7 mm each with 25 % overlap. For the plastic is recommended to perform more than one shot per one location because of possible impurities on the surface or inhomogeneity of the material.
- The laser-energy (33, 64, 78, 99, 135, 145 and 170 mJ)
- The spectrometer delay (0.2; **0.4**; 0.6; 0.8; 1.0; 1.2 and 1.4 μs)
- Detector integration time $(10, 20, 30 \text{ and } 40 \text{ }\mu\text{s})$
- Defocus above the sample for data collection (0.050; 0.100; 0.150; 0.200 and 0.250 mm)
- Data collection spectra as sum of all 125 obtained spectra
- Spectral background subtraction operation: moving minimum

Whereas, some parameters have appeared to be best option (defocus, the detector integration time, mapping raster), others have been chosen conventionally because of no significant differences among the result for individual settings (the spectrometer delay, sum/average of collected spectra, the laser-energy).

Evaluation of selected elemental (atomic/ionic) and molecular emission lines from polymer matrixes.

The table 1 gives the atomic ratios from the emission spectra for individual samples measured under argon atmosphere. The results show good correlation to the relative amount of oxygen in the macromolecule and as well the influence of the inorganic fillers on the O/C and O/H ratio (H I 656.3 nm – Balmer line; C I 247.9 nm; O I 777 nm bundle of 4 lines; only atomic lines have been used). The number of argon washes before the measurement has been optimized to at least 3 as the 5th subsequential argon wash gave comparable results. In figures 2 and 3 are shown the typical detectable emission from a transparent PET sample measured under ambient air conditions and argon atmosphere. Both LIBS spectra for a same sample need a different interpretation and understanding of the optical finger prints (*e.g.*, laser specific/diatomic/molecular emissions versus environment emission lines).

| Table 1. Relative LIBS data from individual | polymeric sam | ples measured under ar | gon atmosphere. |
|---|---------------|------------------------|-----------------|
|---|---------------|------------------------|-----------------|

| Sample | Atomic | # argon | Rel. areas | Rel. areas | Rel. areas |
|-------------------|-------------------------------|---------|------------|------------|------------|
| _ | composition | washes | O/C | O/H | H/C |
| PET – transparent | $C_{10}H_{10}O_4$ | 3 | 1.28 | 0.13 | 9.7 |
| PP- transparent | C ₃ H ₆ | 3 | 0.24 | 0.02 | 13.6 |
| PS – transparent | C_8H_8 | 3 | 0.22 | 0.02 | 10.0 |
| PC – transparent | $C_{16}H_{18}O_3$ | 3 | 0.57 | 0.07 | 8.3 |
| | | 5 | 0.54 | 0.07 | 8.2 |

| HDPE – white | C ₂ H ₄ | 3 | 0.54 | 0.02 | 16.2 |
|--------------|-------------------------------|---|------|------|------|
| Ca/Ti filled | $CaCO_3 + TiO_2$ | | 3 | 0.34 | 0.05 |

Within this work, only C, O and H containing matrixes have been evaluated. Complementary to this, nitrogen containing polymers (polyamide, polyurethane) will be evaluated in the future work.



Figure 2. LIBS spectrum from a transparent PET sample measured in ambient air.



Figure 3. LIBS spectrum from a transparent PET sample measured in argon atmosphere.

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IMPACT OF SILANISING AGENTS ON THE RHEOLOGICAL, VULCANIZATION AND PHYSICAL-MECHANICAL PROPERTIES OF EPDM RUBBER BLENDS CONTAINING LAYERED DOUBLE HYDROXIDES

J. Hronkovič, P. Meluš, J. Oravec, J. Pret'o

VIPO a.s., Gen. Svobodu 1069/4, 95801 Partizanske, Slovak Republic *corresponding author e-mail: <u>pmelus@vipo.sk</u>

Introduction

This work presents some findings of the study of the influence of silanising agents (SA) on the properties of EPDM rubber blends containing layered double hydroxide (LDH) component – a nanofiller able to form lamellar structures in elastomeric matrices. The application of SA was chosen with the intention of improving the ability of LDH to form lamellar structures, positively influencing the application potential of resulting vulcanizates in areas where low permeability to gases and other low molecular weight substances through an elastomeric continuum is required.

Experimental

As an elastomeric matrix EPDM Keltan 4450 was used, the principal filler represented carbon black N-550 and as an LDH component Hydrotalcite 652288 was chosen. This nanofiller is a layered Mg-Al double hydroxide, a laboratory prepared product used in different technical and medicinal areas produced by Sigma-Aldrich Corp., St. Louis, Missouri, USA.

As SA, the following chemicals were used:

- 1. Si 75 bis(triethoxysilylpropyl)disulfide
- 2. MPTES (3-mercaptopropyl)triethoxysilane
- 4. KBE-503 3-(triethoxysilyl)propyl methacrylate
- 5. KBE-1003 triethoxyvinylsilane
- 3. BTEPA bis[3-(triethoxysilyl)propyl]amine

Besides the standard blend (containing no SA), 3 blends for each SA were prepared containing 0.5, 1 and 2 parts of SA per hundred parts of rubber (phr). The rubber blends were prepared in two steps. The first step was carried out in a laboratory mixer Brabender with chamber volume 65 cm³ heated up to 100°C. Components mixed in the first step were: elastomer, carbon black, LDH, softener, antioxidant, and SA. The first step mixing continued for 6 minutes. To carry out the silanising reaction, the mixer temperature was increased to 150°C and the blend was mixed at 50 rpm for 4 minutes.

The second step was carried out in a laboratory double-roll calender at 60°C. The components added in the second step were: the blend from the first step, activators, accelerator, and sulphur. The components were added within 3 minutes and the final blend was thoroughly homogenised by using a calender.

Initially, the following characteristics were chosen for assessing the impact of SA treatment on the properties of EPDM rubber blends containing LDH:

- <u>Rheological characteristics</u>
- 1. Elastic modulus G'
- 2. Loss modulus G"
- 3. Complex modulus G*
- 4. Elastic viscosity η'
- 5. Loss viscosity η "
- Vulcanization characteristics
- 1. Induction time TS2
- 2. 90% of curing time TC90
- 3. Minimum torque S'min
- 4. Maximum torque S'max
- <u>Physical-mechanical properties</u>
- 1. Modules 50, 100, 150, 200, 300 and 500%
- 2. Tensile strength & elongation at break

- 6. Complex viscosity η*
 7. Dissipation factor Tan(δ)
 8. Torque elastic component S'
 9. Torque viscous component S"
 10. Complex torque S*
- 5. Difference maximum torque minimum torque
- S'(max-min)
- 6. Maximum curing speed Peak Rate
- 3. Hardness
- 4. Density

Results and Discussion

1. Rheological characteristics

From the point of view of the industrial processibility of rubber blends the most important parameters are complex viscosity η^* and dissipation / loss factor $Tan(\delta)$. These characteristics were determined at deformation angles from 0.11 to 60°. Relative (with respect to the untreated blend) values of rheological characteristics for the SA MPTES are given in Fig. 1 and 2.



Fig: 1: Changes of relative complex viscosity η^* *with varying concentrations of MPTES*



Fig: 2: Changes of relative dissipation factor $Tan(\delta)$ with varying concentrations of MPTES

The graphs of the dependencies of the complex viscosity η^* and the loss factor $Tan(\delta)$ show at all SA characteristic patterns significantly different from the untreated blend. The practical importance of the observed differences will be possible to assess after the data on gas permeability are available.

2. Vulcanization Characteristics

To assess the impact of SA on the of vulcanisation process the following characteristics were chosen:

a) Time characteristics

- TS2 Scorch period (min)
- TC90 Optimum vulcanization period (min)
- Peak Rate –Highest speed of vulcanization (S'/min)

b) Momentum characteristics

- S'min minimum torque (dNm)
- S'max maximum torque (dNm)
- S'(max-min) difference maximum and minimum torque (dNm)

The relative time vulcanization characteristics are given in Fig. 3.



Fig: 3: Relative time vulcanization characteristics



The relative momentum vulcanization characteristics are given in Fig. 4.

Fig: 4: Relative momentum vulcanization characteristics

From the analysis of vulcanization characteristics follow these conclusions:

- except from the SA BTEPA in concentrations of 1, resp. 2 phr, the scorch time TS2 with the addition of SA is longer than that of the untreated blend
- the period of optimum vulcanization TC90 is significantly longer at SA treated blends than that at the untreated blend
- the blends treated with SA show significantly lower highest speed of vulcanization Peak Rate that the untreated blend
- initial viscosities S'min of SA treated and untreated blends are basically the same
- the SA treated blend, except for KBE-503 in the concentration of 0.5 phr, shows significantly higher maximum torque S'max than the untreated blend
- the vulcanization curve of the untreated blend shows the reduction of torque after the maximum vulcanization reversion

3. Physical-mechanical properties

Of the determined physical-mechanical properties the relative values of moduli at the elongation of 300% are given in Fig. 5 and relative values of tensile strength are illustrated in Fig. 6.



Fig. 5: Relative values of moduli at the elongation of 300%



Fig. 6: Relative values of tensile strength

From the analysis of the physical-mechanical properties of individual rubber blends follow these findings:

- the blends treated with SA show higher modules at the deformation of 50, 100, 150, 200 and 300% as the untreated blend
- the highest modules were observed at the blends treated with MPTES
- the untreated blend shows the highest value of elongation at break
- except for SA MPTES and Si-75 the untreated blend showed higher tensile strength than the SA-treated ones

Conclusion

The analyses of the impact of silanising agents on the rheological, vulcanization and physical-mechanical properties of EPDM rubber blends containing Layered Double Hydroxides show that these agents have prominent effects on these characteristics. However, to select from the five silanising agents tested the one best suited for lowering the permeability to gases will require further research.

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THE MATERIAL RECYCLING POSSIBILITIES OF BIODEGRADABLE MATERIALS SUITABLE FOR 3D PRINTING

<u>Roderik PLAVEC</u>*, Slávka HLAVÁČIKOVÁ, Vojtech HORVÁTH, Leona OMANÍKOVÁ, Jozef FERANC, Andrej BACO, Zuzana VANOVČANOVÁ, Mária FOGAŠOVÁ, Mária MIKULAJOVÁ, Ema MOJŽIŠOVÁ

Institute of Natural and Synthetic Polymers, Faculty of Chemical and Food Technology, Slovak University of Technology, Radlinského 9, 812 37 Bratislava, Slovak Republic *e-mail address: roderik.plavec@stuba.sk

Introduction

Since PLA/PHB biodegradable blends have recently been widely researched in the field of additive manufacturing and also in other branches of the plastics industry due to their positive properties, it is interesting to examine the possibility of their material recycling, especially in terms of a circular economy and environmental protection. Researchers [1] have emphasized that a mechanical recycling strategy is the most appropriate plastic waste management option for the recovery of relatively clean and homogeneous plastic waste as compared with landfill or incineration alternatives. Mechanical recycling allows direct recovery of solid plastic waste for re-use in the production of new plastic products [2] and can use traditional technologies and commonly used processing machines such as conventional extruders and injection molding machines. Due to the fact that the recycling process results in a polymer with varying degrees of degradation, mechanical recycling is limited by the number of repeated processing cycles. Material recycling has commonly been used for many years in the management of plastic waste from the industrial processing of polymeric materials [3].

Material recycling of PLA/PHB blends with the addition of a suitable plasticizer was tested in [4]. It was found that the molecular weight as well as the viscosity of the tested materials decreased due to multiple treatments. Nevertheless, after repeated processing, there was no decrease in the strength characteristics or a change in the thermal properties of the blends.

In this article we focus on the effect of multiple processing on the degradation and consequently on possible process of 3D printing after material recycling of a PLA/PHB blend which was multiple processed in both laboratory and industrial conditions at an industrial partner.

Experimental

This work deals with the study of the recyclability of a biodegradable polymer blend intended for 3D printing technology under the trade name NONOILEN® 3D 3056-2, which is a biodegradable polymeric material prepared from polylactic acid, polyhydroxybutyrate, and oligomer plasticizer.

The process of material recycling (multiple extrusion) of the studied biodegradable polymer blend was carried out in two different processing streams.

For the study of experimental material recycling (under laboratory conditions), first, the material recycling of the tested blend was carried out under laboratory conditions at the Institute of Natural and Synthetic Polymers, Slovak University of Technology, in Bratislava, where the material was blended on a laboratory twin-screw extruder from the Labtech company and the resulting material was cyclically processed on a single-screw extruder (Plasticorder, Brabender, Duisburg, Germany).

In the second processing stream, the blend with the same composition was prepared and further recycled under industrial conditions at the Fillamentum Manufacturing Czech company, Hulín, Czech Republic using a twin-screw extruder LTE 26 from the Labtech company, Praksa, Thailand. The screw diameter was 26 mm and the L/D ratio was 40. The screw speed was set at 400 min⁻¹ and the material was repeatedly processed, firstly by extrusion into filaments, and then by FDM technology (3D printing) into test specimens. Then, the prepared 3D specimens were mechanically ground into granules, from which the filaments were prepared in the next step. The process of mechanical recycling in experimental and industrial conditions is shown in Figure 1.



Figure 1. The process of mechanical recycling in experimental and industrial conditions

To describe the problem of degradation of the studied biodegradable polymer blend based on PLA and PHB, we performed measurements of molecular characteristics of individual processing cycles of the polymer blend, which were processed in experimental, and subsequently, in real production conditions. Figure 2A shows the molar mass distributions for the individual processing cycles of the material tested in both processing conditions. In both cases, due to multiple treatments, the molar masses shift to lower values, which is due to the degradation of the material during the multiple thermomechanical loading. The biggest difference between the molar mass distributions in laboratory (experimental) processing of the tested material and processing in a commercial processing machine is the absence of macromolecules with the highest molar mass (above 10⁶ Da) in the case of industrial processing. This result is consistent with the results described in the processing stability test, where the commercially processed material showed lower complex viscosity values than the material processed under laboratory conditions.

The different influences of processing on the material's molecular characteristics are clearly shown in 2B; the dependence of the molar mass on the retention time of the material in the processing equipment is shown, where a more significant decrease in the molar mass occurs during the experimental processing of the studied material. In both processing alternatives, however, the longer total processing time causes a decrease in the average molar mass.



Figure 2A. Molar mass distribution of individual processing cycles of experimental and industrial types of the NONOILEN® 3D 3056-2 material

Figure 2B. Dependence of the average molar mass as a function of the total retention time of the material in the processing equipment

From the study of material degradation during multiple processing in different processing conditions we found that due to multiple thermomechanical processing, the tested material partially degrades, which was associated with a decrease in its molar mass and a subsequent decrease in material viscosity. It should be noted that the starting blends themselves differed in viscosity. Greater degradation of the material occurs during its processing under industrial conditions, which is due to the different construction of industrial equipment, different shear stress of the material, as well as different retention time of the material in the processing equipment. However, the positive fact is that both in the laboratory and subsequently in the research phase directly at the industrial partner, we were able to realize nine processing passes which would ultimately mean that the tested blend would be usable at least four times under industrial conditions before its ecological recovery in the form of biodegradation would be necessary.

Despite material degradation during multiple processing, it was noted that multiple processing of material had no negative impact on the 3D printing. The recycled material can be printed under the same conditions as fresh (unrecycled) material even after multiple processing (the same printing temperature, pad temperature, and printing speed). There were no increases in side effects such as warping, delamination of layers, or deformation of the 3D-printed model observed during the 3D printing of objects (samples) made of multiple processed material. The tested 3D printed objects after multiple material recycling are shown on figure 3.



Figure 3. 3D printed samples after multiple processing (3rd, 5th, 7th, and 9th processing transition) of the industrial type sample, NONOILEN® Fillamentum for NATURE.

Conclusion

The results obtained in this work indicate that a biodegradable and biobased polymer blend based on PLA and PHB is a suitable candidate for material recycling even in industrial processing conditions. The largest differences in tested rheological and utility properties between the samples processed under experimental as well as industrial conditions were recorded during the actual blending of the biodegradable polymer blend on the different blending devices. The results of this scientific work suggest that the biodegradable polymeric material NONOILEN® 3D 3056-2 is suitable for multiple uses in FDM technology, which could lead to significant savings in input materials in 3D printing, for example in the event of defective prints.

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MODIFICATION OF SILICON SUBSTRATES WITH FUNCTIONAL POLYMERS VIA PHOTO INDUCED ATRP

Nikolaos Konios¹, Darshak Pathiwada^{1,2}, Zuzana Kroneková¹, Jaroslav Mosnáček^{1,2}

¹Polymer Institute, Slovak Academy of Sciences, Dúbravská cesta 9, 845 41 Bratislava, Slovakia

²CEMEA, Slovak Academy of Sciences, Dúbravská cesta 9, 845 11 Bratislava, Slovakia

Requirements for sustainable chemistry involve the development of light induced chemical reactions and the decrease of the amounts of reagents employed^{1,2}. Recent ecological and economical advances include atom transfer radical polymerizations (ATRP) that are light induced, where ppm amounts of catalyst are used and enhanced oxygen tolerance². Regarding surface modifications, the reaction medium may be limited in the microliter scale leading to grafted polymer brushes around 200 nm thickness³.

In the present work, the benefits of the previous advances are focused on poly (2-oxazolines) which are a class of biocompatible polymers with tunable properties ranging from hydrophilic to hydrophobic⁴. For biomedical applications, they are considered an alternative to poly (ethylene glycol) which undergoes oxidation⁴. Specifically, poly(2-isopropenyl-2-oxazoline) (PIPOx), which can be obtained by radical polymerizations, is grafted from silicon wafers via photo induced surface-initiated ATRP and polymer brush layer with controlled thickness up to 77 nm was obtained⁴. It was proved that higher amounts of catalyst led to a slow polymerization, which can be derived from the pedant group trapping of copper. Due to the slow polymerization exhibited by the present monomer, it was found that more active ligand, namely tris[2-(dimethyl amino)ethyl]amine (Me6TREN) is preferred. Dimethyl sulfoxide (DMSO) was proved to be a convenient solvent. Moreover, the substrates exhibited excellent antifouling properties even for the case of 14 nm grafted brushes. Finally, PIPOx was used to extend poly (α -methylene- γ -butyrolactone) brushes that were grafted from silicon wafer and obtain hydrophobic-hydrophilic block copolymers on the substrates.

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RESEARCH IN PREPARATION OF PLA CAST FILMS WITH A CONTENT OF PHOTOLUMINESCENT PIGMENT

Zita Tomčíková*, Katarína Holcová and Dominika Rerková

*Research Institute for Man-Made Fibres a.s., Štúrova 2, SK-059 21 Svit, Slovak Republic tomcikova@vuchv.sk

1 INTRODUCTION

Polylactic acid (PLA) is the first viable thermoplastic which can be produced from a plant-based feedstock such as corn or sugar cane, and be processed by conventional melt processing technologies. Production of PLA requires 25-55% less fossil energy and 20-50% less fossil fuel resources than the production of petroleum-based polymers. PLA polymer is compostable because it easily degrades by simple hydrolysis under the appropriate conditions (around 60°C, 90 % relative humidity). At the same time it is produced at the largest industrial scale from all biodegradable polymers (hundreds of thousand tons of PLA per year)^{1,2}. Applications of PLA are aimed mainly into packaging, agriculture, medicine, electronics, construction, automotive industries and also into fibres (the fibrefills, the nonwovens)³⁻⁶.

Nowadays is a lot of interest in smart textiles which give responsiveness during external stimulation by light, electricity, chemicals, pH, solvent polarity, and temperature⁷. For our research, luminescence (the absorption of light and its subsequent emission) is very interesting precisely photoluminescence. Photoluminescence has as an energy source absorption of photons (electromagnetic radiation). Other types of luminescence are also known depending on the method of excitation: chemiluminescence, crystalloluminescence electroluminescence, mechanoluminescence, radioluminescence and thermoluminescence^{8, 9}.

Photoluminescent pigments, which exist in organic and inorganic forms, are interesting also for the films. They can be used for originality products protection because they are cost-acceptable and effective^{10, 11}.

Our research was focused on the study of PLA film preparation from two types of PLA. The films are sensitive to UV light as a result of photoluminescent pigment content. First PLA masterbatches with protective photoluminescent pigment following PLA films containing the protective photoluminescent pigment were prepared. The conditions of preparation of PLA films and color efficiency of the pigment in two PLA matrixes were evaluated and compared.

2 EXPERIMENTAL AND METHODS

2.1 Materials

Polylactide acid (PLA1) produced by Nature Works LLC with MFR = $27.7 \text{ g/10} \text{ min} (210^{\circ}\text{C}/2.16\text{kg})$, Polylactide acid (PLA2) produced by Total Corbion PLA B.V with MFR = $12.8 \text{ g/10} \text{ min} (210^{\circ}\text{C}/2.16\text{kg})$; and protective organic photoluminescent pigment (FP) of Radiant Color Company were used. PLA have been dried before measurement for 2 hours under 70°C .

2.2 Preparation of PLA masterbatch

Before preparation of PLA1/FP masterbatch the premix has been prepared. The premix consisted of PLA1 carrier and 0.5 wt.% of protective organic photoluminescent pigment. The polymer was milled and dried at 85°C for 4 hours before preparing of the premixes.

The PLA/FP masterbatch was prepared on a Werner-Pfleiderer ZDSK 28 laboratory line with a twin-screw extruder (a screw diameter of 28 mm) in vacuum zone. The preparation process of masterbatch had been carried out at a constant screws rotation speed of 270 min⁻¹ and constant extrusion temperature of 210°C. The output was 0.5% masterbatch of FP with MFR = 31.84 g/10 min (210°C/2.16kg).

2.3 Preparation of cast film

First, from both PLA1 and PLA2, unmodified cast films were prepared as standards for comparison. Then, the photoluminescent PLA cast films from the mechanical mixture of PLA polymer and PLA/FP masterbatch were prepared. The research was carried out by using the Plasticizers laboratory line with an extruder diameter of 18 mm and slot width of 48 mm. The cast films with content of 0.001 wt. %; 0.005 wt. % and 0.010 wt. % of FP were prepared.

2.4 Coloristic properties

Measurement of coloristic properties of unmodified standards and modified PLA films with content of 0.001 - 0.010 wt. % of FP was performed on the device ULTRASCAN PRO under the following conditions: iluminate D65 – daylight with the temperature of 6 500 K, observer 10°, color space CIELab. The following coloristic properties were evaluated: L* (CIELAB) D65 10° - light - color gradient light to dark, a* (CIELab) D65 10° - color gradient from red to green; b* (CIELAB) D65 10° - color gradient from yellow to blue, dE*(CIELab) D65 10° - total color difference, WICIE - whiteness index.

3 **RESULTS AND DISCUSSION**

During the preparation of PLA cast films with and without FP, the technological parameters listed in Table 1 were monitored. The technological parameters were adapted to the type of PLA polymer used in the preparation of the films.

| PLA film | Tempe | erature settin | gs [°C] | Spee | ed [min ⁻¹] | Extenden load [A] |
|----------------|---------|----------------|----------|-------|-------------------------|-------------------|
| designation | I. zone | II. zone | Die head | Screw | Cooled godets | Extruder load [A] |
| PLA1 Standard | 210 | 210 | 210 | 25 | 15 | 1.2 |
| PLA1/0.001% FP | 210 | 210 | 210 | 25 | 15 | 1.2 |
| PLA1/0.005% FP | 210 | 210 | 210 | 25 | 15 | 1.2 |
| PLA1/0.010% FP | 210 | 210 | 210 | 25 | 15 | 1.2 |
| PLA2 Standard | 220 | 220 | 220 | 30 | 16 | 1.8 |
| PLA2/0.001% FP | 220 | 220 | 220 | 30 | 16 | 1.8 |
| PLA2/0.005% FP | 220 | 220 | 230 | 30 | 16 | 1.6 |
| PLA2/0.010% FP | 220 | 220 | 230 | 30 | 16 | 1.3 |

Table 1 Technological parameters of PLA/FP cast films preparation

The preparation of the standard PLA1 film was carried out at the temperature of 210 °C and an extruder load of 1.2 A as shown in Table 1. A defect-free film with a slightly rough surface was obtained, which, as shown in further tests, persisted even with samples containing FP. During the PLA1 film preparation, the processing conditions of PLA1/FP films were the same as the processing conditions of standard PLA1 film. By adding 0.001 % FP to PLA1, the width of the film started to change - the film was narrowed and widened. By further increasing the FP content, this effect was accentuated (Figure 1a).

By changing the polymer to PLA2 a smooth film was prepared without any defects but with a significant yellow coloration in daylight (Figure 1b). PLA2 films were processed at higher temperatures than PLA1 films (Table 1). The standard PLA2 film and subsequently also the modified PLA2/FP films are significantly narrower than the films from the PLA1 matrix (Figure 2a) due to lower melt flow index (MFR) of PLA2 in comparison to PLA1. This is also related to the observed increase in extruder load by 0.6 A compared to PLA1 films.

By increasing the temperature on the die head from 220 °C to 230 °C during the preparation of PLA2/FP films, the extruder load decreased from 1.8 A to 1.6 A for the PLA2/0.005 % FP sample and to 1.3 A for the PLA2/0.010% FP sample. It follows from this, that the pigment has an effect on the flow properties of the PLA mixture. Unlike PP and PE films, PLA films have a distinctive rustling sound due to the fragility of PLA.

The color properties of PLA films were evaluated a) visually under daylight D65 and under UV light and b) by measuring the color coordinates on the device ULTRASCAN PRO.

Photoluminescent PLA films do not differ in color from standard PLA films in daylight, as seen in Figures 1a and a) 2a. Under UV light, the films of the standards do not glow and therefore cannot be seen in Figure 2b. The bright blue effect of PLA films can be seen at the edges of the film already at the lowest content of 0.001 wt. % FP. By increasing the FP content to 0.005 wt. % and subsequently to 0.010 wt. %, the bright blue effect of the films spread over the whole film area with an increasing intensity, as seen in Figure 2b.



a)

Figure 1 a) strips of PLA1 films on the white and black surface; b) PLA1 film (left) and PLA2 film (right)





b)

Figure 2 Strips of PLA1 films (left) and PLA2 films (right) a) under D65 light and b) under UV light

b) The measurement of color coordinates was carried out on films wound in eight layers on plate. The difference in the color coordinates of the photoluminescent films against the standards was compared, as well as the mutual color difference between the standards. Results are listed in Table 2.

| PLA film designation | L* | a* | b* | dE* | Gray scale | Coloring power | WICIE |
|----------------------|-------|-------|------|------|---------------|-------------------|-------|
| PLA1 Standard | 91.75 | -0.45 | 3.40 | | | | 64.28 |
| PLA1/0.001% FP | 92.01 | -0.43 | 3.14 | 0.37 | 5.0 | 96.33 | 66.12 |
| PLA1/0.005% FP | 90.94 | -0.06 | 1.62 | 1.99 | 4.0 | 172.86 | 70.78 |
| PLA1/0.010% FP | 91.30 | -0.03 | 1.17 | 2.31 | 3.5 | 174.61 | 73.71 |
| PLA2 Standard | 88.23 | -0.38 | 3.44 | | | | 55.95 |
| PLA2/0.001% FP | 90.45 | -0.44 | 3.44 | 2.23 | 3.5 | 87.59 | 61.03 |
| PLA2/0.005% FP | 89.98 | -0.35 | 3.05 | 1.80 | 4.0 | 124.26 | 61.80 |
| PLA2/0.010% FP | 90.33 | 0.04 | 0.91 | 3.32 | 3.0 | 314.11 | 74.78 |

Table 2 Color parameters of PLA films dyed with photoluminescent pigment

The PLA1/0.001% FP film has color coordinates practically the same as the standard PLA1 film, the differences between them are minimal. The coloristic coordinates a* and b* point to a weak greenish-yellow coloring of the film due to the negative values of the coordinate a* and the positive values of the coordinate b*. The low values of the a* and b* coordinates, which are particularly low for the a* coordinate, indicate a very weak coloring of the film. The total color difference (dE*) increases and the whiteness index (WICIE) increases with increasing FP content. Low values of color difference max. of 2.31 at a content of 0.010 wt. % FP show a barely noticeable color difference between the standard and the film sample. The values correspond to the gray scale where the value drops from 5.0 to 3.5. PLA1/FP films achieve a high light (L*) comparable to the standard.

The standard PLA2 film has a lower lightness and whiteness than the standard PLA1 film, which corresponds to the visual evaluation of the films in daylight. The addition of FP prominently increases the whiteness index of the film, which at a content of 0.010 wt. % FP reaches the whiteness of PLA1/FP film with the same pigment content. Fundamental changes in this sample can also be seen in the coloristic coordinates a* and b*, which reach the highest deviations from the standard among all evaluated samples, which was also reflected in the achievement of the highest value of the total color difference (dE*) 3.32.

By comparing two types of PLA polymers (PLA1 and PLA2), it was found that, from the point of view of color, PLA1 from Nature Works is more suitable for cast films than PLA2 from Corbion.

4 CONCLUSION

PLA cast films were prepared from two types of PLA polymers PLA1 and PLA2 from competing companies. The mixture for the preparation of films consisted of 0.5 % masterbatch, prepared from PLA1 polymer and photoluminescent pigment, and the type of PLA polymer. During the preparation of the films, the technological parameters of the fabrication process were monitored. It was found that when using PLA2 polymer, it is necessary to use higher processing temperatures by 10 °C to 20 °C than with PLA1 polymer. From the visual evaluation of FP films, it was found that PLA2 cast films are visually narrower compared to PLA1 films with and without additive. The surface of PLA1 films, both standard and with FP content, is rough, while PLA2 films with and without additives have a smooth surface. PLA films make a unambiguous rustling sound when touch it, which is related to the fragility of the PLA polymer.

The color evaluation of the PLA cast films showed, that in daylight D65 the PLA1 films are white, while the PLA2 cast films have a yellow color. Under UV light, all FP films glow blue. The blue intensity of the radiation increases with

increasing pigment content. From the point of view of the CIELab coordinates, films have a weak greenish-yellow color, the a* coordinate takes on values from -0.45 to 0.04 and the b* coordinate takes on values from 0.91 to 3.44.

From the research of the preparation of PLA cast films from two types of PLA polymers (PLA1 and PLA2), it was found that from the process and color point of view, PLA1 type from Nature Works is more suitable for cast films than PLA2 from Corbion.

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PROPERTIES OF PLA MASTERBATCHES WITH INORGANIC PIGMENTS

<u>Mária PETKOVÁ</u>^{*1}, Marcela HRICOVÁ¹, Agáta HUDECOVÁ¹, Anna UJHELYIOVÁ¹, Zita TOMČÍKOVÁ², Roderik PLAVEC¹

¹Department of Plastics, Rubber and Fibres, Faculty of Chemical and Food Technology, Slovak University of Technology in Bratislava, Radlinského 9, 812 37 Bratislava, Slovakia ² Research Institute for Man-Made Fibres a.s., Štúrova 2, 05921 Svit, Slovakia maria.petkova@stuba.sk

Nowadays, our ecological behaviour is about the attitudes to life, the Earth..., what resonates from all sides. New environmentally friendly polymers have been designed with an enhanced sustainability. The improved sustainability could be at first given to input of bio-based row material and at the second used to biodegradable (or compostable) polymers. PLA is both, bio-based and compostable. Therefore, for several years, a lot of research has dealt biodegradable polymers without using polyolefins. Synthetic polymers accumulate in the environment for many decades. Biodegradable plastics burden nature to a much lesser extent, because of made from renewable resources and they would be decomposable by the action of microorganisms¹⁻³.

The investigation of PLA has had the own history. However, biodegradable polymers encounter limitations and disadvantages associated with the processing of biodegradable polymers and the properties achieved. This does not allow using these polymers to a large extent as a substitute for synthetic polymers. Therefore, there is an effort to modification the production process as well as to modify the mass of the polymer with various additives. But we know little about colourful masterbatch of PLA or other biodegradable polymers. The colouring of biodegradable polymers requires a careful selection of pigments that are compatible with European Standard EN 13432. This standard defines the characteristics which the material must have, that to be considered as compostable. For industry, it is very needed to find different roads of colouring masterbatches⁴.

Poly-lactic acid (PLA) is a biodegradable thermoplastic aliphatic polyester. It has a linear character. Its disadvantage is sensitivity to thermal degradation. Because the ester linkages of PLA tend to degrade during melt processing. The optimalization the process parameters must include its thermal and rheological behaviour⁵.

EXPERIMENTAL PART

Materials used:

- Polylactic acid Luminy L175 (PLA L175), MFI 8 g/10 min at 210°C (Total Corbion PLA B.V.)
- inorganic pigments: 1) ferric Fepren TP 303M (F303M) (Precheza a.s.) 2) titanium whiteness AV01SF
- TiO₂ (Ti) (Precheza a.s.); 3) carbon black Printex Alpha (PXA) (Orion, Engineered Carbons GmbH)
- and dispergation agent silicone oil V350 (Azelis Slovakia, s.r.o.).

Preparation of masterbatches:

The preparation of the masterbatches, with 1 and 3% concentration of different pigments, was carried out on Werner-Pfleiderer ZDSK-28 laboratory line with a twin-screw extruder (Ø 28 mm), at an extrusion temperature 185 - 210°C. The extrudate was cooled and pelletised. It was used a stationary dryer and mixer Drais. The composition of PLA masterbatches are presented in Table 1.

| Composition | PLA | Pigments | V350 | | |
|-------------|------|-----------------------|---------|-----------|------|
| | [w%] | TiO ₂ [w%] | PXA[w%] | F303M[w%] | [w%] |
| PLA L175 | 100 | - | - | - | - |
| 1%Ti | 98,7 | 1 | - | - | 0,3 |
| 3%Ti | 96,4 | 3 | - | - | 0,6 |
| 1%PXA | 98,7 | - | 1 | - | 0,3 |
| 3%PXA | 96,4 | - | 3 | - | 0,6 |
| 1%F303M | 98,7 | - | - | 1 | 0,3 |
| 3%F303M | 96,4 | - | - | 3 | 0,6 |

Table 1 The composition of PLA masterbatches

Method used:

The rheological behaviours of the pure PLA and the masterbatches were investigated using Physica MCR 101 rheometer (Anton Paar, Austrie). Experiments were conducted with air- atmosphere. A parallel plate geometry was used with a diameter of 25 mm. The gap was set at 1 mm. All the rheological measurements were performed at 190 °C, at 1% strain from 0,1 to 100 rad.s⁻¹.

Thermal analysis of PLA masterbatches were performed by DSC 1/750 with ceramic sensor FRS5 (Metler Toledo). The samples were heated from 20°C to 190°C, at a rate of 10°C/min. At 190°C the samples were isothermally held for 3 minutes and cooled down to the crystallization temperature afterwards at a rate of 10°C /min. Subsequently after

isothermally holding for 3 minutes at 20°C, the sample was exposed to the second heating from 20°C to 190°C at a rate of 10°C/min. All measurements were carried out in a nitrogen atmosphere. From the melting endotherms of the 1st and 2nd heating, the melting temperatures (T_m) and enthalpies (ΔH_m) and relaxed temperatures (T_{ER}) and enthalpies (ΔH_{ER}). As well as the cold crystallisation (T_{cc}) and crystallization temperatures (T_c) and enthalpies cold crystallization (ΔH_{cc}) and crystallization (ΔH_c) from the crystallisation exotherms were evaluated using software SW STARe.

RESULTS AND DISCUSSION

Table 2 The thermal properties of PLA masterbatches

- a) reached temperatures at the 1st heating and cooling
- b) reached enthalpies at the 1st heating and cooling
- c) reached temperatures at the 2nd heating
- d) reached enthalpies at the 2nd heating

| 1.heating+co | oling | T _{ER} [°C] | T _{CC1} [°C] | T _{CC2} [°C] | T _m [°C] | T _C [°C] | 1.heating+cooling | ΔH _{ER} [J.g ⁻¹] | ΔH _{CC1} [J.g ⁻¹] | ΔH _{CC2} [J.g ⁻¹] | ΔH _m [J.g ⁻¹] | ΔH_{C} [J.g ⁻¹] |
|--------------|--------------------|----------------------|-----------------------|-----------------------|---------------------|---------------------|-------------------|---------------------------------------|--|--|--------------------------------------|--------------------------------------|
| PLA L175 | | 78.16 | | | 177.99 | 103.74 | PLA L 175 | 2.35 | | | 34.43 | -0.28 |
| 1%Ti | | 63.67 | 101.5 | 160.1 | 177.03 | 97.85 | 1%Ti | 2.40 | -27.08 | -5.32 | 41.64 | -0.85 |
| 3%Ti | | 64.14 | 102.16 | 159.59 | 176.32 | 97.86 | 3%Ti | 4.58 | -24.66 | -5.26 | 40.82 | -1.20 |
| 1%PXA | | 66.44 | 102.58 | 159.26 | 176.97 | 100.2 | 1%PXA | 5.73 | -24.52 | -5.27 | 42.30 | -2.08 |
| 3%PXA | | 67.07 | 99.44 | 158.9 | 176.58 | 100.41 | 3%PXA | 5.42 | -22.83 | -5.00 | 42.53 | -3.89 |
| 1%F303M | | 63.61 | 97.57 | 159.46 | 177.46 | 99.48 | 1%F303M | 1.00 | -23.99 | -4.90 | 43.17 | -10.75 |
| 3%F303M | | 63.46 | 96.53 | 158.97 | 176.41 | 101.64 | 3%F303M | 1.14 | -22.17 | -4.30 | 43.45 | -11.45 |
| a) | | | | | | | b) | | | | | |
| 2.heating | T _{ER} [° | C] T _{CC1} | [°C] T _{CC2} | [°C] T _m | [°C] | | 2.heating | ΔH_{ER} [J.g ⁻¹] | ΔH _{CC1} [J | g ⁻¹] ΔH _{CC} | 2 [J.g ⁻¹] | ΔH _m [J.g ⁻¹] |
| PLA L175 | 64.13 | 5 | | 17 | 3.99 | | PLA L175 | 1.93 | | | | 5.11 |
| 1%Ti | 64.03 | 3 103 | .6 16 | 0.1 17 | 5.24 | | 1%Ti | 1.53 | -28.71 | | .64 | 41.24 |
| 3%Ti | 63.70 |) 102. | .77 159 | 0.27 17 | 4.82 | | 3%Ti | 1.26 | -27.05 | 5 _4 | .88 | 40.24 |
| 1%PXA | 63.70 | 0 103. | .53 159 | 0.26 17 | 4.98 | | 1%PXA | 1.26 | -23.60 |) -4 | .99 | 41.30 |
| 3%PXA | 64.00 |) 101. | .03 158 | 3.74 17 | 5.23 | | 3%PXA | 1.04 | -21.50 |) -5 | .23 | 41.31 |
| 1%F303M | 64.12 | 2 102. | .65 159 | 0.11 17 | 5.07 | | 1%F303M | 0.55 | -15.23 | 3 _4 | .36 | 42.88 |
| 3%F303M | 63.98 | 3 103. | 47 159 | 0.62 17 | 5.15 | | 3%F303M | 0.51 | -12.47 | -3 | .56 | 42.00 |
| c) | | | | | | | d) | | | - | | |

At first heating, cold crystallisation was noted in all coloured masterbatches. The presence of pigments makes a significant contribution to cold crystallisation because in the pure PLA L175 any cold crystallisation was not observed. The crystalline phase of the pure PLA is not sufficiently stable and after the first heating the samples have lost the ability to form the original semi crystallization structure. Whereas in the comparison of the 1st and 2nd heating of pigmented masterbatches, the enthalpy of melting is maintained. Compared to pure PLA granules without additives, the masterbatches increase the enthalpy of crystallization during cooling depending on the presence of the various pigments that the changes support (Tab.2).

G' is storage modulus, that represents elastic part of deformation. It is reversible. G'' is loss modulus, which largely represents the plastic component of the deformation. This deformation is irreversible or dissipates as the warm to the surroundings. Therefore, it is important to know how the prepared masterbatches will behave, how the processing conditions need to be set.

Oscillated rheometers are based on the principle of sensing the material's response to a forced sinusoidal strain. The directly measured parameter is the complex torque, based on which the strain in the sample is calculated.

The ratio G' to G" is the closer to 1, the more it presents a material with balanced visco-elastic properties. The masterbatches with inorganic pigment reach this state at higher angular frequency. At lower angular frequencies, the plastic behaviour is much more pronounced. In the flowed behaviour of masterbatches with inorganic pigments compared to pure PLA did not note significant changes (Fig.1a, b). Complex viscosity presents a viscosity curve composed of both components, viscous and elastic part, where we can see the decrease viscosity of masterbatches compared to pure PLA (Fig. 1c).





Figure 1 Dependencies of the rheological properties of PLA masterbatches on angular frequency

- a) Storage modulus
- b) Loss modulus
- c) Complex viscosity

CONCLUSION

The aim of this work was evolution of thermal and rheological behaviours of PLA masterbatches with inorganic pigments regarding industrial use and the need to preserve the status of biodegradable composition. The masterbatches meet the permitted limit quantities according to valid STN, and the influence of pigments on the processing properties is not so great that it prevents the use of pigmented masterbatches for various technological uses.

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b)

PROPERTIES OF PIGMENTED PLA FIBRES

Marcela HRICOVÁ¹*, Mária PETKOVÁ¹, Zita Tomčíková², Agáta HUDECOVÁ¹ and Anna UJHELYIOVÁ¹

¹Department of Plastics, Rubber and Fibres, Faculty of Chemical and Food Technology, Slovak University of Technology in Bratislava, Radlinského 9, 812 37 Bratislava, Slovakia ²Research Institute for Man-Made Fibres a.s., Štúrova 2, 05921 Svit, Slovakia marcela.hricova@stuba.sk

In this work, the influence of the type and concentration of inorganic pigments on mechanical and thermal properties of biodegradable fibres from polylactic acid (PLA) was evaluated.

Synthetic polymers are number one in global problem in waste management. Polylactic acid is one of the ecological biodegradable polymers from renewable sources, which have the assumption to replace synthetic materials¹.

In recent years, research in this area is focused on modifying the production process of PLA fibres by adding various additives (fillers, plasticizers, pigments, nucleating agents, etc.). This is important in terms of improving the final properties of PLA fibres to make them competitive with synthetic fibres.

EXPERIMENTAL PART

Materials used

Polylactic acid Luminy L175 (PLA175), MFI 8 g/10 min at 210°C (Total Corbion PLA B); Polylactic acid INGEO I6100D (PLA6100), MFI 24 g/10 min at 210°C (NatureWorks LLC).

Inorganic pigments: titanium dioxide Pretiox AV01SF (Ti) and iron oxide Fepren TP 303 (Fe), (both produced by Precheza a.s.); carbon black Printex Alpha (PXA) (Orion Engineered Carbons GmbH).

Dispergation agent: silicone oil V350 (Azelis Slovakia, s.r.o.).

Fibres preparation

PLA masterbatches with final concentration of 1 wt.% of pigments were prepared using Werner-Pfleiderer ZDSK 28 laboratory line with a twin-screw extruder (\emptyset 28 mm) at 180-210°C. Before spinning, the PLA granulates were dried in a laboratory oven for 3 hours at 60°C. PLA fibres and additived PLA fibres with final concentration of pigments of 0.1 and 0.5 wt.% were prepared using a laboratory spinning plant at 190°C with the take-up speed 150 m.min⁻¹.

Fibres were drawn using a laboratory drawing machine at maximal draw ratio λ_{max} at drawing temperatures T_{dr} 95°C respective 105°C. The composition of fibres and achieved drawn ratios are presented in Tables 1 and 2. *Method used*

The Instron (Type 3343) was used for the measurements of the mechanical properties (tenacity and elongation at break and Young's modulus) of fibres (according to ISO 2062:1993), evaluated from 15 measurements. The initial length of fibres was 125 mm and the time of deformation was about 20 sec.

Thermal properties were measured by DSC 1/750 with ceramic sensor FRS5 (Metler Toledo) at measurement conditions: 1st heating 20-190°C (at 190°C the samples were isothermally held for 3 minutes), cooling 190-20°C (at 20°C the samples were isothermally held for 3 minutes) and 2nd heating 20-190°C. The speed of heating or cooling was 10°C/min. The measurements were made in inert nitrogen atmosphere. The glass temperature (T_g), melting temperature (T_m) and melting enthalpy (ΔH_m) were evaluated using software SW STARe.

RESULTS AND DISCUSSION

The drawn ratio of the individual pigmented PLA fibres was affected by concentration and the type of pigments (Tables 1 and 2). Content of 0.1% of pigments had minimal or positive effect on the values of λ_{max} at drawing temperature 105°C (Table 1).

Content of 0.5% of pigments caused the worsening of drawing process. The fibres with content of 0.5% of pigments could not be drawn at 105°C. As a suitable drawing temperature for these samples the temperature of 95°C was found. Whereas the fibres with content of pigments 0.5% were drawn at this temperature only on draw ratio λ_{max} 2.5 (Table 2). This influence of pigments was also manifested at the evaluation of mechanical properties of PLA fibres.

Table 1. Mechanical properties (tenacity at break σ , elongation at break ε and Young's modulus *E*) of PLA fibres with **0.1% of pigments**. All fibres were drawn at **105°C** (*T_t* is fineness of fibres)

| No. | Composition of fibres | λmax | T_t [tex] | σ [cN/tex] | ε [%] | E [N/tex] |
|-----|-----------------------|------|-------------|-------------------|-------|-----------|
| 1 | PLA175 | 3.4 | 33.4 | 21.5 | 55.8 | 3.67 |
| 2 | PLA175+0.1% Ti | 3.5 | 26.1 | 28.4 | 44.1 | 4.72 |
| 3 | PLA175+0.1% PXA | 3.2 | 34.8 | 22.0 | 64.7 | 3.87 |
| 4 | PLA6100 | 3.5 | 23.2 | 22.3 | 46.5 | 3.67 |
| 5 | PLA6100+0.1% Ti | 3.6 | 20.1 | 28.2 | 61.4 | 4.76 |
| 6 | PLA6100+0.1% PXA | 3.3 | 18.9 | 30.4 | 49.3 | 4.99 |
| 7 | PLA6100+0.1% Fe | 3.4 | 18.1 | 32.0 | 70.8 | 4.82 |

| 0.0700 | o vo or presidentes i residente interes were drawn de vo e (17 is interess of nores) | | | | | | |
|--------|--|------------------|-------------|-------------------|-------|------------------|--|
| No. | Composition of fibres | λ _{max} | T_t [tex] | σ [cN/tex] | ε [%] | <i>E</i> [N/tex] | |
| 1 | PLA175 | 3.4 | 33.4 | 21.5 | 55.8 | 3.67 | |
| 8 | PLA175+0.5% Ti | 2.5 | 32.2 | 20.6 | 51.1 | 3.35 | |
| 9 | PLA175+0.5% PXA | 2.5 | 29.6 | 19.4 | 56.2 | 3.19 | |
| 4 | PLA6100 | 3.5 | 23.2 | 22.3 | 46.5 | 3.67 | |
| 10 | PLA6100+0.5% Ti | 2.5 | 41.5 | 15.7 | 113.6 | 3.03 | |
| 11 | PLA6100+0.5% PXA | 2.5 | 49.8 | 14.8 | 83.1 | 2.64 | |
| 12 | PLA6100+0.5% Fe | 2.5 | 42.5 | 14.0 | 103.2 | 2.76 | |

Table 2. Mechanical properties (tenacity at break σ , elongation at break ε and Young's modulus *E*) of PLA fibres with **0.5% of pigments.** Pigmented fibres were drawn at **95°C** (*T_t* is fineness of fibres)

All PLA fibres containing 0.1% of inorganic pigments showed higher tenacity than pure PLA fibres (Table 1 and Figure 1a). The content of 0.5% of inorganic pigments caused a decrease of tenacity for all pigmented PLA fibres (Table 2 and Figure 1a). Low content of pigments (0.1%) can act as nucleation agent, increases of the crystallinity and thereby improves the mechanical properties of fibres. On the other hand, the addition of higher content of pigments (0.5%) can lead to higher agglomeration of pigment particles and thus worsen the mechanical properties of fibres. This statement is also supported by the worse drawability of these fibres (λ_{max} only 2.5) as well as the increased values of elongation at break (Table 2 and Figure 1b).



Figure 1. Dependence of tenacity (a) and elongation at break (b) on the composition of PLA fibres

DSC method was used for evaluation of the super-molecular structure of PLA and pigmented PLA fibres. The endothermic and exothermic processes were monitored. The parameters obtained from the 1st heating are influenced by thermal history and unidirectional orientation during the spinning and drawing process as well as by the used additives. During the 2nd heating, only the influence of the composition of the sample becomes apparent.



Figure 2. Dependence of glass transition temperature T_g (a) and melting temperature T_m (b) on the composition of PLA fibres

Due to the asymmetric carbon atom in its molecule, lactic acid (LA) exists in two enantiomeric forms, L-LA and D-LA. The thermal and mechanical properties of PLA depend on the ratio and distribution of L- and D-LA in the polymer chains². Semicrystalline polymer contents more stereoisomer poly(L-lactide) (PLLA), while amorphous polymer contents more poly(D-lactide) (PDLA). The melting temperature (T_m), and the glass transition temperature (T_g) of PLA decrease with decreasing amounts of PLLA³. Glass transition temperature is a significant characteristic of polymer materials. T_g

for both semicrystalline and amorphous PLAs are between 50 and 70°C⁴. The influence of inorganic pigments on more semicrystalline PLA175 is not as marked as in the case of more amorphous PLA6100 where the higher values of T_g for pigmented PLA6100 fibres were found (Figure 2a). Inorganic pigments act as a nucleating agent, which results in an increase of crystallinity, but they probably initiate the formation a lot of small crystallites, which causes a decrease in melting temperature values (Figure 2b).



Figure 3. Dependence of melting enthalpy ΔH_m from 1st heating (a) and 2nd heating (b) on the composition of PLA fibres

When comparing the values of melting enthalpy ΔH_m , we can see that during the 1st heating, the influence of the heat treatment (spinning and drawing) of the PLA samples is manifested. From the Figure 3a we can see that pigmented fibres have higher values of melting enthalpy ΔH_m then pure PLA. It means that the content of inorganic pigments affects and increases the crystallinity of the fibres. During the 2nd heating, only the effect of composition of PLA samples is manifested. This effect of content and concentration of inorganic pigments is stronger for the more amorphous type of PLA6100 (Figure 3b).

CONCLUSION

This work was focused on evaluation of the influence of inorganic pigments on the properties of PLA fibres. Based on the obtained data, the results can be formulated into the following conclusions:

- 1. The lower content of pigments (0.1 wt.%) has positive effect on mechanical properties of pigmented PLA fibres. Higher content of pigments (0.5 wt.%) decreases the tenacity and increases the elongation at break of modified fibres in comparison with pure PLA fibres.
- 2. Inorganic pigments act as nucleating agents, which results in the increase of crystallinity of PLA fibres. This effect is especially evident for the more amorphous type of PLA6100.

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CHEMICAL METHODS FOR REMOVAL OF RUBBER RESIDUES FROM MOLDS

Adam ŠKROBÁK*, Martin NOVÁK and B. HAUSNEROVÁ

Tomas Bata Univerzity in Zlín, nám. T. G. Masaryka 5555, 760 01 Zlín <u>skrobak@utb.cz</u>

In this paper, chemical cleaning methods of the contaminated molds from vulcanized rubber residues are presented. The surface free energy of mold surfaces has been measured and the mold release agents were compared by measuring the force needed for the release of form. The efficiency of sodium hydroxide solvent used in mold cleaning in a project affiliated company is compared with acid-based solvent. The effects of acid on the mold surface are observed. Relative weight loss and change in surface roughness parameters Sa and Sz were evaluated during corrosion testing in acid at different temperatures. Mold wear during a year of use in the company and year of continuous acid exposure was then extrapolated for old tool steel molds and newer stainless-steel ones.

CYTOTOXICITY TESTING OF COMPOSITE SCAFFOLDS PREPARED BY 3D - PRINTING

<u>Ida Vašková¹</u>*, Jozef FERANC¹, Peter FEILER², Zora HAJDÚCHOVÁ², Martina FERANCOVÁ², Mária Mikolajová¹, Vojtech Horváth¹, Mária Fogašová¹ and Marian JANEK²

¹Institute of Natural and Synthetic Polymers, Department of Plastics, Rubber and Fibers, Facuty of Chemical and Food Technology, Slovak University of Technology in Bratislava, Radlinského 9,

812 37 Bratislava, Slovak Republic ²Institute of Inorganic Chemistry, Department of Inorganic Materials, Technology and Materials FCHPT STU, Radlinského 9, Bratislava 812 37, Slovak Republic ida.vaskova@stuba.sk

Abstract

During this work, the thermoplastic ceramic composite scaffold based on synthetic hydroxyapatite was prepared by fused deposition modeling. The thermoplastic polymer binder based on two polymer mixture was loaded with 50 wt.% of commercial hydroxyapatite of pharmaceutical grade. The potential use of this product is aimed in the area of medical hard tissue replacements. The biocompatibility of the material as the necessary condition of scaffolds application in tissue engineering as a matrix for the cell culture growth. Therefore, the agar diffusion test was performed and growth curves were constructed, by usage of biological model – human dermal fibroblasts.

Introduction

This work contributes to the development procedure of the new composite material potentially suitable for preparation of hard tissue, especially the bone tissue replacements, using personalized shape forming by 3D printing. The 3D printing of bioceramics is a relatively novel strategy that may fabricate <u>porous matrices</u> with defined porosity and reproducible degree of precision (1) tailored to specific pacient request. Scaffold porosity provides spaces for cellular growth and attachment. (2) Bone tissue replacements can be needed in medical treatment from several reasons. For example, in case of trauma caused by accidents, osteoporosis, overuse, or degenerative diseases, etc. Hydroxyapatite is a calcium phosphate bioceramic, which is a primary mineral component of teeth and bone and it is known for its ability to interconnect with neighboring tissues and repair damaged cells. (3) Synthetic hydroxyapatite (SHA) is similar to natural component of human bones and is generally considered as suitable biocempatible biomaterial.

Materials and methods

Synthetic hydroxyapatite (SHA), with component ratio Ca/P \approx 1,54 and particle diameter $d_{50} \ge 35 \ \mu m$ was used in this work in combination with biphasic polymer binder for preparation of thermoplastic ceramic composite scaffold by fused deposition modeling method.

The LeapFrog[™] and RaisCube[™] commercial FDM 3D printer were tested to produce the "scaffold" test specimens based on sintered SHA. The prepared specimen was porous with 48 % infill and dimensions of 12.5 x 12.5 x 2.6 mm. The sintering at elevated temperatures followed.



Scheme 1 a) 3D-printed scaffold based on hydroxyapatite b) 3-D printed scaffold after sintering

Biological model – human dermal fibroblasts (HDFs) were obtained from explant cultures prepared at the Department of Burns and Reconstructive Surgery, Faculty of Medicine, Comenius University in Bratislava as is described. (4) The cells were cultured at 37°C in 6% CO₂ atmosphere. The morphology of the HDFs was observed by inverted microscopy (MBL3200, A. Krüss Optronic, Germany). The numbers of cells were evaluated by usage of the Bürker counting chamber.

Agar-diffusion test is based on capability of the cells to hold the vital color - neutral red in their lysosomes. In case of toxic effect of the tested sample on cell viability, the neutral red is released via destroyed cell membranes and discoloration occurs in the near surrounding of the tested sample.

Growth curves construction method describes the development of cell culture in presence of the tested sample in time, in comparison with negative and positive controls from the view of proliferation ability.

Conclusion

Laboratory prepared filaments based on hydroxyapatite were printable on commercial 3D printing device. The scaffolds with 3-D structure were successfully produced by the method of fused deposition modeling by presence of polymer binder. After sintering at elevated temperature, the cytotoxicity tests were performed. As the first, the agar diffusion test was carried out. During this test was observed the influence of the tested scaffold on viability of the HDFs. The studied scaffold did not express toxic effect on HDFs in this test. The growth curves construction followed with usage of the same biological model. During this experiment, the influence of tested scaffold on proliferation of HDFs in comparison with negative and positive controls was evaluated and cell morphology was observed.

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APPLICATION OF PLASTICIZER IN CALCIUM LIGNOSULFONATE-FILLED RUBBER COMPOUNDS

Michaela DŽUGANOVÁ, Ján KRUŽELÁK, Andrea KVASNIČÁKOVÁ, Klaudia JESZEOVÁ, Ivan HUDEC

Department of Plastics, Rubber and Fibres, Faculty of Chemical and Food Technology, Slovak University of Technology in Bratislava, Radlinského 9, 812 37 Bratislava, Slovakia <u>michaela.dzuganova@stuba.sk</u>

Introduction

Lignin is the second most abundant (next to cellulose) renewable natural resource, which can be obtained from various raw materials for instance sugar cane or wood. The ever-increasing environmental awareness drives the research toward finding value-added applications for lignin, which might improve the carbon footprint. Due to its abundance, relatively low cost and high thermal stability, lignin is considered a suitable filler in polymer compounds. Due to its complicated structure, lignin contains various types and several functional groups, so strong self-interactions develop among lignin macromolecules. As a consequence, its miscibility with other polymer matrices is poor^{1–3}.

Plasticizers are low molecular weight molecules, which are miscible with polymers. These molecules occupy space between polymer chains, which leads to the reduction of intramolecular forces, which results in a change in the mechanical properties and permits easier processing of the material. It is known that hydrophilic low molecular substances, with a similar structure to lignin repetition units, can act as plasticizers for lignin. This also means, that lignin is better plasticized by molecules, that can be involved in H bonds^{4–6}. For this reason, glycerol and ethylene glycol were chosen as plasticizers for the studied rubber compounds filled with calcium lignosulfonate.

Experimental

Rubber compounds were prepared by using acrylonitrile butadiene rubber (SKN 3345, acrylonitrile content 31-35 wt.%) as a matrix, filled with calcium lignosulfonate (Borrement CA120, Borregaard Deutschland GmbH, Karlsruhe, Germany) and for cross-linking of rubber compounds, a sulphur-based curing system was used. Glycerol (\geq 99%, Sigma-Aldrich, USA) and ethylene glycol (\geq 99%, Sigma-Aldrich, USA) were individually used as a plasticizer. The content of the ingredients was the same in all formulations, only the content of the plasticizers varied up to 20 phr. The composition of rubber compounds is summarized in Table 1.

The mixing of rubber compounds was performed in a laboratory mixer Brabender (Brabender GmbH&Co. KG, Duisburg, Germany) at a temperature of 90°C. The rubber compounds were homogenized using a two-roll mill as a final step.

The curing process was performed using a hydraulic press (Fontijne, Vlaardingen, The Netherlands) at a temperature of 170°C. The optimum curing time, along with other curing characteristics were investigated from the corresponding isotherms, measured by an oscillatory rheometer (MDR 2000, Alpha Technologies, Akron, OH, USA). During the curing process, thin sheets with 15 x 15 cm dimensions and approximately 2 mm thickness were obtained, which were then used for sample preparation for individual measurements.

Physical-mechanical properties were measured using Zwick Roell/Z 2.5 appliance (Zwick GmbH&Co.KG, Ulm, Germany), according to technical norm ISO STN 37 (62 1436).

| Component | NBR | sulphur | CBS | ZnO | Stearic acid | Calcium lignosulfonate | plasticizer |
|---------------|-----|---------|-----|-----|--------------|------------------------|-------------|
| Content [phr] | 100 | 3 | 1.5 | 3 | 2 | 30 | 0 - 20 |

Table 5: Composition of rubber compounds

Results and discussion

The curing isotherms for the rubber compounds, in which calcium lignosulfonate was plasticized using glycerol and ethylene glycol respectively, are illustrated in Figs. 1 and 2. It is apparent from Fig. 1, that glycerol has a significant influence on the curing isotherms of the studied rubber compounds. The maximum torque shows a decreasing trend with increasing content of glycerol. The maximum curing rate of the reference sample reaches higher values, than of those containing glycerol. Also curing isotherm of the reference sample clearly shows reversion, which suggests crosslink destruction in the compound. On the contrary, compounds containing glycerol show a marching cure for the compound containing 5 phr of glycerol and a plateau for the rest of the compounds. A different outcome can be seen in Fig. 2, where the maximum torque and curing rate show an increasing trend with increasing of ethylene glycol content, in the range of 10 to 20 phr ethylene glycol contained in the rubber compounds.



Figure 10: Vulcanization isotherms for rubber compounds plasticized using glycerol



Figure 11: Vulcanization isotherms for rubber compounds plasticized using ethylene glycol

The mechanical properties of the composites, such as tensile strength and elongation at break, were investigated. Fig. 3 shows the effect of different amounts of plasticizer on the mechanical properties of the studied composites. Glycerol gradually increases mechanical properties up to the point where 15 phr of glycerol was applied. By application of 20 phr glycerol the mechanical properties deteriorate, which is most likely caused by a high plasticizing effect of glycerol on both the filler and the rubber matrix. Weakening inter- and intramolecular forces between macromolecules, along with an increase of free volume between macromolecules could be the plausible explanation. Similarly, composites containing ethylene glycol reach the highest mechanical properties at 15 phr, which are statistically identical to the mechanical properties of the compound plasticized using 15 phr of glycerol.



Figure 12: Influence of plasticizer content on tensile strength and elongation at break of composites

Conclusion

Glycerol and ethylene glycol respectively were applied into rubber compounds based on acrylonitrile butadiene rubber filled with calcium lignosulfonate, to plasticize biopolymer filler for better processing of the compounds. The results revealed that the addition of both plasticizers influences curing characteristics. Mechanical characteristics indicate, that 15 phr of both glycerol and ethylene glycol, is the ideal amount of plasticizer for 30 phr of calcium lignosulfonate used in the rubber composites, since at this specific concentration the composites demonstrate the highest tensile strength as well as elongation at break.

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RHEOLOGICAL AND THERMAL PROPERTIES OF COLOUR MASTERBATCHES PREPARED FROM PLA

<u>Agáta HUDECOVÁ</u> *, Anna UJHELYIOVÁ, Marcela HRICOVÁ, Mária PETKOVÁ, Roderik PLAVEC

Department of Plastics, Rubber and Fibres, Faculty of Chemical and Food Technology, Slovak University of Technology in Bratislava, Radlinského 9, 812 37 Bratislava, Slovakia <u>agata.hudecova@stuba.sk</u>

Polymeric materials can be dyed in mass using colour masterbatches. The colour masterbatches consist of a carrier, a dispersing agent and a pigment¹. When choosing a carrier polymer, it is advisable to choose a polymer with a medium relative molecular weight, which has less bulky and more mobile molecules. At a very low relative molecular weight, particle agglomeration may occur². Today, thanks to its biodegradability, PLA is a suitable carrier polymer for colour masterbatches³. Dispersing agents are substances that reduce adhesion and prevent agglomeration and flocculation⁴. We distinguish between two types of pigments: inorganic and organic. Inorganic pigments are based on inert metal-based compounds. They create acceptable colours with high thermal stability and resistance to UV radiation. Particle sizes are usually less than 1 µm. Inorganic pigments include carbon black, metal oxides, and compounds based on cadmium and lead. Organic pigments are less opaque and less stable to light and heat than inorganic pigments. The particle size is 0.05 µm, which means that they have a smaller particle size than inorganic pigments. Organic pigments include, for example, phthalocyanine, isoindolinone and azo compounds⁵. Pigments must be insoluble in the polymer, chemically stable under processing conditions, compatible with the ingredients used, non-toxic and environmentally friendly⁶.

This article was aimed at the preparation of colour masterbatches from PLA modified inorganic pigments with suitable rheological and thermal properties for further processing.

Experimental part

<u>Materials used</u>: biopolymer: PLA Ingeo 6100D (PLA I6100D); inorganic pigments: Fepren TP 303M (Fe); titanium whiteness AV01SF (TiO₂); carbon black Printex Alpha (PXA); dispersing agent: silicone oil V350.

<u>Colour masterbatches preparation</u>: The preparation of colour masterbatches was carried out on a melting-kneading double screw WP ZDSK D = 28 mm in the temperature range of 180-210°C, using a stationary dryer and a mixer Drais. 1% and 3% content of inorganic pigment and 0.3% and 0.6% content of dispersing agent were used in the preparation.

<u>Method used:</u> Rheological properties were measured using the capillary viscosimeter GÖTTFERT RG20 at 190°C. In the measurement, a capillary with a circular diameter with L/D = 30/1 and a piston with a diameter of 15 mm was used in the range of shear speeds from 90 s⁻¹ to 4500 s⁻¹ with preheating for 5 minutes. Rheological properties were also measured on the rotary rheoviscosimeter PHYSICA MCR 101 with geometry plate/plate with a measuring body diameter of 25 mm in the range of shear speeds from $0.1s^{-1}$ to $100s^{-1}$ at 190°C. Thermal properties were determined using a differential scanning calorimeter from Mettler Toledo in a nitrogen atmosphere and a sample heating rate of 10°C/min and with a sample cooling rate of 10°C/min in the temperature range from 20°C to 190°C with a tempering at the temperature of 20°C and 190°C.

Results and discussion

Figures 1 and 2 show the dependences of the viscosity on the shear rate of the prepared colour masterbatches which was measured on the capillary viscosimeter and on the plate plate rotary rheoviscosimeter. The dependences show a decrease viscosity with increasing shear rate, which is typical for the pseudo-plastic behavior of polymer melts. The coloured masterbatches are polymer systems with non-Newtonian behavior, therefore the Rabinowitsch correction was used to determine the rheological parameters measured on capillary viscosimeter, taking into account the non-Newtonian nature of the flow at the capillary wall.





Figure 1. Dependence of viscosity on shear rate obtained on the capillary viscosimeter for colour masterbatches modified with inorganic pigments a) PXA, b) Fe, c) TiO₂ with 1% and 3% dyeing

By comparing pure PLA I6100D with PLA I6100D blend modified with 1% and 3% content of inorganic pigments PXA (Figure 1a) and Fe (Figure 1b), small changes can be seen in the dependences of viscosity on shear rate. By comparing pure PLA I6100D with PLA I6100D blend modified with 1% and 3% content of TiO₂, we observe a decrease in viscosity by adding pigment. The higher the pigment content (3%), the greater the drop in viscosity.

In the figure 2, it is possible to observe an increase in the viscosity of PLA I6100D blend with 3% content of PXA, Fe and TiO₂ compared to PLA I6100D blend with 1% content of PXA, Fe and TiO₂. By comparing pure PLA I6100D with PLA I6100D blend modified with 1% and 3% content of inorganic pigments PXA (Figure 2a), Fe (Figure 2b) and TiO₂ (Figure 2c), small changes can be seen in the dependences of viscosity on shear rate.

By comparing the measurements on the capillary viscosimeter and the plate/plate rotary rheoviscosimeter, we confirmed the fact that the capillary viscosimeter is more accurate method of measuring rheological properties (Figure 1 and 2).



Figure 2. Dependence of viscosity on shear rate obtained on the plate/plate rotary rheoviscosimeter for colour masterbatches modified with inorganic pigments a) PXA, b) Fe, c) TiO₂ with 1% and 3% dyeing

We determined the thermal properties by DSC analysis. During the measurement, we monitored endothermic and exothermic processes. From the measured thermograms, we evaluated enthalpy relaxation temperature (T_{ER}), cold crystallization temperature (T_{cc}), melting temperature (T_m) and crystallization temperature (T_c) of the prepared colour masterbatches obtained during the 1st heating (Table 1) and 2nd heating (Table 2).

| 1 st heating+cooling | T _{ER} [°C] | T _{CC1} [°C] | T _{CC2} [°C] | T _m [°C] | T _C [°C] |
|---------------------------------|----------------------|-----------------------|-----------------------|---------------------|---------------------|
| PLA 16100D | 70.6 | | 163.1 | 176.7 | 103.8 |
| 1%Ti | 65.9 | 94.8 | 161.2 | 176.5 | 103.4 |
| 3%Ti | 66.2 | 94.8 | 161.1 | 176.4 | 93.6 |
| 1%PXA | 67.1 | 98.2 | 161.6 | 176.8 | 88.4 |
| 3%PXA | 67.5 | 101.9 | 162.5 | 177.4 | 100.4 |
| 1%Fe | 65.4 | 95.4 | 160.9 | 176.9 | 91.1 |
| 3%Fe | 64.3 | 95.9 | 161.2 | 177.3 | 92.4 |

Table 1. Enthalpy relaxation temperature (T_{ER}) , cold crystallization temperature (T_{cc}) , melting temperature (T_m) and crystallization temperature (T_c) of the prepared colour masterbatches obtained during the 1st heating and cooling

During the 1st heating (Tab.1) of pure PLA I6100D, an endothermic peak with a maximum of 176.7°C was detected. Exothermic peak with a maximum of 103.8°C was detected during the cooling. During the 1st heating, cold crystallization was measured for all three colour masterbatches. The higher the inorganic pigment content, the more the thermal properties of colour masterbatches change. Melting temperatures obtained at the 1st heating ranged from 176.4°C to 177.4°C. By adding inorganic pigments and dispersing agent to pure PLA I6100D, we see minimal differences in melting temperatures. During the 2nd heating (Tab.2), pure PLA I6100D showed cold crystallization with a maximum exothermic peak at a temperature of 128.1°C. The difference between the 1st heating and the 2nd heating of pure PLA I6100D is due to the disappearance of the original semi-crystalline structure, PLA I6100D becomes significantly amorphous.

Table 2. Enthalpy relaxation temperature (T_{ER}) , cold crystallization temperature (T_{cc}) and melting temperature (T_m) of the prepared colour masterbatches obtained during the 2^{nd} heating and cooling

| 2 nd heat+cooling | Ter [°C] | Тссі [°С] | Tcc2 [°C] | T _m [°C] |
|------------------------------|----------|-----------|-----------|---------------------|
| PLA 16100D | 64.1 | 128.1 | | 173.9 |
| 1%TiO2 | 63.9 | 93.9 | 159.7 | 174.5 |
| 3%TiO2 | 63.7 | 94.2 | 159.3 | 173.8 |
| 1%PXA | 63.9 | 94.7 | 158.9 | 174.1 |
| 3%PXA | 64.1 | 103.5 | 161.3 | 174.3 |
| 1%Fe | 64.1 | 93.9 | 159.2 | 174.2 |
| 3%Fe | 63.8 | 94.5 | 159.4 | 173.9 |

Conclusion

This work was focused on the preparation of colour masterbatches from PLA and monitoring of the influence of inorganic pigments and the dispersing agent on the rheological and thermal properties prepared colour masterbatches. Based on the obtained data, the results can be formulated into the following conclusions:

- 1. By adding 1% and 3% content of inorganic pigments and dispersing agent to pure PLA I6100D, we observe small changes in the dependence of viscosity on shear rate.
- 2. With DSC analysis, we monitor that the addition of pigments decreases the enthalpy relaxation temperature T_{ER} , affects the cold crystallization temperature T_{CC} obtained during the 1st heating and the crystallization temperature T_C observed during cooling. The higher the inorganic pigment content (3%), the more the thermal properties of colour masterbatches change.
- 3. By adding 1% and 3% content of inorganic pigments and dispersing agent to pure PLA I6100D, we see minimal differences in melting temperatures (T_m).

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COMBINED SULFUR AND PEROXIDE VULCANIZATION OF ELASTOMER COMPOUNDS BASED ON EPDM AND IIR

<u>Andrea KVASNIČÁKOVÁ</u>¹, Ján KRUŽELÁK¹, Michaela DŽUGANOVÁ¹, Klaudia HLOŽEKOVÁ¹ and Ivan HUDEC¹

¹Department of Plastics, Rubber and Fibres, Faculty of Chemical and Food Technology, Slovak University of Technology in Bratislava, Radlinského 9, 812 37 Bratislava, Slovakia <u>andrea.kvasnicakova@stuba.sk</u>

Abstract

In this work, sulfur, peroxide, and mixed sulfur and peroxide vulcanization systems were applied for cross-linking of rubber compounds based on ethylene propylene diene monomer rubber (EPDM) and isobutylene-isoprene rubber (IIR). The goal was to investigate the influence of curing system composition on the cross-linking and properties of tested vulcanizates. The obtained results showed that the crosslink density and physical-mechanical properties of vulcanizates based on EPDM varied depending on the sulfur and peroxide ratio in the curing system. In the case of vulcanizates based on IIR, samples cured only with sulfur reached the most preferred properties.

Introduction

The optimal elastic and tensile properties of engineering rubber materials are achieved during the process of vulcanization, simply termed as curing. Vulcanization occurs by chemical agents, such as sulfur or peroxides. Sulfur vulcanization is the oldest method used for crosslinking of unsaturated rubbers. It is a complex process that leads to the formation of different types of sulfidic cross-links between macromolecules of rubber, namely monososulfidic, disulfidic, and polysulfidic cross-links. In general, sulfur cured vulcanizates exhibit good tensile properties, high tensile and tear strength, good dynamic characteristics, but weak high-temperature stability and poor resistance to aging.

Peroxides can be used to vulcanize both, unsaturated and saturated rubbers. Cross-linking of elastomers with organic peroxides is the radical process, which results in the formation of carbon-carbon bonds between macromolecular chains. Carbon-carbon cross-links have higher bonding energy in comparison with sulfidic cross-links. The main benefit of C-C bonds is their high thermal stability. Therefore, peroxide cured vulcanizates exhibit high-temperature aging resistance and low compression set at elevated temperatures. Simple formulation of rubber compounding, good electrical properties of vulcanizates, good shelf life stability and no staining of the finished parts belong to other advantages of peroxide vulcanization. However, there are also some drawbacks when compared to sulfur cured systems, such as low scorch safety, worse tensile and tear strength, lower elastic and dynamic properties, and lower abrasion resistance of vulcanizates. Cross-linking of elastomers with peroxides can be effectively improved by using co-agents. Co-agents are multifunctional low molecular weight organic molecules with high reactivity toward free radicals. They are used to increase the cross-linking efficiency of the vulcanization process, but to increase the cross-link density of final vulcanizates, as well. As a result, the physical properties and treatability of peroxide-cured elastomers are improved.

When combining vulcanization systems, both sulfidic and carbon-carbon bonds are formed between rubber chains and this gives the real presumption to influence the properties of the final materials in order to suppress the drawbacks of particular vulcanization systems and to highlight their benefits.^[1,2,3]

Experimental

Ethylene propylene diene monomer rubber (KEP 570F, the content of ethylene – 70 wt.%, content of 5-ethylidene-2- norbornene monomer – 4.5 wt.%, Kumho Polychem Co. Ltd., South Korea) and isobutylene-isoprene rubber (X butyl RB 301, content of isoprene 1,85 wt.%, Arlanxeo, Switzerland) were used as rubber matrices. Sulfur curing system consisted of zinc oxide (Slovlak, Košeca, Slovakia), stearic acid (Setuza, Ústí nad Labem, Czech Republic) as activators, N-cyclohexyl-2- benzothiazole sulfenamide (CBS, Duslo, Šaľa, Slovakia) as accelerator, and sulfur (Siarkopol, Tarnobrzeg, Poland) as curing agent. Peroxide curing system consisted of dicumyl peroxide (DCP) as peroxide curing agent and trimethylolpropane trimethacrylate (TMPTMA) as co-agent. Both chemicals were supplied from Sigma– Aldrich, USA. The composition of the rubber compounds and their designations is presented in Tab. 1.

| Component | phr | phr | phr | phr | phr |
|--------------|---------|---------|-------------|---------|---------|
| IIR, EPDM | 100 | 100 | 100 | 100 | 100 |
| ZnO | 0 | 1 | 2 | 3 | 4 |
| Stearid acid | 0 | 0,5 | 1 | 1,5 | 2 |
| Sulfur | 0 | 0,5 | 0,75 | 1 | 1,5 |
| CBS | 0 | 1 | 2 | 3 | 4 |
| DCP | 1,5 | 1 | 0,75 | 0,5 | 0 |
| TMPTMA | 4 | 3 | 2 | 1 | 0 |
| Designation | S0-P1.5 | S0.5-P1 | S0.75-P0.75 | S1-P0.5 | S1.5-P0 |

Tab. 1. Composition and designation of rubber compounds.

The mixing of rubber compounds was carried out in a laboratory mixer Brabender in two mixing steps. The speed of the rotor was set up to 55 rpm and temperature was 80 °C. First, the rubber was plasticated for 1 min, then activators and accelerators of curing systems were introduced. The mixing process then continued for 3 min. After that the blends were homogenized in two-roll mill. In the second step, the accelerator and sulfur were introduced with subsequent compounding for the next 4 min at 55 rpm and 80°C. Similarly, DCP and co-agent were added in the second step. There were prepared five types of rubber compounds. The first one was prepared only with peroxide curing system, by contrast the last one only with sulfur curing system. In the rest three rubber formulations, the mutual ratio of sulfur and peroxide was uniformly changed.

The prepared rubber compounds were cured by using a hydraulic press Fontijne at 180° C and approximately 15 MPa. The rubber compounds were cured in the form of thin sheets (thickness 2 mm, width 15×15 cm). The cross-link density was determined by swelling of vulcanizates in xylene. When equilibrium swelling was reached, the cross-link density was calculated by using of the Flory–Rehner equation. The physical–mechanical properties of the vulcanizates were evaluated by using of Zwick Roell/Z 2.5 appliance at cross-head speed of 500 mm.min⁻¹.

Results and discussion

Both, sulfur and peroxide curing systems exhibit different reaction mechanisms and lead to the formation of different types of chemical cross-links between rubber chain segments. Therefore, there was real presumption that the change in composition of curing could influence the cross-link density and the structure of the formed cross-links within the rubber matrices. From Fig. 1 it can be observed that the highest cross-link density v exhibited the vulcanizate based on EPDM cured with peroxide curing system (S0–P1.5). On the other hand, we can see that the vulcanizate based on IIR cured with peroxide system (S0–P1.5) did not show the networking effect. Higher cross-link density exhibited vulcanizates based on EPDM, while vulcanizates based on IIR were found to have much lower cross-linking degree. Vulcanizates based on EPDM cured with combined sulfur and peroxide curing systems exhibited lower cross-linking degree. The possible explanation of this might be some competitive reactions, which may consume free peroxide radical species and/or sulfur fragments, running simultaneously with the main cross-linking reactions within the rubber matrices into which combined sulfur/peroxide systems were applied for cross-linking. The crosslink density of the vulcanizates based on IIR showed a slight increasing ratio of sulfur system. The chemistry of accelerated sulfur vulcanization is very complex and still not fully understood. Sequences of chemical reactions run during the process, which may have substitutive, addition or even elimination character. Not only initial components of curing systems, but also products of their conversion can participate in these reactions.



Fig. 1. Influence of curing system composition on cross-link density ν of vulcanizates.

The dependence of elongation at break on curing systems is in close connection with dependences of cross-link density. The highest elongation at break showed the vulcanizate based on IIR with designation S0.5-P1 having the lowest cross-link density (Fig. 2). On the other hand, the higher is the cross-link density, the more restricted is the rubber chains elasticity and mobility. Thus, vulcanizates only cured with sulfur or peroxide system with the highest cross-link density exhibited the lowest elongation at break. From Fig. 3 it becomes obvious that the vulcanizate with designation S1-P0.5 was found to have the highest tensile strength. In this way, it must be noted that tensile strength of cured rubber systems is a complex property, dependent not only on cross-link density but also on the type and structure of cross-links formed within rubber matrices. Looking at Fig. 3, it is apparent that vulcanizates cured with combined vulcanization systems exhibited higher tensile strength when compared to their counterparts cured only with sulfur or peroxide system. The achieved results point out to some synergistic effects of combined vulcanization systems.



Fig. 2. Influence of curing system composition on elongation at break of vulcanizates.



Fig. 3 Influence of curing system composition on tensile strength of vulcanizates.

Conclusion

Sulfur, peroxide, and combined sulfur/peroxide curing systems were applied for cross-linking of rubber compounds based on EPDM and IIR. The results revealed that the change in combination of curing systems results not only in the change in vulcanization course but also to the modification of cross-link density and physical-mechanical properties of vulcanizates.

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OXYGEN PERMEATION THROUGH EPDM RUBBER CONTAINING VARIOUS LAYERED NANOPARTICLES

Igor NOVÁK¹, Tuba EVGIN¹, Ján HRONKOVIČ², Jozef PREŤO², Ivan CHODÁK¹

Polymer Institute SAS, Dúbravská cesta 9, 845 41 Bratislavca VIPO, a.s.., Generála Svobodu 1069/4, 958 01 Partizánske <u>upolnovi@savba.sk</u>,

EPDM rubber was modified by addition of various layered nanoparticles, namely organo-modified montmorillonite, graphene, and double layered hydroxides. Standard ultimate properties were investigated with special concern on gas permeation through the polymeric foils.

Several types of graphene in the role of surface filler in EPDM mixtures were investigated in detail. In total, we used four types of graphene, where types G1, G2 and G3 were similar in terms of particle size and specific surface (170 m2/g), but G4 had smaller particles and a significantly higher specific surface (800 m2/g). The recipe of the prepared mixtures is shown in Tab. 1

| Material | content (phr) | Mixing time (minutes) | Supplier |
|---------------------|------------------|--------------------------|--|
| EPDM | 00 | 0-1 | SpecialChem (US) |
| Graphene | 1,3,5,7,10,15,20 | 1-4 | Nanogarafi (Turkey) |
| Carbon black N-550 | 20,50 | 1-4 | MAKROchem S.A. (Poland). |
| Plasticizer | 10 | 4-6 | Unipetrol (Slovakia). |
| AOX-TMQ antioxidant | 1 | | Nord Chemie (Italy). |
| ZnO | 5 | 1-4 | Oddział Huta Oława (Poland). |
| Stearic acid | 1 | | OLEOCHEM, a.s (Czechia). |
| TMTD | 2.5 | 6-6.5 | RDC S.r.l. (Italy). |
| sulphur | 0.5 | 6.5-7 | CHEMICAL PLANTS "Siarkopol" TARNOBRZEG Ltd. (Poland). |

Table 1 Mixture composition and mixing procedure for graphene-based filler testing



Fig. 1 Tensile strength and deformation curves for EPDM filled with 7 phr of different graphenes (picture on the left) and comparison of the tensile curves for EPDM without fillers, containing 20 phr of carbon black and containing carbon black and 7 phr of graphene G1 (picture on the right).

In order to try to explain in more detail the differences and at first glance not entirely logical results of the mechanical properties (especially lower moduli for graphene G4 despite significantly higher surface areas), we performed swelling tests for all mixtures in toluene and evaluated the extractable fraction of the mixture (not presented here), the values of the extractable fraction basically represent the amount of oil. The values of the residual weight of the samples after swelling and subsequent drying are very similar in the range of 88-91 wt.%). The results of the degree of swelling and network density are presented in Tab. 2 and 3.

Table. 2. Degree of swelling (ξ) and calculated crosslink density (v_e) for EPDM mixtures filled with graphene particles of various types. Filler content 7 phr.

| Samples | ξ, % | v_e (mol.m ⁻³) |
|---------|------|------------------------------|
| EPDM | 265 | 168 |
| EPDM/G1 | 232 | 225 |
| EPDM/G2 | 250 | 190 |

| EPDM/G3 | 252 | 188 |
|---------|-----|-----|
| EPDM/G4 | 281 | 147 |

Table. 3. Degree of swelling (ξ) and calculated crosslink density (v_e) for EPDM mixtures filled with various content of G1 type graphene particles. Carbon blacks content 20 or 50 phr.

| G1 (Phr) | EPDM/CB20/G1 | | EPDM/CB50/G1 | | |
|----------|--------------|---------------------------|--------------|---------------------------|--|
| | Ę | ve (mol.m ⁻³) | بخ | ve (mol.m ⁻³) | |
| EPDM | 265 | 168 | 265 | 168.20 | |
| 0 | 198 | 317 | 146 | 592 | |
| 1 | 181 | 380 | 138 | 658 | |
| 3 | 209 | 281 | 141 | 632 | |
| 5 | 193 | 334 | 137 | 673 | |
| 7 | 189 | 349 | 134 | 699 | |

For the study of the fillers effect on the modification of the properties, including the reduction of gas permeability, vulcanizates were prepared for measuring oxygen permeability according to the ASTM D3985-05 "Standard Test Method for Oxygen Gas Transmission Rate through Plastic Film and Sheeting Using a Coulometric Senso".

In total, 6 types of mixtures were used containing layered double hydroxides (LDH) of the Alcamizer P93 and Hydrotalcite 652288 types. Two of the prepared test mixtures contained the silanizing agents (3-mercaptopropyl)triethoxysilane (MPTES) and triethoxyvinylsilane (KBE-1003). In addition, one mixture without LDH fillers was prepared for comparison. In Table 4, the active components of individual test mixtures for measuring oxygen permeability are shown. The concentrations of the components are expressed in parts per 100 phr.

To support the formation of lamellar structures of layered double hydroxides in the matrix of EPDM rubber, 5 types of silanizing agents were used, and EPDM elastomer Keltan 4450 was used as rubber. The following silanizing agents were used to prepare the mixtures: Si 75 – bis(triethoxysilylpropyl)disulfide, MPTES – (3-mercaptopropyl)triethoxysilane, BTEPA – bis[3-(triethoxysilyl)propyl]amine, KBE-503 – 3-(triethoxysilyl)propyl methacrylate, and KBE-1003 – triethoxyvinylsilane.

Determination of gas permeability through polymeric or elastomeric materials is one of the basic parameters for determining the success of possible applications of the materials under question. We modify the materials based on EPDM rubber with three types of layered fillers, preferably nano-sized, with the aim of reducing the penetration of gases through thin layers.

At this stage, in the first phase, we checked both the details of the theoretically known regularities of gas diffusion through polymer thin layers and subsequently some basic attributes of the behavior of (nano) composites as possible additives for adjusting the diffusion parameters or gas permeability. The first results from this research are shown in Fig. 2 and in Table 4. They refer to EPDM-based vulcanized elastomers in which we added different concentrations of layered double hydroxides (DLH) and graphene. In addition to obtaining primary knowledge about the effectivity of individual layered materials as a barrier for gas penetration, we also checked the effect of changing the thickness of the elastomeric film on possible changes in oxygen permeability.



Fig. 2 Relative permeability coefficient normalized to the unit thickness of the sample for vulcanized EPDM filled with 50 phr of N-550 carbon black and the addition of two-dimensional nanofillers or other additives, the identification of which is given in Table 4. Samples G1-5 and G4-5 differ only in thickness (see Table 4).

As seen from the permeability values, compared to the reference value of EPDM vulcanizate with carbon black without other additives, practically all values are higher for the mixtures with the addition of layered fillers, except for the material filled with 10 phr graphene G1, where the trend can be evaluated as a small decrease. In any case, this condition is most clearly manifested in DLH materials, which are also the most polar. However, as seen from Tab. 4, nor the addition of silanes, which should act as compatibilizing agents between DLH and EPDM, not only did not improve the situation, but on the contrary, the measured permeability data are the same or even slightly higher than mixtures with DLH without silanes.

It is seen from the figure, but especially from the Table, thicker samples are more effective in terms of creating a barrier against gas penetration compared to thinner ones, despite the fact that the results were converted to a unit of thickness. The results of the oxygen permeability measurement are to a large extent, because it was assumed that the tested fillers would act as barriers for gas diffusion. More accurate conclusions regarding the reason for this outcome will be made after further tests, primarily of TEM, which should reveal the structure of the fillers in the matrix. It can be assumed that, even if the deposition of layered fillers should reduce gas permeability, in the case that the particles are deposited predominantly perpendicular to the diffusion direction, it seems that many particles are deposited parallel to the diffusion direction, it seems that many particles are formed around the filler particles, sufficient for the passage of gas molecules. This preliminary conclusion is also supported by the higher vapor permeability for the mixtures containing graphene G4 with smaller particles compared to G1, which can be attributed to the significantly higher number of small particles and thus the greater number of cracks in G4.

Table 4 Content of additives in the samples and related values of the relative coefficient of permeability (Kperm) depending on the thickness of the sample (L) for vulcanized EPDM filled with 50 dsk N-550 carbon black. The data in columns 3 and 4 represent the average of three measurements and the standard deviation. Alk – Alcamizer P93 (double layer hydroxide), HT – Hydrotalcite652288 (double layer hydroxide), MPT – (3-mercaptopropyl)triethoxysilane, KBE-503 - 3-(triethoxysilyl)propyl methacrylate

| | Sample | Aditíve, phr | Kperm | L, mm |
|---|---------------------------------------|----------------|------------------------|-----------------------|
| | EP 0 | | $\overline{2938}\pm90$ | $0,283 \pm 0,012$ |
| | EP 5 | Alk 10 | 3083 ± 86 | $0,\!267 \pm 0,\!007$ |
| ſ | EP 6 | HT 0,5 | 3277 ± 63 | $0,271 \pm 0,011$ |
| | EP 8 | HT 3 | 3524 ± 120 | $0,\!249 \pm 0,\!007$ |
| ſ | EP 10 | HT 10 | 3498 ± 27 | $0,255 \pm 0,014$ |
| ſ | EP 15 | HT 10, MPT 1 | 3589 ± 40 | $0,256 \pm 0,019$ |
| ſ | EP 24 | HT 10, KBE 1 | 3907 ± 77 | $0,253 \pm 0,018$ |
| ſ | G1-3 | Grafén1 3 dsk | 3067 ± 124 | $0,\!288 \pm 0,\!019$ |
| ſ | G1-5 -1 | Grafén1 5 dsk | $2265 \pm n/a$ | $0,38 \pm 0,05$ |
| ſ | G1-5 -2 | Grafén1 5 dsk | $2298 \pm n/a$ | $0,\!42\pm0,\!08$ |
| ſ | G1-5 -3 | Grafén1 5 dsk | $3058 \pm n/a$ | $0,\!29 \pm 0,\!03$ |
| ſ | G1-10 Grafén1 10 dsk | | 2530 ± 17 | $0,304 \pm 0,022$ |
| ſ | G4-3 -1 | Grafén4 3 dsk | 3202 ± 110 | $0,332 \pm 0,051$ |
| ſ | G4-5 -2 | Grafén4 5 dsk | $3412 \pm n/a$ | $0,\!30 \pm 0,\!02$ |
| ſ | G4-5 -3Grafén4 5 dskG4-5Grafén4 5 dsk | | $2407 \pm n/a$ | $0,\!39\pm0,\!05$ |
| | | | $2428 \pm n/a$ | $0,\!44\pm0,\!08$ |
| ľ | G4-10 | Grafén4 10 dsk | 3366 ± 37 | $0305 \pm 0,034$ |

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RECYCLING OF TRUCK TYRES

Hamed Peidayesh¹, Ivan CHODÁK¹ and Jozef SOTÁK^{2*}

Polymer Institute SAS, Dúbravská cesta 9, 845 41 Bratislavca RESUMO, Ladislava Hudeca 15326/2A, 974 01 Banská Bystrica <u>upolchiv@savba.sk</u>, <u>sotak@resumo.sk</u>

The recycling of tyre trucks is performed on the production line LJR-5000, a product of China.. Total capacity is around 4000 tons per year.

The tyre rubber powder is prepared from the outer tread of truck tyre. After physical crushing, the particle size of rubber powder is 20~40 mesh. According to the market research on the formula of truck tread, the general average composition consists of natural rubber (67 phr), SBR rubber (19 phr), butadiene rubber (14 phr), carbon black (52 phr) and white fillers, probably silica and calcium carbonate (10 phr).

The rubber powder represents the basic raw material for devulcanization process resulting in reclaimed rubber production. The reclaimed rubber is processable using any technology common for preparation of rubber mixtures, followed by shaping and vulcanization to final rubbery products. It is possible to be modified by identical means as for common rubbers, i.e. by application of reinforcing fillers, softeners, special additives, and components of vulcanizing system.

Several data were selected from a vast collection of experiments showing the examples of possible applications of the produced reclaimed rubber. First, the mechanical properties of the vulvanizate from virgin reclaimed rubber were tested on a model rubber mixture composed of elastomer part (100 phr of reclaimed rubber, in following experiments it is virgin rubber or the summation of reclaimed rubber and virgin rubbers), carbon black N234 (35 phr), accelerator Sulfenax CBS (1 phr), ZnO (3 phr), stearic acid (1 phr) and sulphur (3 phr). To see the reproducibility of product, seven batches of the RESUMO reclaimed rubber were tested, each one prepared as separate process produced in the years 2018 – 2021. From each batch the rubber mixure a 1mm thinck slab was vulcanized and seven specimens were cut from each vulcanized slab for measuring the mechanical properties. The data are shown in Table 1 below.

Table 1 Mechanical properties of vulcanizates prepared from 7 regenerates produced at various times, showing reasonable reproducibility of the regenerate preparation process, even in spite of probable scatter in the compositions of rubber mixtures for recycling.

| Regenerate Sample No | Tensile Stress (MPa) | Tensile Strain (%) | Young's Modulus (MPa) | M 100 (MPa) | M 200 (MPa) |
|-------------------------|----------------------------|--------------------------|-----------------------------|----------------|----------------|
| 1 | 7.9 ± 0.4 | 288.9 ± 12.3 | 3.3 ± 0.1 | 2.4 ± 0.1 | 5.2 ± 0.2 |
| 2 | 8.7 ± 0.4 | 257.0 ± 11.5 | 4.1 ± 0.2 | 2.9 ± 0.1 | 6.6 ± 0.3 |
| 3 | 7.5 ± 0.7 | 285.2 ± 21.2 | 3.1 ± 0.2 | 2.3 ± 0.1 | 4.9 ± 0.3 |
| 4 | 8.0 ± 0.6 | 251.7 ± 15.1 | 3.7 ± 0.3 | 2.8 ± 0.2 | 6.2 ± 0.4 |
| 5 | 7.7 ± 0.7 | 227.0 ± 18.8 | 4.1 ± 0.1 | 3.0 ± 0.1 | 6.7 ± 0.3 |
| 6 | 7.2 ± 0.5 | 255.5 ± 20.3 | 3.4 ± 0.1 | 2.5 ± 0.2 | 5.6 ± 0.3 |
| 7 | 8.9 ± 0.6 | 262.4 ± 20.0 | 4.1 ± 0.1 | 2.9 ± 0.1 | 6.5 ± 0.2 |

Comparison of two regenerates

Next, a comparison of properties were tested between Resumo reclaimed rubber and an Indien product frequently applied in several Italian companies. Three different regenerates were compared, namely, Resumo supplied in 2021, marked as Old Resumo (produced around 2018, grade No 6 in the Table 1), Resumo supplied in April 2022, produced probably in the middle of 2020, marked as New Resumo, and Indian regenerate. The mechanical properties of the regenerate – based mixtures are shown in the Table 2. The mixtures based on reclaimed rubbers in absence of virgin rubbers show difference between Resumo and Indian regenerates, the Resumo vulcanizate exhibits clearly higher both tensile strength as well as strain at break, while modulus 100 for Indian regenerate is slightly higher compared to "old" Resumo regenerate, but more or less the same if compared to "new" Resumo regenerate. The small differences, if compared the old and new Resumo regenerates, can be explained by possible mnarginal degradation of the old Resumo regenerate which has been stored by approximately by 2 years longer time than the "new" Resumo.

Table 2 Reclaimed rubber with all ingredients, no virgin rubbers present

| Sample of reclaimed rubber | Tensile Stress (MPa) | Tensile Strain (%) | M 100 (MPa) | M 200 (MPa) | M 300 (MPa) |
|----------------------------------|----------------------------|-----------------------|----------------|----------------|----------------|
| Old Resumo | 7.2 ± 0.5 | 255.5 ± 20.3 | 2.5 ± 0.2 | 5.6 ± 0.3 | 0 |
| New Resumo | 8.6 ± 0.8 | 232.9 ± 21.5 | 3.1 ± 0.2 | 7.4 ± 0.4 | 0 |
| Indian | 4.0 ± 0.2 | 123.4 ± 8.1 | 3.4 ± 0.1 | 0 | 0 |
Substitution of part of the virgin rubbers by RESUMO reclaimed rubber.

Several model mixtures were tested, based on natural rubber, SBR, or nitril rubber. In this paper, only model mixture based on blend of SBR and NBR 1:1 is presented.

The mixtures were made by two principles. First, the amount of both rubbers (NBR and SBR) decreased by the same portion, either 20 or 35 phr and the particular regenerate was added instead, so that the 100 phr of rubbers consisted from the summation of NBR, SBR, and regenerate.

Second set was designed due to suggestion that the composition of the regenerate (at least Resumo – type) consists of natural rubber, about 67 phr, SBR about 23 phr and BR 10 phr, while no NBR is present. Therefore, we substituted only a part of SBR while the portion of NBR was left constant. By such a way in this case the NBR content was always 50 phr while the contents of SBR and regenerate was 50 / 0 if no regenerate was present, 30 / 20 if 20 phr of the virgin rubber was substituted by the regenerate, or 15 / 35 if the regenerate content was 35 phr. Moreover, in this case also the content of CB was changing, namely it was either left constant for 35 phr of CB in any ratio of NBR / SBR / regenerate, or the ratio of CB being 35 phr was calculated only considering the content of the virgin rubbers, i.e. summation of the NBR + SBR without the regenerate. This attitude was based on the suggestion that in the regenerate, certain portion of CB has been left after devulcanization process.

As the third difference, in the reclaimed rubber, 75 phr of rubber powder (also the product of Resumo produced by simple milling of the tyres without following devulcanization) was added as the reactive filler. This trial was justified by our previous experiments with Resumo reclaimed rubber, where the addition of rubber powder did not affect the mechanical properties and contributed to the other aspects of the final vulcanizate.

Mechanical properties of the mixtures NBR / SBR with substitution of virgin rubbers by reclaimed rubber

In the first set of mixtures part of the virgin rubbers was substituted by Resumo regenerate, in this case amounts of both NBR and SBR were decreased and substituted by the regenerate.

The mixtures were prepared according to composition described above. The mechanical properties of all mixtures are shown in the Table 3 and 4.

It is seen that substitution of 20 phr of virgin rubbers by the regenerate does not result in changing the tensile strength and the decrease in elongation at break is not substantial. On the other hand, substitution of 35 phr of the virgin rubbers leads to significant decrease in the strength. It is worth to mention that a decrease in the CB content on the level corresponding to virgin rubbers without regenerate results in all cases in dramatic decrease in tensile strength.

Further set of samples represents the substitution of only SBR by equivalent amount of regenerate.

Table 3 Mechanical properties of mixtures substituting equal parts of NBR and SBR by Resumo regenerate, CB content either constant calculated to full content of rubbers + regenerate (i.e. 35 phr in all cases), or calculated on phr only of virgin rubbers (28 or 17.5 phr)

| Sample | Tensile Stress (MPa) | Tensile Strain (%) | M 100 (MPa) | M 200 (MPa) | M 300 (MPa) |
|------------------------|----------------------------|-----------------------|----------------|----------------|----------------|
| (NBR-SBR) 100 - CB 35 | 20.4 ± 1.5 | 409.2 ± 19.2 | 3.5 ± 0.2 | 7.9 ± 0.6 | 13.4 ± 1.1 |
| (NBR-SBR) 80 - CB 28 | 18.0 ± 1.0 | 395.7 ± 20.8 | 3.5 ± 0.2 | 7.8 ± 0.4 | 12.9 ± 0.7 |
| (NBR-SBR) 80 - CB 35 | 21.2 ± 1.2 | 335.8 ± 16.3 | 5.0 ± 0.3 | 11.5 ± 0.5 | 18.8 ± 0.8 |
| (NBR-SBR) 50 - CB 17.5 | 13.6 ± 0.9 | 301.7 ± 17.2 | 3.9 ± 0.2 | 8.6 ± 0.4 | 13.5 ± 0.8 |
| (NBR-SBR) 50 - CB 35 | 15.6 ± 1.3 | 217.8 ± 18.0 | 6.8 ± 0.3 | 14.5 ± 0.6 | 0 |

Table 4 Mixtures of NBR - SBR with 35 phr of carbon blacks and either Resumo or Indian Regenerate substituting the virgin SBR

| Sample | Tensile Stress (MPa) | Tensile Strain (%) | M 100 (MPa) | M 200 (MPa) | M 300 (MPa) |
|--------------------------------------|----------------------------|--------------------------|----------------|----------------|----------------|
| NBR 50 - SBR 50 | 24.3 ± 1.2 | 403.4 ± 20.0 | 3.8 ± 0.2 | 9.2 ± 0.5 | 16.1 ± 0.8 |
| NBR 50 - SBR 30 - IND 20 | 21.3 ± 0.7 | 309.7 ± 9.8 | 5.8 ± 0.2 | 12.9 ± 0.3 | 20.7 ± 0.5 |
| NBR 50 - SBR 30 - RES 20 | 22.3 ± 2.4 | 296.9 ± 19.3 | 5.8 ± 0.2 | 13.8 ± 0.5 | 0 |
| NBR 50 - SBR 15 - IND 35 | 19.0 ± 1.8 | 242.1 ± 23.3 | 7.3 ± 0.1 | 15.6 ± 0.3 | 0 |
| NBR 50 - SBR 15 - RES 35 | 19.1 ± 1.9 | 244.9 ± 15.1 | 6.4 ± 0.4 | 15.0 ± 0.8 | 0 |
| NBR 50 - SBR 15 - (IND 75 powder) 35 | 19.9 ± 1.6 | 251.4 ± 14.1 | 7.0 ± 0.3 | 15.4 ± 0.7 | 0 |
| NBR 50 - SBR 15 - (RES 75 powder) 35 | 19.4 ± 1.7 | 243.7 ± 18.1 | 6.7 ± 0.4 | 15.5 ± 0.9 | 0 |

IND Indian regenerate, RES – new Resumo regenerate. In parenthesis the composition of regenerate with addition of 75 phr of rough powder (calculated on the regenerate 100 phr)

It is worth ro mention that in spite of more than double value of tensile strength of the Resumo reclaimed rubber compared to the Indian material (see the Table 2), the comparison of the mechanical properties of the mixtures containing also virgin rubbers with the two regenerates, i.e the Indian and new Resumo, shows that mechanical parameters for all mixtures are almost identical. Certain decrease of mechanical parameters are seen for both regenerates if subsituting the SBR part of the rubbers,

I tis seen that the substitution of part of SBR by the reclaimed rubber results in statistically significant but not dramatic decrease in both tensile strength and strain at break. At the same time, the moduli M100 as well as M200 were found to be higher for mixtures with regenerate presence.

Conclusions

Generally during the mixing of the blends following comments were reported by the staff performing the laboratory preparation:

All mixtures containing Indian regenerate exhibited higher adhesion to metallic parts of both mixing chamber of the Brabender as well as to two-roll mill. The sticking onto Brabender chamber walls was somewhat more pronounced, obviously due to higher temperature of the blends during mixing (around 60 °C) compared to calendering.

The smell of the materials during mixing was more intensive for mixtures containing the Indian regenerate, also the vulcanizates after curing smelled more intesively if containing the Indian regenerate.

The reproducibility of properties of Resumo regenerate prepared by the same processes in several batches during approximately two years shows that the differences in the values of mechanical properties of the regenerate-based vulcanizates are very reproducible, justifying that the process of regenerate production is well mastered.

The data presented above may lead to following conclusions and recommendations:

- The substitution of virgin rubbers by regenerates has almost negligible effect on the mechanical properties (decrease in tensile strength) up to regenerate content of 20 phr for both Indian as well as Resumo regenerates.
- Substitution up to 35 phr of virgin rubbers could be considered if marginal decrease of strength would be acceptable.
- Higher reclaimed rubber content might be achieved if more substantial changes would be applied in the mixture composition, especially regarding the filler content and perhaps changes in vulcanization system.
- All conclusions mentioned above have been supported by DMTA data which are not presented here due to extensive space

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THE USE OF RECYCLED POLYETHYLENE IN ASPHALT MIXTURE

Czímerová, A.^{1,*}, Lukáčová E.², Víghová A.², Kovács R.¹ And Fónod A.¹

VÚRUP, a.s., Vlčie hrdlo P.O.BOX 50, 820 03 Bratislava 23, Slovakia e-mail address: eva.lukacova@vurup.sk, <u>anita.vighova@vurup.sk</u>

Recycling of any kind has become a must in last decades of human being. Production of waste increases enormously from year to year. Polymers except of their great processing properties is perfect material for recycling and reusing it repeatedly in different fields of daily life. This poster presents a short review of using recycled polyethylene (PE-LD) for asphalt modification as a way for sustainability and lowering the environmental impact. There have been already issued various application studies of PE-modified asphalt since the 1980s even though PE as an asphalt modifier has received less attention compared to other polymer potential modifiers because the non-polar and non-aromatic nature of PE limits its ability to blend with asphalt binders. Anyway we decided to use recycled PE-LD fraction for modification of asphalt mixtures since it has a large presence in polymer waste, can be quite easily sorted out and pretreated before final application in asphalt mixtures (energetically less demanding because it's melting temperature is close to the mixing temperature of asphalt mixture). With the right choice of physical-chemical parameters of recycled materials and using a suitable reaction condition we can them incorporate into the asphalt mixtures. In our study, recycled plastic granulate was used, originally from films and various packaging materials. Subsequently, this recycled material was blended into the asphalt mixture under appropriately selected reaction conditions. A commercially available polymer of similar chemical composition to the recycled material was used as a comparison sample.



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