Introduction

Disposal of waste tyres is a serious environmental problem since tyre rubber as other polymeric materials does not decompose easily. Two major approaches to solve this problem are the recycling and reclaiming of waste rubber. Tyre rubber is a complex material consisting of natural rubber (NR), styrene-butadiene rubber (SBR), polybutadiene rubber (BR) and several additives whose purpose is to improve physical properties of the final product. The average composition of tyre rubber varies with the type of tyres. The mechanical recycling of waste tyre consists in their shredding, grinding and removing steel cords and textile parts and gives ground rubber. This material can be used, e.g., in road construction as additive in hot mix asphalt and the rate of degradation of this material can significantly influence the performance and service life of road surface.

Mobility of polymer chains in rubber is restricted by crosslinks. The optimum cross-linking gives rubber good flexibility and elasticity. The ageing processes in rubber lead to chain scission and/or increased cross-linking giving weaker, brittle polymer. Information about the segmental motion in rubber can be obtained from the measurements of temperature dependence of NMR spin-lattice relaxation time $T_1$ of protons in polymer chains. At the temperature minimum of the relaxation time $T_1$ the condition $\omega t_\pi = 0.62$ is fulfilled, where $\omega$ is the Larmor frequency and $t_\pi$ is an average (local) segment reorientation time. With increasing degree of cross-linking $t_\pi$ increases and $T_1$ minimum shifts to higher temperature. Information about the molecular motion can be also obtained from the proton spin-spin relaxation time which is related to elasticity and flexibility of material. The more restricted a molecules motion is, the faster the system will return to its initial condition after being excited, so the shorter is $T_2$.

The aim of this study is to quantify the degradation of ground rubber from waste tyres by means of NMR spin-lattice relaxation time $T_1$ and spin-spin relaxation time $T_2$ determined for protons in methylene groups of rubber chains.

Experimental

The $^1$H and $^{13}$C NMR experiments were performed in the temperature range 22–100 °C on Varian NMR spectrometer operating at 400 and 100 MHz, respectively, using 4 mm rotor and a magic angle spinning (MAS) rate of 6 kHz and 10 kHz. $^{13}$C NMR spectra were obtained with 90° pulse (1.9 $\mu$s), a high power proton decoupling of 92.6 kHz, a recycle delay of 6 s, and averaging over 4000–6000 scans. $^1$H MAS NMR spectra of sufficient resolution were obtained with 90° pulse (4.75 ms), using a recycle delay of 4 s and averaging 20 scans. An inversion recovery pulse sequence was used for $T_1$ measurements. $T_2$ was obtained from the experiments using MAS rate of 10 kHz and 90-t-180 sequence in which spin-echo was detected after a delay time $t$. The spectra measured for $t$ from the range 100 µs – 40 ms were deconvoluted using MestReNova software and the areas under the peak given by methylene protons were plotted versus the delay time $t_d = 2t$.

The curve fitting was performed in SciDavis programme using scaled Levenberg-Marquardt algorithm.

The samples of ground rubber were supplied by V.O.D.S, Kechnec, Slovakia. The material underwent a standard recycling procedure. Prior to NMR measurements the traces of metallic parts in the samples were removed using permanent magnet. The measurements were carried out on the as-supplied sample (GR-0) and the samples GR-3 and GR-8 which were thermally treated at 85 °C for 3, and 8 days, respectively, in Ecocell oven with natural convection. The spectra were recorded also for new tyre rubber (TR).

Results and discussion

The $^{13}$C MAS NMR spectra of ground rubber are qualitatively the same (spectrum of GR-0 is shown in Fig. 1) and consist of lines with chemical shifts of 134.8, 125.3, 32.5, 26.7, and 23.6 ppm assigned to $C_1$, $C_2$, $C_3$, $C_4$ and $C_5$ carbons in cis-1,4-isoprene units of NR and lines with chemical shifts of 129.6, 30.4 and 27.6 ppm assigned to SBR carbons.

The chemical shift pattern is in accordance with the tyre rubber $^{13}$C NMR chemical shifts.

The $^1$H NMR spectra of ground rubber samples display three dominant lines with chemical shifts of 1.6, 2.0 and 5.1 ppm assigned to the methyl, methylene and unsaturated methine protons of cis-1,4-isoprene units of natural rubber, the $^1$H lines of aromatic and methine protons in SBR are visible in the spectra and are marked by circles in Fig. 1.

Fig. 1. $^{13}$C MAS NMR spectrum of GR-0 sample recorded at room temperature
ble in the spectra of these samples as a broad line at 7 ppm, and a shoulder at 5.3 ppm, the line of methylene protons has
the shift of 2.0 ppm so it overlaps with the line of NR methylene protons (spectrum of GR-0 sample is shown in Fig. 2).

The values of spin-lattice relaxation time $T_1$ for protons in methylene groups versus $1/T$ are plotted in Fig. 3. The $T_1$
minimum of new tyre rubber (TR) is below room temperature. The shift of $T_1$ minima to higher temperatures for GR samples
indicates the increase of cross-linking in these samples since higher temperature is required to achieve the $\tau_s$ value fulfilling
the condition for $T_1$ minimum. The minima of thermally treated samples show a slight tendency to move to higher
temperature and longer $T_1$ values with longer thermal treatment and hence higher degradation of the polymer structure.

The values of spin-spin relaxation time of methylene protons were determined from the deconvoluted $^1$H MAS NMR spectra recorded with increasing delay time. The plots of the areas under the peaks given by methylene protons versus $t_d$ time are shown in Fig. 4. The curve fitting required the sum of two exponential decay functions:

$$M(t)/M(0) = A \exp(-t_d/T_{2A}) + B \exp(-t_d/T_{2B})$$

The values of function parameters are listed in Table I. The parameters A and B are proportional to the fractions of samples with different degree of cross-linking. The $T_2$ values in both fractions decrease with longer thermal treatment inducing further rubber degradation. The fitting of transverse magnetization of new tyre rubber (TR sample) was successful with one exponential function providing as expected a long $T_2$ value characteristic for highly elastic and flexible materials. The spin-lattice and spin-spin relaxation times reflect the changes in the structure of ground rubber induced by even a short thermal treatment at relatively low temperatures and can be used for quantifying the ground rubber degradation.

This study was supported by funding from the Project of the State Program of Research and Development No. 2003SP200250203, Slovakia. The paper presents results of the research activities of the Centre „Progressive Constructions and Technologies in Transportation Engineering”. The Centre was supported by the Slovak Research and Development Agency under the contract No. SÚSP-0613-09 and the companies Inžinierske stavby and EUROVIA SK.

REFERENCES

P-23
ELECTRICAL CONDUCTIVITY OF COMPOSITES DURING MECHANICAL DEFORMATION

JURAJ KRAJČI and IVAN CHODÁK
Slovak academy of sciences, Dúbravská street 9, 845 41 Bratislava, Slovakia
juraj.krajci@savba.sk

Electroconductive composites are formed by mixing electroinsulating polymeric, mainly thermoplastic and rubber matrix with electroconductive filler. In this work we investigated the composite styrene-butadiene rubber filled with carbon blacks N 234. The influence of mechanical deformation on changes of electrical conductivity and current was investigated online during mechanical deformation of the composite. Changes in electrical conductivity of composite were observed in dependence on mechanical deformation in process of simple uniaxial tensile deformation, followed by stress relaxation and recovering after the release of tension. This process is not simple, but we observed interesting changes of current during mechanical deformation, relaxation and recovery. The results were considered taking into account the destruction of conductive paths as a result of small movement of styrene-butadiene rubber chains and possible recovery of the paths during deformation, relaxation and recovery. Changes of electrical conductivity were markedly dependent on degree of deformation. The shape of the curves were not monotonous but exhibited maxima and minima which correspond to certain patterns on the stress-strain curves. Research of this changes conductive paths can lead to produce electroconductive composites, which are sensitive towards changes of mechanical deformation.

This work was supported by projects APVV 51-010405 and VEGA 2/0185/10.

REFERENCES

P-24
MECHANICAL AND ELECTRICAL PROPERTIES OF COMPOSITES BASED ON LOW DENSITY POLYETHYLENE AND EXPANDED GRAPHITE

JÁN KRATOCHVÍLA*, IGOR KRUPA**, ZDENKO ŠPITALSKÝ*, and JAN PROKES

* Polymer Institute, Slovak Academy of Sciences, Dúbravská cesta 9, 84541 Bratislava, Slovakia,
** Charles University Prague, Faculty of Mathematics and Physics, V Holešovickách 2, 182 00 Prague 8, Czech Republic
upolkrup@savba.sk

Over the last years, the conducting polymer/graphite composites and nanocomposites have attracted considerable interests because of their exceptional properties. Polymer micro and nanocomposites prepared from high aspect ratio layered graphite nanofillers achieve significant improvements in mechanical, thermal, electrical and barrier properties at very low filler concentrations, compared to conventional composites, without a significant increase in density.

Here we discuss various aspects of electrical and mechanical behavior of composites based on the low density polyethylene (LDPE) matrix filled with various grades of expanded graphite having an average size 5, 50 and 500 µm. The aspect ratio of the fillers varies dependently on degree of exfoliation. We also compare the influence of various routes of preparation on the final mechanical and electrical properties.

The research was supported by the Scientific Grant Agency of the Ministry of Education of Slovak Republic and the Slovak Academy of Sciences (project No. 2/6114/26) and by Science and Technology Assistance Agency under the contract No. APVV-0478-07. This work is a part of the research plan MSM0021620834 that is financed by the Ministry of Education, Youth and Sports of the Czech Republic.

REFERENCE

P-25
APPLICATION OF LIGNIN IN NATURAL RUBBER- BASED BLENDS

JANKA KUBAČKOVÁ*, IVAN HUDEC, and JOZEF FERANC

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
janka.kubackova@stuba.sk

Introduction

It is well known that lignin is a polydisperse natural amorphous polymer consisting of phenylpropane (C6-C3)
units and that some differences in its molecular mass and type of functional groups exist dependent on the genetic origin of the wood and the method of isolation. Lignin is readily available and relatively inexpensive material due to the fact it obtained as by-product of pulp production during delignification, which presents environmental problems and give altered lignin. Nevertheless, another important source of lignin exists, straw, a very diffuse and very low cost agricultural residue, which allow to obtain a less altered lignin.

Lignin has many functions in wood, but its commercial utilization is relatively low, usually it is burnt as an energy source. However, various properties of lignin designate it for different technical purposes. Lignin can be utilised as stabilizer (antioxidant) for plastics and rubber, the modified lignins have been used in crosslinked polyurethanes or phenolic resin or as a mechanical properties modifier for rubber mixtures. Most studies of lignin as an additive to rubber compounds have investigated carbon black replacement in order to achieve similar reinforcement of rubber composites, but important problem is producing rubber composites with sufficient stability. Lignin, as the most stable cell-wall polymer of wood, may have great potential to be a filler with a stabilizing effect.

The present work deals with the possibility of application of commercially available lignins in rubber blends. There was studied influence of different types of lignin in natural rubber-based model blends on cure characteristics and mechanical properties.

**Experimental**

The formulation used in this study is given in Table I. Rubber blends were prepared by mixing dry lignin powder and other ingredients with natural rubber. Six types of lignin (Table II) were used in range from 0 to 30 phr.

**Results and discussion**

Influence of lignin on cure characteristics – scorch time $t_s$ and optimum cure time $t_{90}$ were studied. Fig. 1 shows that the increasing of lignin content causes a decrease of scorch time $t_s$ for every type of lignin.

The same trend is seen from Fig. 2 where optimum cure time $t_{90}$ decreases as well. The $t_{90}$ of maximum filled rubber blend with Li-Ca lignin decreased in about 35% and the $t_s$ in about 42% in comparison with unfilled blend.

More significant decrease of the $t_s$ in about 53% was observed in case of rubber blend filled with 30 phr of DP 991 lignin. This results indicate that lignin may affect the curing behavior, probably due to the interaction of lignin with vulcanization system.

The effect of lignin on the mechanical properties of the prepared vulcanizates is illustrated in Fig. 3 and 4.

The properties such as tensile strength at break (Fig. 3) and elongation at break (Fig. 4) improved remarkably with the increasing amount of lignin from 10 phr in case of vulcani-

<table>
<thead>
<tr>
<th>Ingredient</th>
<th>phr</th>
</tr>
</thead>
<tbody>
<tr>
<td>SMR 20</td>
<td>100</td>
</tr>
<tr>
<td>Lignin</td>
<td>0, 5, 10, 15, 20, 25, 30</td>
</tr>
<tr>
<td>Zinc Oxide</td>
<td>5</td>
</tr>
<tr>
<td>Stearic Acid</td>
<td>2</td>
</tr>
<tr>
<td>Sulfur</td>
<td>3.5</td>
</tr>
<tr>
<td>CBS</td>
<td>3.5</td>
</tr>
</tbody>
</table>

**Table II**

<table>
<thead>
<tr>
<th>Lignin</th>
<th>Ca content %</th>
<th>pH of 10% sol.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li-Ca</td>
<td>Calcium lignosulfonate</td>
<td>5</td>
</tr>
<tr>
<td>DP 624</td>
<td>Calcium lignosulfonate</td>
<td>5</td>
</tr>
<tr>
<td>DP 625</td>
<td>Calcium lignosulfonate</td>
<td>5</td>
</tr>
<tr>
<td>DP 850</td>
<td>Calcium lignosulfonate</td>
<td>1.8</td>
</tr>
<tr>
<td>DP 990</td>
<td>Calcium lignosulfonate</td>
<td>7.5-9</td>
</tr>
<tr>
<td>DP 991</td>
<td>Natrium lignosulfonate</td>
<td>7.9-10.5</td>
</tr>
</tbody>
</table>

Fig. 1. Effect of lignin content on scorch time $t_s$ of rubber blends

Fig. 2. Effect of lignin content on optimum cure time $t_{90}$ of rubber blends
zates filled Li-Ca and DP 624 lignins. The tensile strength at break and elongation at break of vulcanizates filled with lignin up to 10 phr were comparable or increased moderately in comparison with lignin free vulcanizates. The addition of other types of lignin had only very slight effect on an increase of evaluated properties. The values illustrated in Fig. 3 indicate that optimum lignin concentration for maximum reinforcement is about 20 phr for Li-Ca and 30 phr for DP 624 lignin.

**Conclusion**

The obtained results show that lignin has significant influence on cure characteristics as well as mechanical properties. The final results indicate a great potential for the use of Li-Ca lignin as a filler for NR rubber blends.

This work was supported by Ministry of Education of Slovak Republic project No. 2622020091 by the Research & Development Operational Programme funded by the ERDF.

**REFERENCES**


**P-26**

**SIMULATION OF RUBBER INJECTION MOLDING PROCESS**

**KAMIL KYAS, MICHAL STANĚK, MIROSĽAV MAŇAS, DAVID MAŇAS, MARTIN KRUMAL, and ZDENĚK HOLÍK**

Tomas Bata University in Zlín, Department of Production Engineering, Nam. T.G.Masaryka 273, 762 72 Zlín, Czech Republic
kyas@ft.utb.cz

**Abstract**

Simulation analysis of injection moulding are a good tool for improving the quality of polymeric products and manufacturing equipment, an instrument to reduce the time to prepare new products for market. The poster point out that in terms of computational resources, nothing precludes the injection of the rubber compounds could be analyzed already in the design development stage of production and were thus achieved positive gains, which have been applied to thermoplastic parts. Reliable tool for analyzing injection moulding of rubber compounds is software Cadmould Rubber, a product developed by German company Simcon GmbH.

1. **Introduction**

Injection moulding is now a well-established fabrication process in environmental industry. It has more advantages in most situations over the older processes of compression and transfer moulding. These advantages comprise reduced labour cost, better dimensional control and shorter cure times for injection moulding process. This process is still improved and other materials (not only thermoplastic) are used for example elastomeric compound.

The injection moulding process is a cyclical process, each cycle comprises several operations: feeding, melting and homogenization of polymer grains inside the plasticizing cylinder mould closing, injection under pressure of melt in mould's cavities and cooling or heating of polymer inside the mould, mould opening and ejection of moulded piece. In figure 1 there is shown time influence for each parts of cycle. It is necessary to realize, that rubber injection moulding cycle is several times longer than for thermoplastics. It is evoked by long time period of heating (curing) of a compound.
During injection moulding process, melt is subjected to more severe processing conditions than during compression or transfer moulding. Values of temperatures, pressures, and shear stresses are higher, though cure times are shorter in rubber compound. Control over process variables can be more precise.

The cycle time can be minimized by independently controlling barrel temperature, screw speed, mould temperature and injection pressure. That is the reason why the analysis of injection moulding process should be improved and understood.

2. Experiment

As it was told, elastomeric mixtures consist of different additives and different quantities, therefore each compound is the "original" and they have differences at flow characteristics. These properties can be measured by Rubber Process Analyzer (RPA 2000). The amount sample of mixtures should be approximately 100 g. These prepared samples of rubber compound which weighs about 5 g is placed into the measuring device and is closed by force 15 kN. Top and bottom of the mould are heated with accuracy ± 0.3 °C.

Rubber compound with vulcanization system is used for measuring the curing characteristics (Fig. 2) and without the vulcanization system is used for measuring the complex dynamic viscosity (Fig. 3).

These Data are processed and imported to Cadmould Rubber programme, where analysis of injection moulding process can be done now. The basic input format for importing components is STL. Before setting up process parameters is necessary to create a computational network and assign the measured material characteristics. These simulations of injection moulding process were optimized to finally form several times. Profitable last setting is shown in Table I.

3. Results and discussion

With using the colour spectrum is filling time displayed in Fig. 5. According to these results weld lines and air traps can be predicted. But software Cadmould Rubber displays these results automatically. It is easier and more comfortable especially for analyses of products with difficult shape.

Temperature and curing closely related together and it is important to know these values during injection moulding process of elastomeric compound. Program Cadmould Rubber has great advantage that it can show the temperature and percentage of crossed-links in each moment during injection moulding cycle and in the individual layers of the product. It is necessary to consider how many layers use before setting analyse. With large number of layers time of computing increase rapidly on the other hand the results are more accurate.

On a Fig. 5 there is shown a detail of part. For the better understanding of injection moulding process is necessary to
know how elastomeric compound behave in each places of part and sensors are right tools to show behaviour of material. It can rendered results of pressure, temperature, viscosity, shear rate and in Fig. 6 there are rendered curves of cure rate for each of used sensors.

These results can help to set up injection moulding cycles of injection moulding machine. Especially cure rate is necessary for setting of the longest and most energy-consuming cycles and it is heating time.

4. Conclusion

Software Cadmould Rubber can show more important and interesting result of analyse. Results show very similar tendency as in real process. It can be told that Cadmould Rubber is good and helpful computational tool for injection moulding process of elastomeric compound.

This article is financially supported by the Czech Ministry of Education, Youth and Sports in the R&D projects under the titles ‘Modelling and Control of Processing Procedures of Natural and Synthetic Polymers’, No. MSM 7088352102 and ‘CEBIA Tech’, No. CZ.1.05/2.1.00/03.008.

REFERENCES


P-27

PROPERTIES OF COMPOSITES OF LOW DENSITY POLYETHYLENE FILLED WITH MAGNESIUM HYDROXIDE

ZUZANA NÓGELLOVÁ and IVAN CHODÁK

Polymer Institute, Slovak Academy of Sciences, Dúbravská cesta 9, 845 41 Bratislava, Slovakia
zuzana.nogelova@savba.sk

Several types of magnesium hydroxide in composites with low density polyethylene matrix were tested. Three types of magnesium hydroxide were modified with various agents. These experimentally prepared fillers were compared with two commercial types of this filler. Moreover, an attempt was done to increase rather low toughness of the composites by crosslinking initiated by thermal decomposition of organic peroxide. This would be beneficial also if considering possible application for fire-resistant cables. 2,5-dimethyl-2,5-di(tert-butylperoxy)hexyne(3) was used as the initiator of crosslinking.

Mechanical properties of composites filled with experimental types of magnesium hydroxide show only marginal differences. The differences are more remarkable for composites containing commercial fillers.

Crosslinking leads to a significant increase of tensile strength and elongation at break indicating improving the interactions between polymeric matrix and filler. Young’s modulus is lower in this case, in accordance with lower crystallinity caused by restriction of macromolecules mobility in crosslinked matrix. Effectivity of crosslinking was determined from values of insoluble portion. Insoluble portion of un-crosslinked samples is increasing with concentration of filler in composites only slightly and it is related to formation of physically bonded polymer. In crosslinked samples the increase of insoluble portion with a filler content was substan-
tial and it reached almost 100 wt.% of insoluble portion at the highest concentration of a filler (70 wt.%).

The research was supported by project APVV 0203-07.

P-28
POLYETHYLENE MEMBRANES
HYDROPHILIZATION BY ATMOSPHERIC LOW-TEMPERATURE PLASMA

IGOR NOVÁK*, IVAN CHODÁK*, MILENA ŠPIRKOVÁ*, GALINA ELYASHEVICH*, ALEXEJ OLIIFIRENKO*, ANTON POPELKA*, ANGELA KLEINOVÁ*, and VLADIMÍR POLLÁK*

a Polymer Institute, Slovak Academy of Sciences, 845 41 Bratislava 45, Slovakia, b Institute of Macromolecular Compounds, Russian Academy of Sciences, Saint Petersburg, Russian Federation, c Institute of Macromolecular Chemistry, Academy of Sciences of the Czech Republic, v. v. i., Praha, Czech Republic

Igor.Novak@savba.sk

Abstract

The contribution deals with surface modification of high density polyethylene (HDPE) porous film by surface barrier discharge plasma in nitrogen and oxygen. It was observed that the surface energy of HDPE porous film modified by diffuse surface barrier discharge plasma increased even for short time of modification.

Introduction

The hydrophobicity of polyethylene represents a permanent problem which cannot be solved without modification of polymer. The securing of good adhesion of more polar liquids to HDPE porous film surface necessitates increasing its surface energy by convenient modification methods. The most advanced method of modification of HDPE porous film surface, due to its practical usability, suitability to continuous modification processes, and efficiency the modification, is based on modification by electric discharge plasma1–4. The aim of the paper is presentation of research results relating to the change in surface and adhesive properties of HDPE porous film modified by diffuse surface barrier discharge plasma in the medium of N_2 or O_2 at atmospheric pressure.

Experimental

The experiments were carried out with HDPE porous film (Stavrolen, Russia) prepared by melt extrusion process with subsequent annealing and uniaxial extension. The thickness of HDPE porous film was 14 μm and it contained through channels 100–300 nm in size.

The modification of HDPE porous film was performed in static conditions by diffuse surface barrier discharge (DSBD) plasma. The modification of polymer was realized at atmospheric pressure in N_2 or O_2 of a technical purity.

Measurement of the surface energy of polymer was carried out by direct measurements of contact angles of testing liquids set (re-distilled water, ethylene glycol, formamide, methylene iodide, and α-bromo naphthalene) using Surface Energy Evaluation System (Advex, Czech Republic). The surface energy and its polar component were evaluated by Owens-Wendt-Rable-Kaelble (OWRK) modified by method of least squares3.

Results and discussion

The surface properties of HDPE porous film modified by DSBD plasma in O_2 and N_2 are shown in Fig. 1. The surface energy of HDPE porous film tracted by DSBD increased markedly after a short treatment time (5 s) in comparison with unmodified polymer. The total surface energy of SBD plasma modified HDPE porous film increased from 33.2 mJ m^{-2} (unmodified sample) up to 51.8 mJ m^{-2} (DSBD, O_2, 10 s) and 53.9 mJ m^{-2} (DSBD, O_2, 20 s), or 48.9 mJ m^{-2} (DSBD, N_2, 10 s) and 51.3 mJ m^{-2} (DSBD, N_2, 20 s), respectively. The degree of modification of HDPE porous film by DSBD discharge plasma was more pronounced with longer time of modification.

Conclusions

The significant increase of the surface energy and its polar component of HDPE porous film modified by DSBD plasma in O_2 and N_2 at atmospheric pressure was observed. This increase was important even for short times of polymeric porous film modification by DSBD plasma, and for longer times of modification was more pronounced.

Fig. 1. Surface energy of HDPE porous film modified by DSBD (50 W) plasma in O_2 and N_2 vs. time of activation

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The research was supported by the Slovak Scientific Agency project VEGA, No.2/0185/10, by the Slovak Research and Development Agency, project VSMP-P-0023-09, by the Grant Agency of the Academy of Sciences of the Czech Republic (grant A 400500505), and the Russian Foundation for Basic Research (Grant No. 07-03-00177).

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P-29
ANTIBACTERIAL MODIFICATION OF MEDICAL/ GRADE PVC BY ATMOSPHERIC PLASMA AND POLYSACCHARIDES

IGOR NOVÁK*, MARIÁN LEHOCKÝ†, IVAN CHODÁK*, ANTON POPELKA*, ITA JUNKAR*, ALENKA VESEL†, and IVICA JANIGOVÁ‡

*Polymer Institute, Slovak Academy of Sciences, 845 41 Bratislava 45, Slovakia, †Tomas Bata University in Zlín, T.G.M. Sq. 3555, 760 01 Zlín, Czech Republic, ‡Department of Surface Engineering, Plasma Laboratory, Jozef Stefan Institute, Jamova cesta 39, SI-1000 Ljubljana, Slovenia

Igor.Novak@savba.sk

Abstract

Medical-grade polyvinyl chloride was coated by polysaccharides through a novel physicochemical approach. An initial surface activation was performed foremost via diffuse coplanar surface barrier discharge plasma in air at ambient temperature and pressure. Radical graft copolymerization of acrylic acid through grafting-from pathway was directed to render a well-defined brush, and finally chitosan monolayer and chitosan/pectin alternating multilayer were bound onto the functionalized surfaces.

Results and discussion

A highly surface sensitive technique is contact angle analysis which enables a convenient assessment of the surface wettability. PVC exhibits a hydrophobic characteristic (θw = 85.9°), which after being treated by plasma, an evident change in θw = 64.9° arises, and hydrophilicity ascends as anticipated. This trend continues in the case when polyacrylic acid (PAA) chains are grafted where more hydrophilic propensities are shown inferred from θw = 46.5°. The elevated hydrophilicity upon multistep modifications is assumed to come from the inclusion of superficial hydrophilic entities. The hydrophilicity then decreases as polysaccharides are coated onto the investigated polymer (θw = 50.5°).
Conclusions

DSBD plasma is capable of raising surface energy of PVC, and introducing oxygen-containing functionalities anchored onto the polymeric surface. A structured PAA brush of high graft density is synthesized using surface-initiated approach to further improve hydrophilicity and develop a stable brush-like assembly to yield a platform for biomolecular binding. Surface-sensitive analyses evidence the presence of chitosan and chitosan/pectin multilayer.

Financial supports by the Slovak Academy of Sciences (Grant VEGA 2/018510), by Slovak Research and Development Agency, project VSMP-P-0023-09, the Ministry of Education, Youth, and Sports of the Czech Republic (Grant VZ MSM 7088352101 as well as Grant MPO 2A-1TP1/126), and the Ministry of Higher Education, Science, and Technology (Program P2-0082-2) are gratefully acknowledged.

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P-30
THE INCREASE IN EFFICIENCY OF CURING SYSTEMS Vulcanized AT LOW TEMPERATURES

DARINA ONDRUŠOVÁ,* MARIANA PAJŤAŠOVÁ,
TATIANA BAZYLÁKOVÁ, MÁRIA KOPCOVÁ,
MICHAELA ĎURČEKOVÁ, MARTINA ČECHOVÁ,
and EUGEN JÓNÁ

Faculty of Industrial Technologies, TnU AD, I. Krasku
491/30, 020 01 Púchov, Slovakia
ondrusova@fpt.tuni.sk

Increasing the efficiency of rubber compounds curing systems and effect of application new types of accelerators, or their combinations, has been intensively studied. Dithiocarbamates used in the curing process of rubber compounds form a group of ultra-accelerators. Several new metal N-ethyl-N-phenyldithiocarbamates have been prepared recently, their structural properties and influence on the kinetics of cure were studied. The kinetically most active Co(III) N-ethyl-N-phenyldithiocarbamate (Fig. 1) (Co(epdtc)3) was mixed into commercial rubber compound – coupler, especially used for cold tire retreading, which is Vulcanized at lower temperatures of 95–100°C.

Four new curing systems of rubber compound named with the addition of new dithiocarbamate accelerator Co (epdtc)3 were prepared. Their efficiency was evaluated testing the vulcanization characteristics and physical and mechanical properties of vulcanizates before and after accelerated thermal aging in air. The optimal values of characteristics tested showed vulcanization system containing of 1.67 phr Co (epdtc)3, specifically slightly decreased but comparable values of modulus 300 % and hardness in comparison with original vulcanization system, increased and thus better elongation value, tensile strength and elasticity. Obtained results are clearly positive for the possibility of increasing the efficiency of vulcanization systems by addition of Co(epdtc)3.

REFERENCES

P-31
THE ATMOSPHERIC PLASMA TREATMENT OF THE POLYMER FILMS

ANDREA ORAVCOVA* and 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

The purpose of this work was to improve surface energy and wettability of the films before printing by plasma treatment. The printability of polymer materials is dependent upon the chemical and physical properties of the polymers. The surface of polypropylene consists solely of carbon and hydrogen. Using appropriate plasma treatment, the surface of the non-polar polymer material may be activated to contain the variety of functional groups including oxygen-based functionalities (carbonyl, carboxyl, ether, peroxide etc.) or nitrogen-based groups resulting in modification of the surface properties. Low-functionality polypropylene surfaces become more reactive by enhancing the concentration of polar groups on the surface.

The result of plasma modification of the polymer film is the increase of the surface energy of the polymer and the improvement of surface wetting by liquids. The minimum value of the surface free energy of the material being printed using the solvent-based inks is 38 mJ m⁻².
The advantage of the plasma treatment is the ability to change the surface properties of the most external layers of the material without modifying its bulk characteristics. The transparent PP film (monaxially oriented polypropylene, 30 μm thickness, CHEMOSVIT FOLIE, a.s. Svit) determined for packaging various products was studied. The films were activated by atmospheric pressure plasma treatment by the diffuse coplanar surface barrier discharge DCSBD (350W input) using ambient air and nitrogen. The treatment time varied from 1 s to 5 s.

Surface properties were characterized by the contact angle measurement of sessile drop (4 μl, liquids; water, glycerol, α-bromonaphthalene, formamide, ethylene glycol) using CCD camera (SEE software 6.1, MU Brno, Czech.Rep.).

As it can be seen in the Fig. 1a, polar liquids, such as water, do not wet the surface of the untreated hydrophobic PP film in comparison with the treated film sample (Fig. 1b).

The dyne test pen Quick Test 38 was used to confirm changes in wetting of the films, too. In the Fig. 2 there are shown an untreated and a wettable 5s-plasma treated film.

The contact angles of testing liquids with different polarity and PP films largely decreased with increasing treatment time. The values of total surface energy, calculated by Owens-Wendt regression method, were increased, as shown in Fig. 3 and Fig. 4.

There was a significant increase in the polar (AB) component of the surface energy after the treatment.

The required surface energy for printing using solvent-based inks (38 mJ m⁻²) was detected by all the investigated samples.

The surface functionalities were also detected by attenuated total reflection (ATR) technique of FTIR spectroscopy. Fig. 5 shows the influence of plasma discharge on chemical composition of the surface of polypropylene films.

Fig. 3. Influence of the time of plasma treatment on the surface energy of the polymer surface using nitrogen as a working gas

Fig. 5 shows the influence of plasma discharge on chemical composition of the surface of polypropylene films.

There are some small surface changes of PP films, before and after plasma treatment, in the region of carbonyl and carboxyl groups (1520–1750 cm⁻¹). It confirms creation of small amount of polar functional groups on the film. AFM technique was used to study changes in morphology of PP films as it can be seen in Fig. 6b and Fig. 6c in comparison with untreated sample in Fig. 6a. There are changes in roughness, the value of middle roughness (RSM) increased.
As it was expected, plasma treatment has no significant influence on mechanical properties ("bulk properties"). The values of tensile strength at break varied from 21.9 (3 s) to 23 MPa (1 s), the value for untreated sample was 23 MPa.

Based on obtained results it is possible to note that the plasma treatment at atmospheric pressure by diffuse coplanar surface barrier discharge seems to be a successful technique for improving wettability of hydrophobic polymer film materials.

As performed experiments showed, the contact angle of the treated polypropylene films decreased and the surface energy of the samples increased in comparison with the plasma untreated samples. Improved wettability of the samples was also obtained by using the dyne test pen. The proper surface energy for printing using solvent-based inks (38 mJm⁻²) was detected by all the investigated samples after plasma treatment in ambient air. It was confirmed that plasma treatment has no significant influence on mechanical properties of polypropylene films.

REFERENCE


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REFERENCE


Introduction

A multitude of rubber composites, especially in technical applications, are based on filler containing rubber blends. Effective dispersion and distribution as well as optimized phase selective filler localization in rubber blends has been recognized as one of the most important facts for achieving high quality and consistent product performance. Rubber type, rubber-filler interaction and also technological parameters during the mixing process control the filler distribution in the different blend phases. The local filler distribution in vulcanized blends can be characterized by means of different direct and indirect methods. Transmission electron microscopy (TEM) was used by Sahakaro and Suzuki. Sircar analyzed the filler migration in S-SBR/BR, NR/BR and CIIR/BR blends by atomic force microscopy (AFM). Nuclear magnetic resonance (NMR) and differential scanning calorimetry (DSC) in combination with bound rubber measurements were used by Massie for BR/NR blends. Dynamic mechanical analysis (DMA) was used by Meier and Sirisinha to analyze the filler distribution in different rubber blends.

Experimental

The selective extraction in connection with thermogravimetric analysis (TGA) is presented in this work as new method for the characterization of the phase selective silica distribution in low filled S-SBR/NBR and NBR/NR blends. For the quantification of the different wetting behavior of the used rubber types, the so called rubber layer \( L \) was estimated by means of solubility measurements. The effect of the mixing regime on the phase selective silica distribution was investigated by the methods described above and checked by atomic force microscopy for the S-SBR/NBR blends. For the NBR/NR blends, the effect of the viscosity of the NR phase and the effect of the polarity of the NBR phase on the filler localization were investigated. The infiltration rate \( b \) and the wetting parameter \( \omega_s \) were used for the prognosis of the phase selective filler distribution in binary blends.

The wetting parameter \( \omega_s \) was calculated by the Young equation (Eq. 1).

\[
\omega_s = \frac{\gamma_{\text{silica-rubber}} - \gamma_{\text{silica-rubber}}}{\gamma_{\text{rubber-rubber}}}
\]
By application of eq. (1) the following cases could occur:

- \( \omega_1 < -1 \) : silica is concentrated in the phase of rubber 2,
- \( \omega_1 > 1 \) : silica is concentrated in the phase of rubber 1,
- \( -1 < \omega_1 > 1 \) : silica is concentrated in the interface of both phases.

The interfacial tension between two phases was calculated by the Girifalco-Good equation (Eq. 2)

\[
\gamma_{12} = \gamma_1 + \gamma_2 - 2\sqrt{\gamma_1 \gamma_2}
\]

For the selective extraction 0.2 g uncured blend material were dissolved in 100 ml cyclohexane at 70 °C for 12 h in laboratory oven. The S-SBR respectively the NR phase of the blends are in solution. The gel of NBR phase was analyzed by TGA with regard to the residual filler. The investigations on S-SBR/NBR blend show a silica localization in the NBR phase already after short mixing time (Fig. 1). The S-SBR phase was free of silica. The reason is the high affinity of the acrylonitrile groups to the silica surface.

Furthermore, no effect of the viscosity of the NR phase and the polarity of the NBR phase was found on the silica localization in the binary blends. In addition, silica was determined in the NBR phase after short mixing time. The prognosis of the phase selective filler distribution by infiltration rate and wetting parameter \( \omega \) were confirmed by experimental values by the selective extraction.

REFERENCES


P-33
THE POSSIBILITY OF USING NON-AROMATIC OILS AND DITHIOPHOSPHATES IN RUBBER COMPOUNDS

MARIANA PAJTÁŠOVÁ*, DARINA ONDRŮŠOVÁ, JANA PALIESKOVÁ, SLÁVKA ĽALÍKOVÁ, ZUZANA JANUKOVOVÁ, and ANDREA FERIANCEOVÁ

Faculty of Industrial Technologies, TnU AD, I. Kraska 491/30, 020 01 Púchov, Slovakia

The ecological requirements are closely linked to the issue of environmental protection and human health, which attaches currently the greatest importance. One of a number of measures is to use products that are not harmful to health. Using high-aromatic oils in the rubber industry is increasingly criticized, especially because of health risks, because these oils contain polycyclic aromatics (PCA), most of which are carcinogenic. The subject of the introduced work is to investigate the effects of non-aromatic oils of the type (TDAE – modified aromatic oils distilled, MES – Extract refined oils, RAE – residual aromatic oils) on the processing properties, physico-mechanical, dynamic-mechanical properties and vulcanization characteristics of the tread compound designed for winter use.

The measured results showed improvement of some observed properties of the compound with application of organic and commercially produced plasticizers.

The creation of Nitrosamine-free vulcanization systems is one of the important environmental problems in the car tyres production. Present work deals with ecologisation of vulcanization system of rubber compoud for passenger car tyres. The formation of Nitrosamine-free vulcanization system was providet by the way of substitution of commercially used benzothiazolic accelerator (Vulkacit DZ) with some new accelerators on the base of Dithiophosphates, that do not form dangerous Nitrosoamines.

Dithiophosphates tend to form monosulfidic or disulfidic crosslinks which, because of their higher bond energies, are much more resistant to reversion, so they added to enhance heat stability. The results of measurements show in...
majority of studied properties the synergistic effects of combination Zn-dithiophosphate with Vulcakit DZ. On the base of evaluated results two optimal synergistic vulcanization systems were selected.

REFERENCES


P-34
MODIFICATION OF PROCESSING AND MECHANICAL PROPERTIES OF POLYLACTID ACID/POLYHYDROXYBUTYRATE BLENDS

MIROSLAVA PAVLAČKOVÁ, KATARÍNA TOMANOVÁ, FRANTIŠEK BENOVIČ, RODERIK PLAVEC, and PAVOL ALEYX

Institute of Polymer Materials, Faculty of Chemical and Food Technology, Slovak University of Technology, Radlinského 9, 812 37 Bratislava, Slovak Republic
miroslava.pavlackova@stuba.sk

Introduction

Plastic materials have found wide range of applications in different aspects of life and industries. However, most conventional plastics such as polyethylene, polypropylene, poly (vinyl chloride), polystyrene, poly (ethylene terephthalate) etc. are non biodegradable, and their increasing accumulation in the environment has been a threat to the planet. One possibility how to solve this problem can be production of biodegradable polymers. On the other hand, these materials usually exhibit problematic processing properties following partially sensitive to thermal degradation as well as lower mechanical properties. These problems can be reduced by blending of two or more polymers as well as by addition of modifiers.

In our work PLA/PHB and PLA/PHB/TAC blends were studied. Styrene-acrylate copolymer containing epoxy groups was used as modifier. The aim of our work was study of influence of modifier on rheological and mechanical properties of PLA/PHB blends.

Materials and methods

PLA 4042D from NatureWorks, LLC, USA was used as polylactide acid, PHB from Biomer, Germany was used as polyhydroxybutyrate, Triacetine was used as plasticizer and Joncryl ADR-4368 from BASF, Asia was used as modifier (styrene-acrylate copolymer containing epoxy groups).

Preparation of blends

The blends of polylactide acid/polyhydroxybutyrate and polylactide acid/polyhydroxybutyrate/triacetine with content of polyhydroxybutyrate 5, 10, 15, 30 and 50 wt.% were prepared using twin screw extruder with screw diameter 16 mm, L/D = 40 with three kneading zones. The content of triacetine was 10 wt.% These blends were modified by addition of Joncryl ADR-4368 (2 wt.% as well.

Rheological measurements

Rheological parameters of blends were measured using oscillation rheometer RPA 2000 from Alpha Technologies. Two types of tests were used in our work – strain sweep and timed test. Frequency was set up to 50 cpm during the strain sweep, while angle of strain varied from 0–60°. Timed test was done at constant angle of strain 30° and constant frequency 60 cpm. Time period of test was 20 min. Temperature of measurement for all prepared blends was 200 °C.

Mechanical properties measurement

For tensile test according to ISO 527 the Zwick machine was used at cross-head speed 1mm/min while deformation range was of 0–3 % and after this value of deformation the speed increased up to 50 mm min⁻¹. The tensile strength of break (σb), elongation at break (εb) and tensile strength at yield (σy) were determined based on recorded tensile curves.

Results and discussion

The dependencies of mechanical properties on PHB content in the blends of PLA/PHB, PLA/PHB/J 4368, PLA/PHB/TAC and PLA/PHB/TAC/J 4368 are shown in Fig. 1–3.

Tensile strength at yield (Fig. 1) of pure PLA is near to 60 MPa. After addition of 5 % of PHB, yield point disappear
from tensile curve of PLA/PHB blends. The PLA/PHB blends exhibit no yield point up to 30 wt.% of PHB content in the blends. Value of tensile strength at yield is about 50 MPa if concentration of PHB is from 30 to 50 wt.% where the yield point appears on tensile curve and its value is about 35 MPa, e.g. logically lower than in case of blends without plasticizer. Considerable improvement was obtained after application of Joncryl 4368. Dependency of $\sigma_y$ on PHB content exhibit strong maximum around 10 % of PHB in the blend and value of maximum is about 50 MPa. If concentration of PHB is over 15 wt.%, $\sigma_y$ again falls down to approx. 15 MPa. It can be assumed that position of maximum can be influenced by concentration of modifier Joncryl 4368. Similar dependencies were obtained also in case of tensile strength at break (Fig. 2). Addition of PHB to PLA without plasticizer causes increasing of $\varepsilon_b$ from 50 MPa at 15 wt.% of PHB. Application of TAC also causes decreasing of $\sigma_b$. Addition of modifier do not improve absolute values of $\sigma_b$, but similarly like in case of $\sigma_y$ it shift position of maximum to lower concentration of PHB. Most significant improvement was observed in case of elongation of break if both additives (TAC as well as Joncryl) were applied in the PLA/PHB blends. While PLA/PHB blends exhibit in whole studied range of concentration practically 0 or very low values of $\varepsilon_b$, application of TAC logically causes increasing of it. Improving of $\varepsilon_b$ in case of PLA/PHB/TAC blends starts from 15 wt.% of PHB if no Joncryl 4368 was used. Addition of Joncryl 4368 (2 wt.%) gives blends with $\varepsilon_b$ more than 200 % already at concentration of PHB 5 wt.% and at higher concentration of PHB elongation at break is constant and higher in comparison with blends without Joncryl.

Discussed effects of Joncryl on mechanical properties of PLA/PHB and PLA/PHB/TAC blends are probably cause by chain extending of degrading polymer, preferably PHB, during its thermal processing. This assumption was confirmed also by rheological measurements.

The flow curves of blend containing 30 wt.% of PHB are shown on Fig. 4 and results of degradation (timed) tests in form of dependency of relative complex viscosity on time are shown on Fig. 5. Both figures show that the viscosity of blend
containing 30 wt.% of PHB quickly decreases with shear rate as well as with time of thermal loading. Addition of TAC has only marginal effect on both characteristics. Addition of Joncryl markedly inhibits degradation process of the blends (see Fig. 5) and also it is able to keep higher viscosity of the blends at low shear rates (see Fig. 4). Application of TAC in PLA/PHB/Joncryl composition logically reduces viscosity as well as it decreases effect of Joncryl as processing stabilizer.

Conclusion

High sensitivity of PHB during its thermal processing was confirmed in our work. The negative effect of degradation of PHB which causes decreasing of mechanical properties of PLA/PHB blends can be significantly reduced by application of plasticizer and/or by application of chain extenders. Mainly epoxided styrene-acrylate copolymer (Joncryl 4368) increases viscosity of the melt as well as mechanical properties. The best results in mechanical properties were achieved if both additives were applied in the PLA/PHB blends. Combination of plasticizer TAC and chain extender Joncryl 4368 give a good chance to prepare PLA/PHB blends with properties suitable for practical use of such materials in packaging for example.

This work is supported by Norwegian Financial Mechanism, Financial Mechanism of EEA and State budget of Slovakia - project No. SK 0094.

REFERENCE


P-35
THE INFLUENCE OF SURFACE-ACTIVE CHEMICALS ON PHYSICO-MECANICAL PROPERTIES OF ELASOMERIC MIXTURE WITH UTILIZATION OF LIGNIN AS BIO-FILLER

PETER POČAROVSKÝ*, IGNÁC CAPEK*, IVAN CHODÁK*, PAVEL KOŠTIAL†, JANA ĎURFINOVÁ*, LUBOŠ KRIŠŤÁK*, SILVIA KOIŠOVÁ†, JANKA JURČIOVÁ†, ROMAN BREŠER*, and MARTINA ŠARLAJOVÁ†

* Slovak university of technology in Bratislava, The Faculty of Chemical and Food technology, Radlinskeho 9, Bratislava 812 37, † Slovak Academy of Sciences, Institute of Polymers, Bratislava 812 37, ‡ Technical University in Zvolen, Faculty of Wood Science and Technology, T.G.Masaryka 24, 960 53 Zvolen, Slovak Republic, § VSB-Technical university of Ostrava, Faculty of Metallurgy and Material Engineering, 17. listopadu 15/2172, 70833 Ostrava-Poruba, Czech Republic, Department of Materials Engineering, † Saar Gummi Slovakia spol. s r.o., Gumarenska 397/21, Dolne Vestenice 972 23, Slovak Republic, † Department of Inorganic Materials and Environmental Engineering, Faculty of Industrial Technologies, University of Trenčín, 02001 Púchov, Slovakia peter.pocarovsky@stuba.sk

Abstract

The given work is focused on the influence of surface-active chemicals on vulcanization characteristics and physico-mechanical properties of rubber mixtures where the natural rubber was used as a matrix and Lignin was used as an alternative bio-filler. Ethoxone AF5, Lauryl sulfate sodium salt and Cetyltrimetylamonium bromide are the tensides which were chosen by us. During the process of preparation of samples for infrared spectroscopy, the emulsion of Ethoxone AF5 and rubber SMR20 got blue after the heating (aging process) to temperature 140 °C and it means that there was the chemical reaction. We were adding the tensides which are mentioned hereinbefore and the adding of these tensides was from 0.5 to 4 hm.%. This mentioned weight was the weight from the total weight of prepared mixture and we were observing the changes of resultant properties of final vulcanizates.

1. Experimental work

Materials

Natural rubber of type SMR-20, which was used as the elastomeric matrix, was obtained from Malaysia. The natural Lignin, which was used in a function of reinforcement bio-filler is a commercial product of global company firm Borregaard Lignotech. The powder of pale brown colour Calcium lignosulfonate is derived from eucalyptus wood, pH in solution was 7.4 and molecular weight was 1500 g mol⁻¹. Ethoxone AF 5 – anionic tenside C₁₂H₂₅ – OCH₂ CH₂ – OCH₂ CH₂ – OSO₃Na , Cetyltrimetylamonium bromide – cationic
surfactant, white powder with the molecular weight $p364, 45 \text{ g mol}^{-1}$ were used as the surface-active chemicals. Lauryl sulfate sodium salt $C_{12}H_{25}OSO_2ONa$, anionic tenside with the molecular weight 288.37 $\text{ g mol}^{-1}$ was used as last one surface-active chemical. All agents were used directly without any further purification and modification.

The preparation of samples for investigation by IR spectroscopy

The preparation of the sample (SMR 20 + surface-active chemicals) before the aging: 1 g of natural rubber and 25 ml of toluene (used as a solvent) were mixed together and the given mixture was left for two days because of its swelling (imbibition). The 2 % of surface-active investigated substance were added into the mixture. Then, the thin film (layer) of this solution was deposited on KBr tablet which was placed into the dryer at temperature 100 °C for 2 minutes. After this process, the given KBr tablet was taken from the dryer and it meant that the sample was prepared for investigation and testing with help of IR spectroscopy. The mentioned testing of given sample had to be done until the KBr tablet absorbed the humidity from the air.

Preparation of sample (SMR 20 + surface-active chemicals) after the aging: 1 g of natural rubber and 25 ml of toluene (used as a solvent) were mixed together and the given mixture was left for two days because of its swelling (imbibition). The 2 % of investigated substance were added into the mixture after the two-day process of swelling of mentioned mixture. Then the thin film (layer) of this solution was deposited on KBr tablet which was placed into the dryer at temperature 100 °C during the two-hour process of reaction—process of aging. Then the given sample was taken from the dryer and 25 ml of toluene was added there and then the sample was left for two days because of its swelling (imbibition). The process of swelling (imbibition) was followed by depositing of the thin film (layer) of the given solution on KBr tablet which was placed into the dryer at temperature 100 °C for 2 minutes. After this process, the given KBr tablet was taken from the dryer and it meant that the sample was prepared for investigation and testing with help of IR spectroscopy. The mentioned testing of given sample had to be done until the KBr tablet absorbed the humidity from the air.

2. Results and discussion

Characterization of infrared spectroscopy for natural rubber with Ethoxone AF 5

The process of preparation of sample is concerned with heating (aging process) at which the temperature was 140 °C and the given heating process took two hours. During this process of preparation for IR spectroscopy, the emulsion of Ethoxone AF 5 together with the rubber SMR 20 became blue and it means that there was chemical reaction.

Fig. 1. The violet colour shows IR spectrum of Ethoxone as a pure substance. The red colour is IR spectrum of the natural rubber together with Ethoxone—it is before the process of aging. Blue colour represents IR spectrum of natural rubber together with Ethoxone—it is after the process of aging which was at temperature 140 °C and it took two hours.

Characterization of rubber compounds with surface-active chemicals

The results of measured cure characteristics ($M_l$, $M_{Hl}$, $t_90$, $t_{00}$, $R_v$) of prepared rubber compounds with lignin as bio-filler and surface-active chemicals are present in Table I.

According to the obtained values in Table I, it can be seen, that the selected type of filler acts as an reinforcing filler in prepared rubber compounds. The shown values confirm that there is the fluctuation of viscosity because of different types of surface-active chemicals which were added to the mixture (increase of values $M_l$ and decrease of values $M_{Hl}$) and moreover, there is the change of the optimal time of vulcanization ($t_{00}$) – the highest value was obtained after the adding of Lauryl sulfate sodium salt. The values of rate coefficients of vulcanization ($R_v$), which characterize "activity" of ingredients in rubber compounds with lignin and surface-active chemicals are also markedly lower.

The results of measured physico-mechanical properties of prepared rubber compounds with surface-active chemicals and lignin are presented in Table II.

Table I

<table>
<thead>
<tr>
<th>Variable</th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
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</thead>
<tbody>
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<td>$M_l$ [N m]</td>
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<td>17</td>
<td>4</td>
<td>9</td>
</tr>
<tr>
<td>$M_{Hl}$ [N m]</td>
<td>32</td>
<td>24</td>
<td>24</td>
<td>31</td>
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<tr>
<td>$t_90$ [min]</td>
<td>7</td>
<td>4,5</td>
<td>7</td>
<td>1</td>
</tr>
<tr>
<td>$t_{00}$ [min]</td>
<td>9</td>
<td>11</td>
<td>25</td>
<td>7,5</td>
</tr>
<tr>
<td>$R_v$ [min$^{-1}$]</td>
<td>50</td>
<td>15,38</td>
<td>5,5</td>
<td>15,38</td>
</tr>
</tbody>
</table>

A – standard rubber compounds
B – rubber compounds with Ethoxone AF 5
C – rubber compounds with Lauryl sulfate sodium salt
D – rubber compounds with Cetyltrimethylammonium bromide
The mixtures on the basis of lignin together with Etoxone and Lauryl sulfate sodium salt have almost the same values and it was found according to the measured values of physico-mechanical parameters (see Table II). In comparison to standard, much higher value was found out in the case of mixture where the additive agent was Cetyltrimetylamonium bromide and this fact can be closely connected with positively charged particles of mentioned additive agent and there is the reaction of these particles with the matrix. The highest tensibility was obtained at mixture with Lauryl sulfate sodium salt and it means that it can be understood as a softener. On the other side, the values of hardness were quite low at the mixture with Lauryl sulfate sodium salt and it means that there less interaction between the polymer and filler. The comparison of the other two additives with the standards, there was the increase of values characterizing the hardness.

### Table II

<table>
<thead>
<tr>
<th>Variable</th>
<th>A</th>
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<td>Tensile strength</td>
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<td>[MPa]</td>
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<td>Tensibility [%]</td>
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<td>1044</td>
<td>720</td>
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<tr>
<td>Hardness [IRHD]</td>
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<td>39</td>
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<td>40</td>
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<tr>
<td>Modulus 300 [MPa]</td>
<td>4.09</td>
<td>3.55</td>
<td>3.2</td>
<td>5.78</td>
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### Introduction

The analysis of results, which were obtained during the measuring of rubber mixtures, showed that Lignin with its interaction with surface-active chemicals can not be used as reinforcement filler. It also changes the course of vulcanization and it changes the physico-mechanical properties of vulcanizates after adding of surface-active chemicals. The physico-mechanical properties of vulcanizates are mainly changed because of composition of mentioned substances.

### References


### P-36

**MODIFICATION OF LDPE SURFACE BY POLY(2-ETHYL-2-OXAZOLINE) USING LOW-TEMPERATURE PLASMA**

**ANTON POPELKA, JURAJ KRONEK, IGOR NOVÁK, MATEJ MÍČUŠÍK, and IVAN CHODÁK**

Polymer Institute, Slovak Academy of Sciences, Dubravská cesta 9, 845 41 Bratislava 45, Slovakia
anton.popelka@savba.sk

**Abstract**

Modification of polyolefins by a low-temperature discharge plasma is very frequently used in automotive industry, for upholstery production, bumpers covering by varnishes as well as in the production of plastics elements for car interiors. The worldwide production of low-density polyethylene (LDPE) reaches the highest value among the polymers produced for many industrial applications including the automotive industry (bumpers or steering wheels manufacture). However, it is polymer with chemically inert and hydrophobic character, what is limiting to the further processing. This lack of LDPE properties can be removed by the surface modification of LDPE by the low-temperature plasma. Moreover, the plasma discharge can be used for surface treatment by biocompatible materials such as poly(oxazoline) to improve the adhesion of the laminating materials.
The surface changes of LDPE films can be achieved by various methods of surface modification, such as by low-temperature discharge plasma, and by substances containing polar functional groups, such as 2-oxazoline polymers. Thus surface of LDPE treated by discharge plasma is homogenous without the bulk changes. As working gases for plasma treatment can be used oxygen, nitrogen, argon, and carbon dioxide. Polymers poly(2-ethyl-2-oxazoline) (PETOX) (Scheme 1) containing polar amide groups on the backbone were prepared by cationic polymerization of 2-ethyl-2-oxazoline and it belongs to biocompatible materials.

Scheme 1. PETOX structure

Experimental

Following materials and treatment conditions were used in our experiment:
Foil of LDPE BRALEN FB 2-17 (Slovnaft MOL, Slovaka) containing no additives. The thickness of LDPE film was 20 μm. PETOX with the degree of polymerization equals 100 was prepared by cationic polymerization 2-ethyl-2-oxazoline, which was initiated by methyl-p-benzenesulfonate at 110 degrees Celsius, and 24 hours in N,N-dimethylacetimide with molar concentration equals 4 mol per liter.

The LDPE foil modification were carried out by DCSBD equipment (made in Comenius University, Bratislava, Slovakia) under dynamic conditions, power supply = 200 W, treatment time = 20 s, in oxygen atmosphere. The surface properties of modified LDPE were carried out by the measurements of contact angles of testing liquids set, such as water, ethylene glycol, glycerol, formamide, and methylene iodide by Surface Energy Evaluation System (See system, Advex Instruments, Czech Republic). The surface energy was calculated by Owens-Wendt-Rabel-Kaelble model. The structure changes of the modified surface were monitored by X-ray photoelectron spectroscopy (XPS) (model K-Alpha, monochromated high-performance XPS spectrometer, Thermo Fisher Scientific).

The adhesive properties, namely peel force and peel strength (force per unit width) of adhesive joint of modified LDPE by PETOX using DCSBD to poly(2-ethylhexyl acrylate) deposited onto polypropylene foil, were carried out by measurements of 90° peel test using Instron 4301 (England).

Results and discussion

The water contact angle changes of LDPE treated by DCSBD plasma, and subsequently modified by PETOX before and after washing in H2O are shown in Fig. 1. The water contact angle of modified LDPE surface by PETOX using discharge plasma significantly decreased in comparison with unmodified polymer. The treated samples were washed in H2O to remove weakly bounded PETOX from LDPE surface. The water contact angles of LDPE treated by PETOX after washing were higher than before washing in H2O, what is caused by removal non-covalently bounding chemical substances from LDPE surface. Analogously, the surface energy significantly increased with PETOX content increasing from 1 % w/v up to 10 % w/v before washing in H2O, but after washing was independent on content of PETOX, such as shown in Fig. 2.

This decrease of the water contact angle and increase of the surface energy of LDPE modified by PETOX is caused by the increase of hydrophilic character after this surface treatment, which is caused by the presence of polar functional groups in PETOX.

Fig. 1. Contact angle of water: a) LDPE untreated, b) LDPE plasma treated, c) LDPE treated by PETOX via plasma before washing, d) LDPE treated by PETOX via plasma after washing vs. PETOX content in dichloromethane solution

The modification of LDPE by PETOX via plasma discharge resulted in an increased adhesion to more polar polymer, specifically to poly(2-ethylhexyl acrylate) deposited onto polypropylene foil, when peel force and peel strength significantly increased (Fig. 3). It is also obvious that peel force and peel strength negligible decreased after samples washing in H2O, as a result of chemically and structure changes in the surface layers.

Fig. 2. Surface energy vs. PETOX content in dichloromethane solution (description see Fig. 1)
The survey spectra from XPS measurements with the corresponding surface atomic compositions of LDPE treated by plasma and by PETOX are provided in Fig. 4. Carbon spectrum of untreated LDPE has only one peak due to C-C bonds. After plasma treatment of LDPE foil, new peaks due to different carbon-oxygen bonds appear. Also the small amount of silicon was found supposedly coming from plasma parts as a pollutant. Moreover, after PETOX bounded on LDPE surface via plasma discharge, some carbon-nitrogen bonds were found. Also the presence of carbon-nitrogen bonds was apparent for LDPE treated by PETOX after washing in H$_2$O, which corresponds with amide’s group of PETOX.

**Conclusions**

The significant decrease of the water contact angle as well as an increase of surface energy of LDPE foil grafted by PETOX via DCSBD plasma in O$_2$ at atmospheric pressure were observed. The hydrophilicity of LDPE after surface treatment significantly increased. The PETOX remaining on LDPE surface after washing was covalently-bonded. The presence of amide group in PETOX introduced onto surface of LDPE using DCSBD plasma was verified by XPS measurements. The presence of polar functional groups of PETOX grafted onto LDPE surface has been confirmed, because peel strength of adhesive joint modified LDPE-polyacrylate due to introduction of polar PETOX groups onto polymer surface markedly increased.

**REFERENCES**


**P-37**

**ECOLOGICAL ASPECTS OF USED SOFTENERS FOR RUBBER COMPOUNDS**

**JOZEF PRETO**, JAN ORAVEC, and JAN HRONKOVIC

*VIPO a.s., 958 01 Partizanske, Slovakia*

*jpreto@stonline.sk*

The European directive 2005/69/EC restricts the use of certain Polycyclic Aromatic Hydrocarbons in oils used in tyre production. The directive was applied to tyres produced after January 1$^{\text{st}}$ 2010. Extender and processing oils may not be used for production of tyres if they contain more then 1 mg kg$^{-1}$ of benzo(a)pyrene (BaP) and/or more than 10 mg of the sum of all listed Polycyclic Aromatic Hydrocarbons (PAHs). Many authors deal with replacement of aromatic oils with oils having low content of harmful components$^{1-5}$, or look for application of different, environmentally friendly softeners$^{1,2}$.

Several types of oils with low content of PAHs in various rubber blends (e.g. apex blend, inner liner blend) were tested for purpose to replace highly aromatic processing oils.
The oils were selected with respect to the viscosity gravity constant (VGC) value and to the aromatic extract PAHs value. The physical and chemical properties of tested blends are in correlation with values of VGC. A higher VGC value means a higher content of naphthenic and aromatic structures and relatively higher polarity in comparison with paraffinic oils, what is beneficial to the oil-elastomer compatibility. It means, that compound consisting of SBR containing oil with higher value of VGC gains higher physical properties.

The tensile strength gradually decreases with lower VGC values, only one blend with higher sulfur content in used oil reached higher tensile strength values probably affected with this extra content of sulfur

The experimental results showed that tested physical properties of evaluated rubber blends after replacement of usually used aromatic oil are:

- in correlation with VGC values of used oils,
- affected with residual sulfur content also and,
- mostly reached the required physical parameters.

This publication was prepared as part of the project MŠSR-3933/2010-11 „Application of Knowledge-based Methods in Designing Manufacturing Systems and Materials – MANUSMAT“ co-funded by the Ministry of Education, Science, Research and Sport of the Slovak Republic within the scheme constituted by Act No. 185/2009 Coll. “Research and Development Incentives”.

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P-38
EMISSION TESTING OF NON-METAL VEHICLE MATERIAL ACCORDING TO VDA 278
FRANKY PUYPE and JIŘÍ SAMSONEK
Institute for Testing and Certification – Zlín, testing division - laboratory of analytical chemistry, Trída T. Bati 299, 764 21 Zlín-Louky, Czech Republic
fpupye@itc.zlin.cz

Introduction

VDA (Verband der Automobilindustrie) is the German quality management system for the automobile industry which is concerned about the passengers’ health, comfort and protection. To monitor the emissions from the non-metallic parts of car interior on passengers’ health, all car interior material needs to be tested under conditions that simulate real conditions in the vehicle.

The standard VDA 278 requires emission testing from non-metallic materials intended for use in automotive industry and is based on analytical thermal desorption by a semi-quantitative method. This test is based on dynamic desorption of analytes from the solid phase (sample) to a vapor phase (emissions)\(^1\).

Thermal desorption is a sampling technique that utilizes heat to increase the volatility of analytes so they can be removed (separated) from the solid matrix (plastics, rubber, wood, textile, extracts, foam, hair, gel, paint, etc.). Analytical thermal desorption connected to gas chromatography with mass spectrometry detection (TD-GC-MS) is a highly developing sampling technique in modern chromatography.

Thermal desorption allows analysis of almost all sorts of materials including insoluble and complex materials. No solvent extraction or other pre-treatment is needed and a small amount of sample is required (approx. 20 mg).

The analytes/emissions are trapped in the GC injector on Peltier-cooled sorbent trap (filled by Tenax TA sorbent). After trapping emissions (concentrating), analytes are transferred from the injector towards the analytical column of the gas chromatograph by quickly heating of this trap (12 K/sec.). After chromatographic separation mass spectrometry detects the compounds and helps to identify them.

Typical emissions from automotive parts are firstly the oligomers or matrix related compounds and secondarily the additives and their degradation products.

Technical parameters

The principle of VDA 278 can be divided into two parts. Both parts are applied on the same sample.

The first part describes the volatile organic compound analysis (VOC) with thermal desorption of the sample at 90 °C for 30 minutes. The peaks are quantified on toluene equivalent and integrated from \(n\)-hexane till \(n\)-ecosane. This is the total VOC region (VOC) and partly the semi-VOC region (SVOC). The VOC unit is expressed as \(\mu g \cdot g^{-1}\) of toluene equivalent.

The second part describes the semi-volatile organic compound analysis (SVOC/FOG) with thermal desorption of the sample at 120 °C for 60 minutes. The peaks are calibrated with an \(n\)-hexadecane standard and integrated from \(n\)-hexadecane till \(n\)-dotriacontane. The FOG unit is expressed as \(\mu g \cdot g^{-1}\) of \(n\)-hexadecane equivalent.

The thermal desorption parameters defined in VDA 278 do not intend a full thermal extraction, these smooth parameters are limited in thermal desorption time and temperature. VDA 278 is intended to compare samples and to simulate the emissions of non-metal compounds during their life-time.

For measurement of VDA 278, a TD-20 thermal desorber unit coupled to a GC-MS 2010 (Shimadzu, Kyoto, Japan) was used. This system is fully automatized and its performance is screened regularly by inter-laboratory testing.

Expected values and trends

It is logical that the emission behavior of the material is different for each type of sample. Purity of the polymer (recycled polymer!), quality of additives, amount of additives, reactivity and stability of additives (UV), thermal stability during desorption, presence of brominated flame retardants and impact of plasticizers are only a few impact factors on the
In Fig. 1, final VOC/FOG value.

In Fig. 1 is shown an overview of VOC values sorted by matrix. The standard deviation ($\sigma_{n-1}/\sqrt{n}$) of the matrix is given just to show the expected range of test results. In first view there is a difference between the VOC emissions from the hard polymers (ABS, POM and PBT) and softer polymers (PU and rubbers).

Harder matrixes have more ability to retain emissions (low emission rate) and usually contain fewer components. The softer matrixes are mostly loaded with more components and generally have a higher diffusion rate through the polymer matrix.

Defect analysis - smell characterization

However the VDA 278 is initially developed to screen emissions from non-metallic material to assure the passengers’ health, this method is also useful for defect analysis. Due to the long sampling time and low emission temperature, defects like smell and blooming can be fully characterized.

It is recommended for defect analysis to compare a reference sample with the defect sample. The VDA 278 is used as a screening method, making an “emission fingerprint” of the material, in most cases it helps to get to know the reason of a defect and the answer for further defect prevention. This method can save the manufacturer lots of money, if the results are properly interpreted.

Firstly a description of the smell can help the analyst to get to know the type or target analyte. Further identification of the emissions can be done by mass spectrometry. In Fig. 2 is shown a chromatogram of a PU foam sample with a slight “amine” smell causing fogging on the car parts around. After analysis in VOC there was detected the amine catalyst triethylenediamine (TEDA).

Emission equivalents - another approach

For homogenous matrixes, a model based on emission equivalents can be used to predict the emission value of individual compounds. For a certain amount of compound (ng) there is a corresponding maximum VOC value (ng of toluene). The use of emission equivalents can help to ban additives for “risky” formulations or optimize a mixture to ensure that the VOC value is lower than a fixed limit.

The VDA 278 measurement is performed by electron impact ionization mode (70 eV) and all compounds are compared relatively to one chemical. The electron impact fragmentation mechanism of alkanes is completely different from the electron impact fragmentation of aromatic amines. According to the type of fragmentation for a same amount of compound the signal, and so VOC/FOG value, might be completely different.

In Table I are given some VOC emission equivalent values. 2-ethyl-1-hexanol, a typical hydrolysis product from di-ethylhexylphthalate has a lower impact on the final VOC value than $n$-decane. Aniline, a degradation product from phenylamine antidegradants or thiazole accelerators in rubber has the lowest impact on the VOC value. It is up to the operator to make decisions but the use of these VOC emission equivalent values can help in case of looking for better replacements of additives. Using emission equivalents might be very practical in use to check if the replacement gives a higher VOC value.

<table>
<thead>
<tr>
<th>Chemical</th>
<th>VOC emission equivalent (ng toluene/ng compound)</th>
<th>% RSD $(n=3)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aniline</td>
<td>1.6</td>
<td>5</td>
</tr>
<tr>
<td>$n$-Decane</td>
<td>4.3</td>
<td>6</td>
</tr>
<tr>
<td>2-Ethylhexanol</td>
<td>2.8</td>
<td>8</td>
</tr>
</tbody>
</table>

Table I: VOC emission equivalent values for some typical emissions

Many problems with high VOC values in polyurethanes might be related to the choice of amine catalysts. For rubbers the VOC emissions are mainly depended on the choice of accelerators and low MW anti-degradants.

Emissions from degradation products

By use of VDA 278 a comparison of additives and their VOC values can lead to important decisions to choose for a certain type of additive. Also the degradation products from
original substances can have a high impact on the VOC value. This is the case for many rubber applications.

In the Fig. 3 is shown a typical VOC chromatogram of SBR (VOC 667 μg g⁻¹ toluene equivalent). The emissions seen in the VOC fraction are mainly based on degradation products from rubber accelerators used for vulcanization.

2,2’-Dibenzothiazoledisulfide (MBTS) creates after thermal breakdown products like aniline, benzothiazole and 2-(methylthio)-benzothiazole (Fig. 4). The high peaks of cyclohexane and isothiocyanato-cyclohexane are typical fragmentation products from cyclohexyl-dithiocarbamate based accelerators (Fig. 5). These accelerators give generally high emissions. Not the substance itself but the degradation products give high VOC values. The VOC emissions and area % value of these degradation products are given in Table II. In many cases a trace of the original substance is visible in the FOG analysis due to its higher boiling point.

As aniline (mutagene/carcinogene class 3) is limited till a VOC level of 1 μg g⁻¹ toluene equivalent, the dosage of 2,2’-dibenzothiazole disulfide in the rubber mixture is critical. The operator should be aware of this potential risk that the automotive will not accept the final product due to fact that a mutagenic compound has been detected after VOC analysis despite the fact that no CRM substances are in the recepy!

Table II
VOC emission values from accelerator degradation products in SBR as shown in Fig. 3

<table>
<thead>
<tr>
<th>tₜ  (min.)</th>
<th>ID</th>
<th>VOC value (μg g⁻¹ toluene equivalent)</th>
<th>VOC % (area %)</th>
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<tr>
<td>3,9</td>
<td>cyclohexylamine</td>
<td>169,0</td>
<td>24</td>
</tr>
<tr>
<td>5,6</td>
<td>aniline</td>
<td>1,1</td>
<td>0,2</td>
</tr>
<tr>
<td>9,5</td>
<td>benzothiazole</td>
<td>36,4</td>
<td>5,2</td>
</tr>
<tr>
<td>9,6</td>
<td>isothiocyanato-</td>
<td>65,0</td>
<td>9,6</td>
</tr>
<tr>
<td>14,5</td>
<td>2-(methylthio)-</td>
<td>13,7</td>
<td>2,0</td>
</tr>
<tr>
<td></td>
<td>benzothiazole</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Fig. 3. VOC emissions from SBR showing mainly degradation products

Fig. 4. Thermal breakdown of 2,2’-dibenzothiazoledisulfide (MBTS accelerator) making high VOC emissions

Fig. 5. Thermal breakdown of a dithiocarbamate accelerator making high VOC emissions

Target values; Limiting values for individual substances

The VDA 278 is for many years already a reference for the European automotive industry. It requires a limit of 100 μg g⁻¹ toluene equivalents for VOCs on test parts and a limit of 250 μg g⁻¹ n-hexadecane equivalents for FOG. For some matrixes (rubbers) these limits are difficult to reach. Some concerns have even lower limits in their specification list. But it is more than VOC and FOG values.

Other criteria based on this analysis like limit values and targets for individual substances like carcinogens, reprotoxics or mutagens (CRM) are set from 1 μg g⁻¹ till 8 μg g⁻¹ toluene equivalent. The sum of phthalate esters which are toxic for reproduction are limited till 20 μg g⁻¹ toluene equivalent. Regarding the formation of nitrosoamines the sum of selected
secondary aliphatic amines should not be higher than 3 μg g⁻¹ toluene equivalent. These limits are depending on demand of the car producer².

Conclusion

New trends in modern analytical chemistry are based on quickness, trueness and quality. The sampling and quantification of the VOC and FOG values are relatively quick and easy. However the interpretation and information which this semi-quantitative method gives is in many cases underestimated. Its broad application range from quality control to defect analysis makes this method a nice source of information for material engineers dealing with automotive.

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P-39
COMPOSITE MATERIALS WITH MAGNETIC FILLERS AND ELASTOMERIC MATRIX FOR CONSTRUCTION OF INTELLIGENT TYRES

JANA REKOŠOVÁ, IVAN HUDEC, JAN KRUŽELÁK, and RASTISLAV DOSOUDIL

a Slovak University of Technology in Bratislava, Fakulty of Chemical and Food Technology, Institute of Polymer Materials, Radlinského 9, 812 37, Bratislava, Slovak Republic
b Slovak University of Technology in Bratislava, Faculty of Electrical Engineering and Information Technology, Ilkovičova 3, 812 19 Bratislava, Slovak Republic

Introduction

The influence of preparation of magnetic hard ferrite fillers on the properties of filled mixtures used in construction of tyre sidewall was studied.

The advantage of elastomeric magnetic composites are possibility of modification their properties for the requirements of specific applications. Rubber magnets can be applied in intelligent tyres, in microwave and radar technology, also in other technological applications. As a sensors of intelligent tyres are able to take of tyre deformation, resp. side forces directly in the tyre and to transfer them directly to electronic equipment of the vehicle and like this obtain information on the adhesion of tyres to the ground, about the forces acting on the tyre or about the deformation of the tyre respectively. They inform the driver of changes while driving, able of the feedback reaction to optimize the movement of the vehicle on the road³.

Experimental

For preparation of composites commercially produced sidewall rubber mixture made by Continental Matador Rubber s.r.o. Puchov base on butadiene rubber BR SKD 2 and natural rubber was used. Two types of rubber mixture were prepared – mixtures I. – ferrite filler and vulcanization system were added into first grade of sidewall rubber mixture and mixing in laboratory mixer (chamber of Brabender mixer), mixtures II. – magnetic filler was added into second grade of sidewall rubber mixture and mixing in laboratory mixer (chamber of Brabender mixer).

Anisotropic magnetically hard strontium ferrite FD 8/24 made by ceramic technology of wet grinding with addition of poly vinyl alcohol, dried by spraying was used in this work as magnetic filler.

Results and discussion

From physical – mechanical properties of vulcanizates tensile strength at break, elongation at break, hardness and modulus M300 were evaluated.

As it can be seen from Fig. 1 modulus M300 with the increasing content of ferrite filler in elastomeric mixtures decreased slightly.

In the mixture type II., where the magnetic filler was added into second grade of sidewall rubber mixture, the influence of the filling on module M300 was observable only very little.

In the case of tensile strength, which dependence on the filler content is showed on Fig. 2, is clear that with increasing of content of ferrite filler tensile strength slightly decreased and the differences between the vulcanizates I and II are minimal.

From the dependence of the elongation at break of vulcanizates on the magnetic filler content (Fig. 3) is clear that in the case of vulcanizates I elongation not changes with increasing of contents of ferrite filler, but in the case of vulcanizates II with the increasing of content of ferrite the elongation slightly decreased.

From the determination of hardness IRHD (Fig. 4) is shown that the hardness of vulcanizates increasing by the increasing content of magnetic filler in the mixture.

Magnetic properties of the vulcanizates were evaluated on a vibrating magnetometer TVM-1, at a laboratory temperature and maximum coercivity Hm = 750 kA m⁻¹.

Fig. 1. Influence of content of ferrite on rubber modulus M300 vulcanizates I, II.
The coercivity $H_c$, which specifies the level of energy necessary for cancellation of residual magnetism, maximum magnetic flux $\Phi_m$ and remanent magnetic flux $\Phi_r$ were subtracted from hysteresis loops.

Maximum magnetic polarization $J_m$ (in saturation) and remanent magnetic polarization $J_r$ were calculated by following equations:

$$J_m = \frac{\Phi_m}{S} \cdot D \ [T]$$  \hspace{1cm} (1)

$$J_r = \frac{\Phi_r}{S} \cdot D \ [T]$$  \hspace{1cm} (2)

where $S$ – surface of a sample $S = 3.2 \times 10^{-5} \ m^2$

$D$ – constant factor of the equipment TVM-1 characterizing its demagnetizing effects.

Maximum magnetic induction $B_m$ and remanent magnetic induction $B_r$ was calculated using the following equations:

$$B_m = \mu_0 H_m + J_m \ [T]$$  \hspace{1cm} (3)

$$B_r = \mu_0 H + J_r \ ak \ H=0 \Rightarrow B_r = J_r \ [T]$$  \hspace{1cm} (4)

where: $\mu_0$ – permeability of vacuum [N A$^{-1}$], $H_m$ – maximum intensity of magnetic field [kA m$^{-1}$], $H$ – intensity of magnetic field [kA m$^{-1}$].

From dependence expressing the influence of contents of ferrite filler on maximum magnetic induction $B_m$ (Fig. 5) and remanent magnetic induction $B_r$ (Fig. 6) come through that in the case of remanent magnetic induction and maximum magnetic induction there is a big rise of its values with the increasing content of ferrite filler in the elastomeric composites.

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Fig. 2. Influence of content of ferrite on tensile strength of vulcanizates I, II

Fig. 3. Influence of content of ferrite on elongation at break of vulcanizates I, II

Fig. 4. Influence of content of ferrite on hardness of vulcanizates I, II

Fig. 5. Influence of content of ferrite on remanent magnetic induction $B_r$, vulcanizates I, II

Fig. 6. Influence of content of ferrite on remanent magnetic induction $B_r$, and remanent magnetic polarization $J_r$, vulcanizates I, II
Higher values were reached in the case of adding the filler into the first grades (vulcanizates I) in comparison with the magnetic characteristics of composites in which the filler was added into second grade, what is apparently related to the process of dispersion of the filler and uniformity of its distribution in the branched matrix of vulcanizates.

Conclusion

From the evaluation of the physical – mechanical properties, tensile strength at break and rubber modulus M300, has been concluded that by increasing the contents of ferrite FD 8/24 are all these parameters decreasing, but hardness with increasing of content of ferrite increasing slightly. Bigger differences in physical – mechanical characteristics show, that the addition of magnetic active filler into the first grade sidewall tyre mixture is preferable, what is connected with a better dispersion of the filler in the non cross-linked elastomeric matrix.

Magnetic characteristics has markedly rising with the increasing ratio of ferrite filler. This shows, that materials filled with magnetic hard ferrite potentially can be used for valuation of the tyre deformation by building it into the tyre sidewall.

The obtained results are showing the possibility to prepare elastomeric magnetic composite materials to be used as a sensor in intelligent tyres.

This work was supported by grant agency VEGA, project No.1/0575/09.

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P-40
STUDY OF THERMOELASTIC PROPERTIES OF ACRYLATE COMPOSITES IN AUTOMOTIVE INDUSTRY – PART II

BRANISLAV JURAČKAa, SAYA RUSNÁKOVÁb, IVAN LETKOC, PAVEL KOŠTIAc, IVAN RUŽIAKC, and JANNA JURČIOVÁd

a VACUUMSCHMELZE, s.r.o., 916 24 Horná Sreda 1325/14, Slovak Republic, b Tomas Bata University in Zlín, Faculty of Technology, T. G. Masaryka 275, 762 72 Zlín, Czech Republic, c VŠB-Technical university of Ostrava, Faculty of Metallurgy and Material Engineering, 17. listopadu 15/2172, 708 33 Ostrava-Poruba, Department of Materials Engineering, Czech Republic, d Saar Gummi Slovakia spol. s r.o., Gumárenska 397/21, Dolně Vestenice 972 23, Slovak Republic rusnakova@ft.utb.cz

Abstract

The wide spectrum of composite materials application in automotive, aerospace and military industry, heterogeneous and their large –scale utilization requires necessary demanding accurate knowledge of material parameters those materials.

The thermal expansion behaviour and elastic properties of acrylate resin MODAR reinforced by glass fibre are studied. MODAR – Modified Acrylic Resins offers a series of unique thermostet polymers used in many markets such as automotive, mass transit, railways, building, rods for optical cable, structural parts and profiles and optical fire retardant / low smoke / low toxicity composite parts. MODAR resins offers: low viscosity, rapid cure, fast cycle times, superior physical properties, and resistance to cracking, long shelf-life and stability (valuable for hot climate countries).

Results and discussion - Part B

The diagrams of work for the sample B are described on the schemes 6–9.
The primary field of application for fibre reinforced polymer composites is the aerospace industry. For several years, however, composite materials have been increasingly used for various other technical tasks, where it is beneficial to use the low density of the matrix resins used, and the high strength and stiffness characteristics. The favourable specific properties of fibre reinforced polymer composites are based on the low density of the matrix resins used, and the high strength of the embedded fibres. Composites are unconventional material with those we have only short-term experiences with their using resulting in new methods their testing. These results to bad reproducibility of tests and comparison materials suitable to the same standard in various countries can offer very different values. Gradually unification testing methods is performing by parameters being used to testing and quality evaluation of composite materials we should have in mind anisotropy the properties of materials reinforced with continuous glass fibres are used those standards:
- Young’s modulus of elasticity, strength, maximal deformation – tensile test ISO 3268, ISO 527, ASTM 3039,
- tensile strength ASTM D 638,
- coefficient of thermal expansion ASTM D 696, DIN 51005, DIN 52612.

On the basic of results tensile strength between samples A and B we can constant, that composite material B is firmer like sample A. During classification influence of reinforced compound to properties of unreinforced acrylate resin Modar (the solid stage), which has tensile strength 56 MPa we constant, that none reinforcement do not improve strength of MODAR. Vice-versa strength of reinforced acrylate resin is lower (strength of sample A is 21, 42 MPa a strength of sample B is 36, 90 MPa. Actual tensile strength samples A and b are lower compared to value Re, reinforced laminate with reinforcement UNIFILO, Re = 93 MPa, mentioned in material paper of the producer Ashland. Relative elongation unreinforced acrylate resin MODAR is 6,5 % and reinforced acrylate resin with reinforcement UNIFILO is 1,4, what are higher values like mentioned the producer Ashland. From the measured values by bursting test with extensometer located on investigated samples we obtained Young’s modulus of elasticity to samples A and B. The values are to the sample A E = 5,861 GPa and to the sample B E = 7,106 GPa. The calculated values E on the basic measurements of flexure rod are to the sample A E = 4,907 GPa a to the sample B E = 5,977 GPa. As we compare with values mentioned in material list of the producer to reinforced laminate with fabric UNIFILO E = 10,4 GPa we found, that Young’s modulus of elasticity of the samples A and B is lower.

To the achieving same deformation those composite materials we need lower strain like is mentioned in materials list of the producer. By the comparison E of the samples A and B unreinforced resin MODAR (E = 2.2 GPa) we can constant, that the application of reinforcement increase Young’s modulus of elasticity and so on the same deformation we need higher strain.

The aim of this paper was obtain by experimental measurement thermoelastic properties of acrylate composite MODAR reinforced with continuous glass fibres. The seriousness of determination of materials parameters of composite materials was confirmed as well as experimental results because they are distinctive diversity from physical values in material parameters of producer. In generic term some experimental studies consider reinforced composite materials like isotropic if reinforcement meets the criteria is very simplifying fact. Consequently in other measurements of composite materials we should have in mind anisotropy the properties of composite materials and the samples should be prepared to the testing method in various directions to the reinforcement orientation. During measurement of deformation (elastic and plastic) and the relative extension of samples and subsequent calculating of Young’s modulus of elasticity it could think of application biaxial extensometer, which provide simultaneously measurement the changes of sample size upon loading in longitudinal and transverse direction with regard to loading direction. For a consideration results of experimental measurements and diagrams of work on Dilatometer DIL 402 PC realized on the same samples predicate, that the thermal ex-

<table>
<thead>
<tr>
<th>Table I</th>
<th>The average values for the sample A</th>
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</thead>
<tbody>
<tr>
<td></td>
<td>sample A</td>
</tr>
<tr>
<td></td>
<td>measurement Nb. 1</td>
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<tr>
<td>T₁(°C)</td>
<td>32,55800</td>
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<tr>
<td>T₂(°C)</td>
<td>35,60300</td>
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<tr>
<td>α × 10⁻² 1/K</td>
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</tr>
<tr>
<td>σₕₐᵢₜₑᵢᵩ × 10⁻⁵</td>
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<tr>
<td>εₕₐᵢₜₑᵢᵩ (°C)</td>
<td>0,00186</td>
</tr>
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</table>

T₁ – beginning of the linear part, σₕₐᵢₜₑᵢᵩ – hysteresis between curves of coefficient of thermal expansion, T₂ – finish the linear part, εₕₐᵢₜₑᵢᵩ – hysteresis between curves of specific elongation, α – coefficient of thermal linear expansion.

<table>
<thead>
<tr>
<th>Table II</th>
<th>The average values for the sample B</th>
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<tbody>
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<td>sample B</td>
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<tr>
<td>T₂(°C)</td>
<td>27,37300</td>
</tr>
<tr>
<td>α × 10⁻² 1/K</td>
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<tr>
<td>σₕₐᵢₜₑᵢᵩ × 10⁻⁵</td>
<td>2,60440</td>
</tr>
<tr>
<td>εₕₐᵢₜₑᵢᵩ (°C)</td>
<td>0,00994</td>
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</table>

T₁ – beginning of the linear part, σₕₐᵢₜₑᵢᵩ – hysteresis between curves of coefficient of thermal expansion, T₂ – finish the linear part, εₕₐᵢₜₑᵢᵩ – hysteresis between curves of specific elongation, α – coefficient of thermal linear expansion.
pansion our investigated material is change in dependence on number of temperature cycles of loading. At the same time the measurement demonstrate, that dependency of change size to the temperature and dependency of thermal expansion coefficient to temperature is characteristic by sizeable nonlinearity and so coefficient of thermal expansion is not constant, it changes in dependence on the applied thermal cycle.

So for objective evaluation of thermal expansion acrylicate resin MODAR reinforced by continuous glass fibres is necessary realized a series another measurement with repeated thermal loading the same samples and simultaneously with monitoring influence of reinforcement orientation to thermal expansion.

REFERENCES

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EXPERIMENTAL TIRE TEMPERATURE-PRESSURE MEASUREMENTS IN REAL DRIVING CONDITIONS - PART B

JANA ŽURFÍNOVÁ, PAVEL KOŠTIAL, IVAN RUŽIJA, ZORA JANČÍKOVÁ, MARTIÁNA FARKÁŠOVÁ, LUBOŠ KRISTÁK, JANKA JURČÍOVA, SOŇA RUSNAKOVA, and IVAN LETKO

a Slovak University of Technology in Bratislava, The Faculty of Chemical and Food Technology, Radlinského 9, Bratislava 912 37, b VŠB-Technical University of Ostrava, Faculty of Metalurgy and Material Engineering, 17. listopadu 15/2172, 70833 Ostrava-Poruba, Czech Republic, Department of Materials Engineering, c Technical University in Zvolen, Faculty of Wood Science and Technology, T.G.Masaryka 24, 960 53 Zvolen, Slovak Republic, d Saar Gummi Slovakia spol. s r.o., Gumárenska 397/21, Dolné Vestenice 972 23, Slovak Republic, e Tomas Bata University in Zlín, Faculty of Technology, T. G. Masaryka 275, 762 72 Zlín, Czech Republic

Abstract
In this contribution we present measurements of external and internal tire temperature as well as the internal tire pressure by complex system for the simultaneous contact less measurement of these values (CTPA). The measurement is fully automatic, controlled by a personal computer and installed “in situ” on the car. The global position system, which is connected to a PC, further allows us to measure also the car speed in synchronized regime with other measured parameters. All external temperatures under investigation were independently tested by other contact thermometers.

Results and discussion - Part B

The same kind of dependence for the left wheel (sample A) is in the Fig. 5, to demonstrate decrease of measured outdoor temperature in this case caused by left tire release. In the Fig. 6 (B) and 7(C) are right wheel temperature-speed dependences for tires of other producers. On the Fig. 8 is a dependence of internal tire temperature versus time. Due to relatively small pressure changes we don’t present the pressure/speed changes which are also registered by the CTPA system.

The results of “peak” outdoor (T_{ext,Max}) right wheel temperature as well as the onset time of internal temperature (t_{onset}) increase are in Table I (see also the Fig. 9). This Table also contains fitted value of experimental relaxation time \( \tau_{exp} \). Values of \( \tau_{exp} \) are mean values of fitted data.

From experimental outdoor temperature decay curves we can determine the experimental “relaxation time”. In every case it depends on the heat capacity and sample density as material constants (for convective heat transport characterized by constant \( h \) relaxation time is possible to express in the form \( t = \rho c_p V / h S \). The slowest tire temperature decay is observed for sample A (\( \tau_{exp} = 76,2 \)) which is accompanied by tire overheating (\( T_{ext,Max} = 338,8 ^\circ C \)). The onset time (\( t_{onset} = 60 s \)) signals quick energy transfer (also through tire sidewall) from rubber composite to the air inside a tire. As we said this fact is probably caused by improper breaker angle.

Different situation is for samples B and C. The smallest value of relaxation time (\( \tau_{exp} = 53,8 \)) was observed for the sample B and a \( \tau_{exp} = 65,6 \) for the sample C. In both cases the tire overheating is sufficiently smaller than in the case A which is seen on values of \( T_{ext,Max} = 236,4 \) for the sample B and 236,3 for the sample C.

![Fig. 5. Left wheel temperature-speed curves for sample A](image-url)
Table I
The data of maximum external tire temperatures, as well as the onset time of internal temperature increase $t_{\text{onset}}$ and experimental relaxation time $\tau_{\text{exp}}$.

<table>
<thead>
<tr>
<th>Sample</th>
<th>A</th>
<th>B</th>
<th>C</th>
</tr>
</thead>
<tbody>
<tr>
<td>$T_{\text{ext}}$(MAX)[°C]</td>
<td>338,8</td>
<td>236,4</td>
<td>236,3</td>
</tr>
<tr>
<td>$t_{\text{onset}}$[s]</td>
<td>60</td>
<td>289</td>
<td>1281</td>
</tr>
<tr>
<td>$\tau_{\text{exp}}$[s]</td>
<td>76,2</td>
<td>53,8</td>
<td>65,6</td>
</tr>
</tbody>
</table>

Conclusion

CTPA is useful, fully automatic instrument for “in situ” monitoring of both internal and external tire temperatures and tire pressure. The CTPA system allows the easy data matching and offer constructors interesting information about tire temperature trends in real driving conditions.

REFERENCES