

POSTERS

P-01 SURFACE MODIFICATION OF TEXTILE REINFORCING MATERIAL BY PLASMA TREATMENT AND PLASMA POLYMERIZATION

IHSSAN AMIR, IVAN HUDEC, and MILAN VOLOVIČ

*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
ihssan.amir@stuba.sk*

Polyester cords play an important role in the modern tyre industry as a reinforcing materials because of their extraordinary mechanical and physical properties. Many problems concerning to the adhesion between polyester cords and tyre rubber come from the relatively low surface energy of polyethyleneterephthalate (PET) and also its chemical inertness. The standard method for the improvement of adhesion strength between polyester cord yarns and the rubber matrix are based on RFL system – the fibre surfaces are treated with a solution or emulsion consisting of resorcinol-formaldehyde resin and vinyl-pyridine latex^{1,2}. The next change of improvement of adhesion cords to rubber is surface modification of cords by plasma treatment, where is a change to creation new group, eventually new polymeric layer at the surface cords when reactive monomer are applied as working gas in plasma polymerization process³⁻⁵.

The aim of this work is presentation of some results obtained by the studying of the influence of plasma treatment conditions on the static adhesion strength and adhesion strength after dynamic stress of polyester high modulus low shrinkage cord yarn (HMLS – Slovokord 1440 Dtex 1x2, twists 380/380 produced by SH Senica, Slovakia) to rubber. The rubber compounds contained natural rubber, SBR and polybutadiene rubber was used for fabric coating. The static adhesion strength to rubber and adhesion strength after dynamic stress (the sample was exposed to a cyclic flexural stress with frequency = 7.5 Hz for 12 h in a chamber at 80 ± 1.5 °C) to rubber was studied by means of Henley test method according to STN 62 01464.

Polyester cords were treated by Difusion Coplanar Surface Barrier Discharge (DCSBD) at atmospheric pressure. A sinusoidal high-frequency high-voltage ($\sim 1-15$ kHz, up to 10 kV peak to peak) was applied between the electrodes. Such a discharge electrode arrangement and energization were found to generate visually almost uniform plasmas in nitrogen and ambient air at atmospheric pressure. DCSBD was powered by the high voltage harmonic source with the frequency of 10 kHz (LIFETECH, Ltd., Brno, Czech Republik). The polyester cords were modified by plasma treatment in ambient air, technical air or nitrogen and by plasma polymerization process in gas of propane-butane with nitrogen admixture in flow rate ratio 0.5 to 3 liters per minute. The power of discharge was set to 350W and time of treatment varies in the range from 1 to 20 seconds. Cords were treated from both

sides between electrodes.

The results of the influence of plasma treatment time and plasma polymerization time on the static adhesion strength and adhesion strength after dynamic stress of polyester cord to rubber in the case of distance of electrodes 0,5 mm are summarized in Fig. 1 and Fig. 2.

The results of the influence of plasma treatment time and plasma polymerization time on the static adhesion strength and adhesion strength after dynamic stress of polyester cord to rubber in the case distance of electrodes 1,0 mm are summarized in Fig. 3 and Fig. 4.

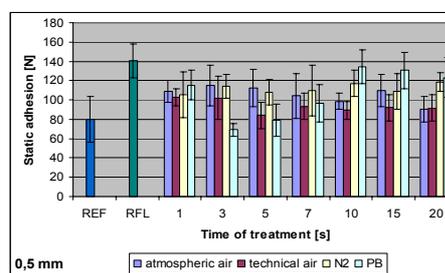


Fig. 1. Graphical comparison of static adhesion strength of plasma modified PET cords to rubber compound

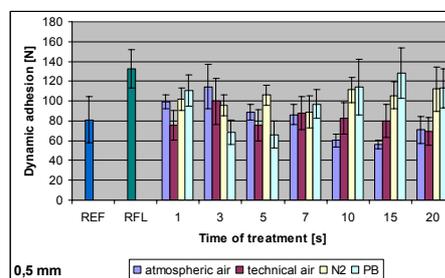


Fig. 2. Graphical comparison of adhesion strength after dynamic stress of plasma modified PET cords to rubber

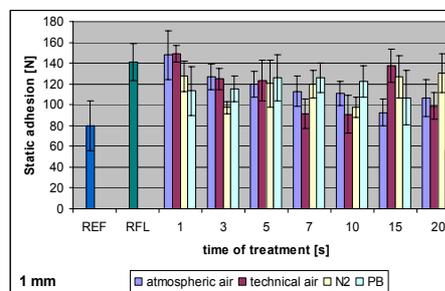


Fig. 3. Graphical comparison of static adhesion strength of plasma modified PET cords to rubber compound

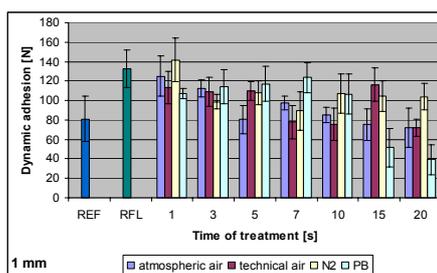


Fig. 4. Graphical comparison of adhesion strength after dynamic stress of plasma modified PET cords to rubber compound

Static adhesion strength of cords to rubber and adhesion strength after dynamic stress (dynamic adhesion) of plasma treated cords were compared with adhesion strength of cords treated with resorcinol-formaldehyde latex (RFL) system. From Fig. 1 and 3 is evident that the maximum static adhesion strength of polyester cords modified in technical air and ambient air plasma (difference is only in humidity content) was observed in very short time of plasma treatment (1second) when distance of electrodes was 1mm. In both type of plasma treatment obtained level of static adhesion were comparable with the static adhesion when resorcinol formaldehyde (RFL) system was used for surface modification of polyester cord (Fig. 3). As Krump³ mentioned before, under sufficient conditions, the relatively short contact between the PET cords and plasma is sufficient for increasing of surface energy and adhesion to rubber. Higher exposure by plasma treatment caused decrease of static adhesion strength.

From results of the influence of activation time on adhesion strength after dynamic stress obtained from plasma treatment in technical air and ambient air plasma (Fig. 2 and 4) is clear that the higher exposure time by plasma treatment decrease of adhesion strength after dynamic stress too.

From the experimental data of adhesion testing it is clear, that with plasma polymerization technique is possible to obtain adhesion strength comparable with nitrogen plasma treatment process. In comparison with untreated virgin cords it is possible to obtain more than 30 % increasing in static and 50 % increasing in dynamic adhesion strength.

Conclusion

From measured data it is evident that plasma treatment and plasma polymerization has strong influence on the adhesion strength of polyester cords to rubber. From the results it is clear that adhesion strength of plasma treated cord achieved the adhesion level of RFL system treated cords. Plasma treatment process can lead to the chemical changes on the surface layer of polyester cords yarn.

As a result of plasma polymerization a new non-polar layer with different chemical structure as well as higher roughness has been create on the surface of polyester cords. In the deposited layer – rubber interface several mechanisms can occur that can result in increasing of adhesion to rubber. The polymer chain of deposited layer and the rubber matrix can form a diffusive layer due to chain diffusion and mechanical interlocking of the rubber matrix on the roughness surface can form too. These changes can contribute into increasing of

adhesion of polyester cords modified by plasma polymerization to rubber compound.

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P-02

MAGNETIC FIELD SENSITIVE RUBBER NANOCOMPOSITES

DENISA BELLUŠOVÁ, TIMO STEINKE, THOMAS ALSHUTH, and ROBERT H. SCHUSTER*

*German Institute of Rubber Technology, Eupener Strasse 33, 305 19 Hannover, Germany
denisa.bellusova@dikauschuk.de*

A particular group of magnetic materials, for which the interest have been regained in the last few years are the composites consisting of magnetic particles dispersed in a non-magnetic, elastomeric matrix during the cross-linking process. Composites made of ferromagnetic particles and a soft matrix belong to specific class of smart materials where the mechanical properties can be changed under different magnetic environments. The one of the aims of this work is investigate dispersion of ferrite magnetic particles in butadiene rubber. Various types of ferrites (Ba, Sr) prepared in laboratory using coprecipitation and auto-combustion method and for the comparison wet milled commercial ferrite (Sr) were used as a magnetic fillers for magnetoactive elastomers. The morphology of the ferrite particles was observed. The atomic force microscopy and stress-strain measurements were used to obtain the results displaying the homogeneity of the magnetoactive elastomers. The change in the stiffness, elasticity on the content and particle size dependence in the presence and without the presence of the magnetic field is shown in this work.

Introduction

The magnetic particles (which may be aligned during the composite production by means of an external magnetizing field) within the non-magnetic, elastic matrix exhibit unique properties, which are not characteristic of the monolithic magnetic materials, such as strong dependence of the magnetic permeability on stress, together with good mechanical characteristics^{1,2}. Due to the above mentioned magnetoelastic characteristics, as well due to their ability to be: manufactured into complex shapes (using for example the mold injection methods) and easily machined, these composites have already found many applications as sensors, high strain actuators, converters, controlled vibration dampers, variable stiffness components, etc^{3–5}.

Experimental

Ferrites (4–11 vol.%) were embedded in 1,4-cis butadiene as a magnetic filler. The M-type barium ferrite was synthesized from iron and barium chlorides using a chemically reliable co-precipitation method. The commercial strontium ferrite was prepared using wet milling with the addition of polyvinylalcohol on the surface. The morphology of magnetic powders was studied using a combined field-emission (scanning) transmission electron microscope LIBRAO 120, Zeiss. Characterized ferrites powders were incorporated into 1,4-cis butadiene rubber in internal mixer Haake Rheocord System 90 under the following conditions: temperature: 50 °C, rotation speed: 50 min⁻¹ and mixing time: 10 min. The dispersion of the magnetic particles in isotropic and anisotropic magnetoactive composites was observed using high-resolution type of scanning probe microscopy - atomic force microscopy. Stress-strain measurements of the samples were carried out using an universal testing instrument (Zwick Typ 1445). The measurements were carried out according to DIN 53504 with 5 specimens (S3A) per material with a deformation velocity of 200 mm min⁻¹ at temperature of 23 °C. Dynamic-mechanical properties of the samples were studied using a Servohydraulic 1000 Hz Elastomer test System MTS 831.50. Testing was carried out at 10 Hz with and without an external magnetic field of 0.35 T.

Results and discussion

Fig. 1 represents the transmission electron microscope image (a) and optical microscope image (b) of the ferrites morphology used for magnetoactive elastomers. TEM image (Fig. 1a) shows the co-precipitated barium ferrite consisting of hexagonal platelet crystallites mostly in the 300–400 nm size. Commercial strontium ferrite for the comparison was chosen. Commercial strontium ferrite (Fig. 1b) is micro-sized in the range from 30 to 200 micrometer and the particles are in spherical shape.

In the absence of an applied magnetic field the magnetic moments are randomly oriented and thus the composites has no magnetization. In an external field, two distinct types of interactions can be identified, field-particle interaction as well as particle-particle interaction.

From the AFM image (Fig. 2a) it is evident the vulcanization without the presence of the magnetic field results in magnetoactive elastomer with isotropic properties. The particles are dispersed randomly in elastomer matrix. On the other side the application of the magnetic field during the vulcani-

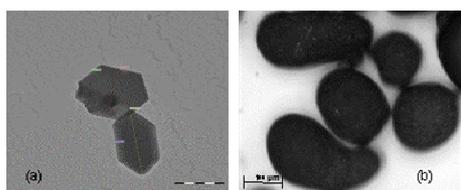


Fig. 1. The morphology of (a) barium ferrite (b) strontium ferrite

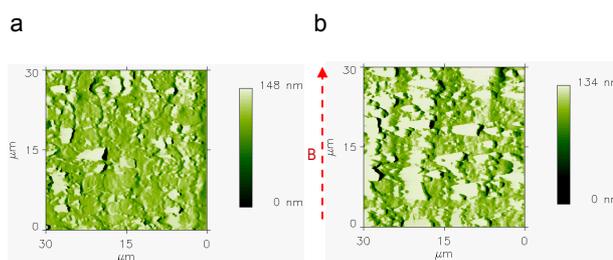


Fig. 2. AFM images of barium ferrite magnetoactive elastomers vulcanized (a) without the presence of the magnetic field, (b) in the presence of the magnetic field

zation leads to the formation of the columnar structure of the magnetic particles in elastomer matrix. Particles are aligned and fixed to the direction of the applied magnetic field. The anisotropic magnetoactive elastomer was obtained (Fig. 2b).

The effect of the alignment of the ferrite particles to the direction of the applied magnetic field during vulcanization on the mechanical properties is shown (Fig. 3). The results show that the higher content of strontium ferrite causes the higher tensile strength at break and this increase is even better if the ferrite magnetoactive elastomers are vulcanized while applying magnetic field.

From the dependencies it is evident that the particle size has an influence on the tensile strength at break, also. It is clear observed the higher tensile strength at break thus better particle dispersion and homogeneity of the sample by the application of ferrite nanosized particles in comparison with micro-sized commercial strontium ferrite. The tensile strength at break is influenced to a high degree of +70 % to +100 %.

The application of the magnetic field gives rise to a magnetic dipole-dipole interaction between the ferrite particles causing the apparent changes in stiffness and damping. The strong magneto-sensitivity can be viewed in both Fig. 4a, b for the magnitude of the storage modulus. For the case of barium nanoferrite +15 % increase is observed, while for the second case strontium microferrite it is a little less, yet strong. Furthermore, it will subsequently be shown that the increase

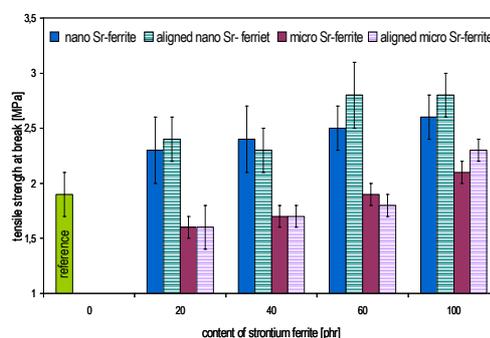


Fig. 3. The dependence of the tensile strength at break on the content of the nanosized and micro-sized strontium ferrite in isotropic and anisotropic magnetoactive elastomers

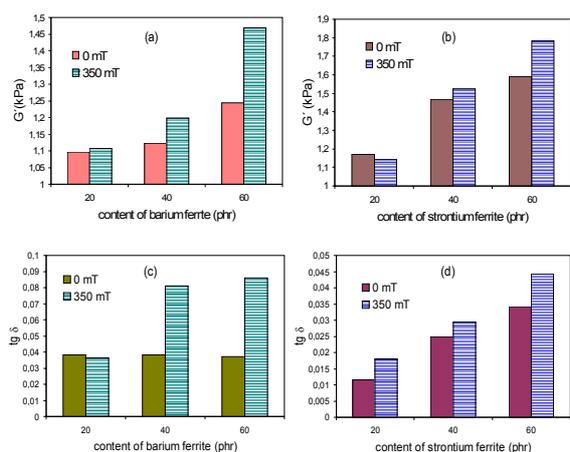


Fig. 4. The dependence of (a), (c) the storage modulus and (b), (d) the loss modulus of the magnetoactive elastomers on the content of barium and strontium ferrite in the absence and presence of magnetic field (0.35T) at 10Hz frequency

in storage modulus magnitude with magnetic field grows with the concentration of the ferrite particles. The small amount of ferrite filler influences the change of storage modulus on the magnetic field dependency too small. The higher content of ferrite filler indicates that the change of storage modulus in the presence of magnetic field become much larger. Subsequently, the intensity of magnetic field was switched of and the magnitude of storage modulus decreases to origin magnitude of storage modulus and it means the rheological change is entirely reversible. The loss factor (Fig. 4c, d) displays an ferrite content dependence in the presence of magnetic field that is very large (110 %) for relatively small content of 40 phr (7.5 vol.%) of barium nanoferrite.

Conclusions

Analysis of the results leads to the following: under the influence of the magnetic field a characteristic structuring of magnetic particles within the composite during curing takes place. Particles can move under the influence of the field to form magnetic structures of chains and it leads to the change of the physical-mechanical properties. The columnar structure of the particles in the elastomer matrix gives rise to tensile strength at break. An increasing content of ferrite gives rise to an increasing storage modulus and loss factor while applying magnetic field. The effect grows stronger with the smaller ferrite nanoparticles then with the microsized strontium ferrite. Thus it can roughly be said that the stronger the magneto-rheological effect, the higher content of magnetic particle with smaller particle size.

The financial support of Deutsche Kautschuk -Gesellschaft is gratefully acknowledged.

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P-03

ANALYSIS OF RUBBER-FILLER GEL FOR CHARACTERIZATION OF SILICA LOCALIZATION IN RUBBER BLENDS

DANIEL HEIDENREICH, HAI HONG LE, SYBILL ILISCH, ANDRÉ WUTZLER, and HANS-JOACHIM RADUSCH

*Center of Engineering Sciences, Martin Luther University Halle-Wittenberg, D-06099 Halle (Saale) Germany
hans-joachim.radusch@iw.uni-halle.de*

Silica as a filler for rubber has a great reinforcing capability. It leads to improved abrasion resistance, tear strength, aging resistance and adhesion properties. In tire treads silica yields a lower rolling resistance by maintaining a high wear resistance and wet grip. Currently, a number of rubber blends filled with silica are commercially used. The distribution of filler in rubber blends is one of the most important factors affecting the physical properties of rubber final products. Generally, it can be assumed that the main factors controlling the filler distribution into each phase of the blends are the nature of rubber, filler-rubber interaction and the mixing sequence. Several techniques have been developed for determining the filler distribution in blends¹⁻⁵. However, the most of the methods are time consuming and need a complicated sample preparation. The other common problem for the determination of the filler distribution is related to the fact, that along the mixing process the filler undergoes a large change in their size. There is a broad spectrum of large agglomerates and aggregates at short mixing time, and a narrow spectrum of small aggregates at longer mixing time. The analysis of the phase specific filler distribution could be done only for the finished compounds containing only small aggregates. At shorter mixing time, when the agglomerates themselves are larger than the blend phase, the available methods failed. Thus, the kinetics of the filler distribution in binary blends along the mixing process has not been investigated so far.

In our previous works^{6,7} a new method – the so-called wetting concept – was proposed for determination of the selective wetting behavior of filler by the blend phases. Based on the thermogravimetric analysis (TGA) of the rubber-filler gel the phase selective carbon black (CB) distribution in rubber blends could be quantified. Using the wetting concept it became possible to characterize the free CB fraction and the fraction of CB in separated blend phases as function of mixing time regardless of the agglomerate size. However, the

TGA technique is usable only when the two rubber components demonstrate distinctly different degradation temperatures. In order to overcome this problem in the present work we have used the Fourier transform infrared (FTIR) spectroscopy for evaluation of the rubber-filler gel of silica filled SBR/NR blends. The effects of the material and technological parameters on the wetting behavior of rubber and the kinetics of the phase selective distribution of silica in NR/SBR blends were investigated in detail. The results received from FTIR method will be compared with those received from TGA method.

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P-04

STRUCTURE AND PROPERTIES OF THE POLYPROPYLENE/CARBON NANOTUBES COMPOSITES AND COMPOSITE FIBRES

MARCELA HRICOVÁ*, ANTON MARCINČIN,
and ALENA HOFERÍKOVÁ

*Slovak University of Technology in Bratislava, FCHFT, IPM,
Department of Fibres and Textile Chemistry, Radlinského 9,
812 37 Bratislava, SK
marcela.hricova@stuba.sk*

The carbon nanotubes (CNT) with regard of their unique properties (mainly electrical and mechanical properties) are attractive fillers for electroconductive polymer composites and composite fibres¹. The multiwall carbon nanotube (MWCNT) have been used for reinforcing and enhancement of electrical conductivity of the engineering polymers and polymer fibres such as polypropylene (PP), polyamide (PA6), polyethylene terephthalate (PET) and others^{2–4}. The low concentration of the CNT is sufficient for improvement of the tensile properties of composite fibres. The essentially higher concentration of the fibrous particles is needed for formation of the electroconductive composite fibres with electrical conductivity higher than 10^{-2} S cm⁻¹. However, higher concentration of CNT affects negatively processing of composites at spinning and drawing. Therefore, the combination of CNT with others suitable additives, such as carbon black pigments (CBP) or organoclays, was used to get electrical conductivity of fibres at lower concentration of CNT⁵.

In this paper, the spinning and electrical properties of the PP/MWCNT composites and composite fibres, as well as their supermolecular structure, thermal and mechanical properties are presented. The laboratory twin-screw extruder $\Phi = 28$ mm was used for preparation of PP/MWCNT composites before spinning. PP composite fibres were prepared using laboratory spinning plant with extruder $\Phi = 16$ mm and drawn at maximal draw ratio. The supermolecular structure and thermal properties of fibres have been investigated by DSC analysis. Electrical conductivity of PP composites and fibres was evaluated using two methods: four-contact method (FCM) and method of resistivity of the linear textiles (RLT). The mechanical and electrical properties of the PP composites and fibres in dependence on concentration of electroconductive fillers and compatibilisers-dispersants were evaluated.

The results show that melt viscosity of the PP/MWCNT composites increases gradually with content of the MWCNT (1–8 wt.%) in PP matrix (Fig. 1). The worsening of spinning of the composite melt containing concentration of MWCNT above 6 wt.% was observed and only low spinning speed was possible.

Similarly, the low deformation gradient and temperature 140 °C in drawing process for PP fibres with MWCNT content above 1 wt.% was used. The fibres were drawn on relative high drawing ratio in this case (Table II). To improve spinability of the PP/MWCNT composites the series of the PP composites containing 3.0 wt.% of MWCNT and 3.0 wt.% of CBP PL6 with polar oligomers-dispersants based on polyglycols was prepared. Total content of electro-conductive carbon particles in the composite was 6.0 wt.%. The positive effect of MWCNT on tensile properties of PP fibres was found for low content of nano filler in PP fibres up to 1.0 wt.%. Some selected compatibilisers also contribute to mechanical properties of composite fibres (Table I).

Tenacity and Young's modulus of PP/MWCNT composite fibres decrease gradually with content of the fibrous particles in PP fibres. The low elongation at break (about 15%) and high non-uniformity of the mechanical properties are characteristic for the fibres (Table II). The compatibilisers-dispersants (PEG and NOV) have significantly improved spinability and deformation of the fibres in drawing. In addition, they have improved the non-uniformity of the composite

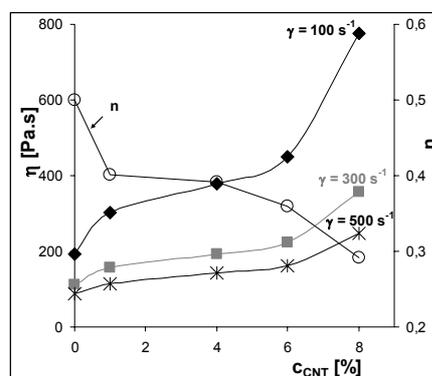


Fig. 1. Dependence of viscosity η and power law exponent n on concentration of MWCNT in PP500R/MWCNT composites at 250 °C

Table I

Tenacity T, elongation E and Young's modulus YM of the PP500R/MWCNT composite fibres (λ_{\max}). Content of MWCNT in fibres 0.1 wt.%

Additive in PP fibres	Draw ratio λ_{\max}	T [cN/tex]	E [%]	YM [N/tex]
PP standard	7.0	64.8	22.6	7.2
MWCNT	7.0	65.1	22.6	7.3
MWCNT+Boehmite D40	7.2	76.1	20.7	8.7
MWCNT+layered silicate C15A	7.5	72.8	21.6	7.9
MWCNT+C15A+der. siloxane	7.5	81.2	21.7	9.5
MWCNT+PP-g-MA+der. silox.	7.2	76.6	22.0	8.9
MWCNT+der. oxazoline	7.5	74.0	20.0	8.8

fibres expressed by lower CV_T and CV_E in comparison with PP/MWCNT fibres without compatibilisers-dispersants.

Thermal analysis of the PP/MWCNT fibres showed on double melting endotherm of the fibres with higher content of filler (1–6 wt.%) and the same shape of the endotherms for PP fibres modified by mixture of MWCNT and CBP PL6 with dispersant. Double melting endotherm of the PP/MWCNT composite fibres shows on heterogeneity in the supermolecular structure of fibres and can corresponds with worsening of their spinability and drawability. The MWCNT act as nucleating agent with high efficiency and shifts the crystallisation temperature about 10–20 °C higher, gradually with concentration of MWCNT.

Electrical properties of the PP/MWCNT composites and composite fibres were measured using two methods: standard four contact method (FCM) and resistivity of the linear textile method (RLT). Both methods show that electrical conductivity increases with the content of MWCNT. The percolation threshold is dependent on shape of sample measured and shifted from the PP composites to PP composite drawn fibres within the nanofiller concentration of 4.0–8.0 wt.%. The electrically conductive composites were obtained already at 4.0 wt.% of conductive particles, but 8.0 wt.% was insufficient for conductive drawn fibres (Fig. 2). Improvement of the rheological properties and spinability of the PP/MWCNT/CBP PL6 composite fibres by polar additives (PEG and

Table II

Tenacity T, elongation E and Young's modulus YM of the PP500R/MWCNT composite fibres, drawn at low gradient of deformation

Content of MWCNT [%]	Draw ratio λ_{\max}	T [cN/tex]	E [%]	YM [N/tex]
1.0	7.6	47.5	15.7	4.36
4.0	6.8	38.4	14.8	4.24
6.0	9.3	35.0	13.1	4.27
8.0	7.0	33.3	14.3	4.14

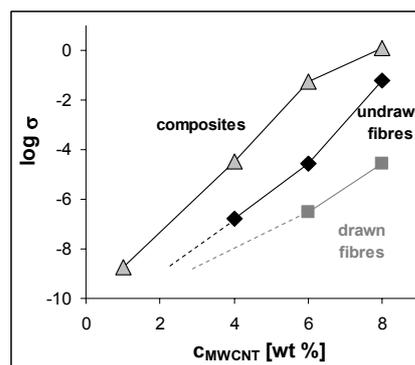


Fig. 2. Dependence of the log of conductivity σ on concentration of MWCNT in the fibres

NOV) led to decrease their electrical conductivity compared to PP/MWCNT fibres. This phenomena can be explained by separation and flocculation of the fibrous nanofiller in the PP matrix what shifts the percolation threshold to higher concentration of electrically conductive additives.

The experimental work was supported by EC, FP6 Project: NMP3-CT-2005-516972 and Grant Agency VEGA: 1/4456/07 and 1/0444/09.

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P-05

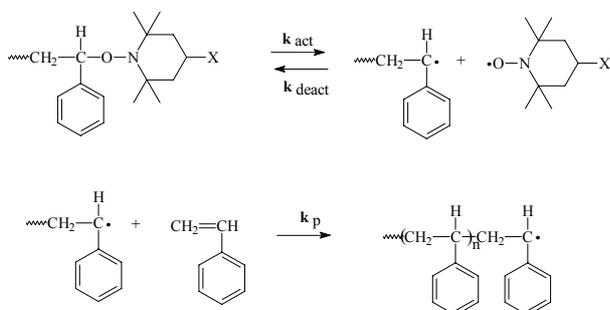
DETERMINATION OF ALKOXYAMINE CONCENTRATION IN POLYSTYRENES PREPARED BY NITROXIDE MEDIATED POLYMERIZATION

ĽUDMILA HRČKOVÁ, ŠTEFAN CHMELA, JOZEF KOLLÁR, and MAREK STACH

Polymer Institute, Slovak Academy of Sciences, Dubravská cesta 9, 842 36 Bratislava, Slovakia
upollud@savba.sk

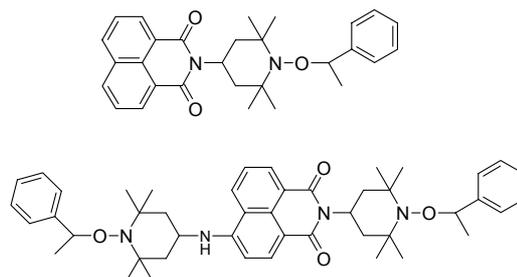
Over the past several years attempts to moderate the reactivity of the propagating species in radical polymerization have been multifold. Nitroxide mediated radical polymerization (NMP) offers simple method for preparation of polymers with programmable construction of macromolecules^{1–4}. This method permits molar mass regulation, offers polymers with rather low molar mass distribution, allows polymer preparation with desirable choice of end groups and allows preparation of block copolymers. Contrary to the anionic polymeriza-

tion it does not require precise purity of monomers and is not sensitive to the moisture. NMP is based on the ability of nitroxide to trap growing radical under the production of an alkoxyamine dormant end-functionality. Alkoxyamine at higher temperature (90–130 °C) decomposes into nitroxide and growing radical which is able to admit a part of monomer according to the following scheme:



Steady-state concentration of growing radicals is markedly lower than at common radical polymerization. Reversible reaction of macro radicals with nitroxides eliminates non-reversible termination reactions of macro radicals (recombination, disproportionation and transfer on monomer). Polymerization can be terminated at the consumption of monomer or by decreasing of temperature. Resulted polymer contains at the chain end nitroxyl radical in the form of alkoxyamine, which is able of additional growing reaction. Quantification of active chain ends represents serious problem. Up to now used approaches are problematical. NMR spectroscopy is not sufficiently precise and post-polymerization is indirect way. The last approach required substitution reaction of chain-end nitroxyl radical by another radical, which could be detectable by spectrophotometry.

In this work we prepared polystyrenes by NMP using combined molar mass regulators containing besides alkoxyamine part the structure of fluorescence mark. Stable nitroxyl radical represented 2,2,6,6-tetramethylpiperidine-*N*-oxyl and covalently bonded fluorescence mark is 1,8-naphthylimide – Scheme 1. Concentration of marked polystyrene chain ends in polymers was measured directly by UV-absorption or emission spectroscopy. Theoretical molar masses of polystyrenes were calculated from these concentrations on the assumption that all polystyrene chains are terminated by alkoxyamine dormant end-functionality bearing fluorescence probe. Comparisons of these data with the molar masses from GPC gave us the range of the marked active polymer chain ends. Fractions of active polymer chain ends depended on the conversion. With increased conversion the fraction of alkoxyamines was decreased. At lower conversion (10 %) roughly 90 % of polymer chain ends contained alkoxyamine while at higher conversion (60 %) this value represented just 50 %. In this case just each second polymer chain is terminated by alkoxyamine. From this follows that the „livingness“ of polymerization process was decreased with the increasing of conversion. It should result in the increase of polydispersity with increased conversion. Despite this polydispersity was the same for all conversions and reached value ca. 1.3.



Scheme 1. Structures of unimolecular initiators

The authors thank Grant Agency VEGA for financial support through grant 2/0082/08 and through APVV project 0562-07.

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P-06

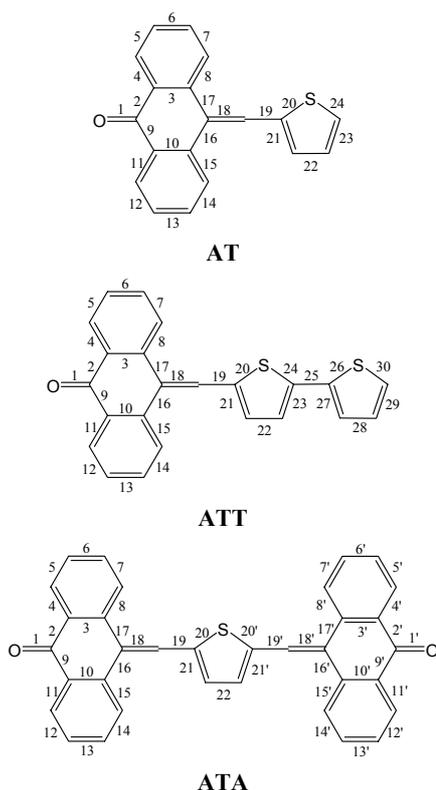
THE SYNTHESIS AND ELECTRONIC STRUCTURE OF OLIGOTHIOPHENES TERMINATED WITH (10H-ANTHRACENE-9-ONE)METHYLENE CHROMOPHORES

VLADIMIR LUKEŠ^a, IVAN HRABLAY^a, ROLAND ŠTOLC^a, DANIEL VĚGH^b, PAVOL HRDLOVIČ^c, and VILIAM LAURINC^a

^a Department of Chemical Physics, Slovak University of Technology, Radlinského 9, SK-812 37 Bratislava, ^b Department of Organic Chemistry, Slovak University of Technology, Radlinského 9, SK-812 37 Bratislava, ^c Polymer Institute, Slovak Academy of Science, Dúbravská cesta 9, SK-842 36 Bratislava, Slovak Republic
upolhrdl@savba.sk

The automotive industry is a material intensive industry. A wide variety of metal, fillers, plastics, pigments and dyes are required to meet specific applications. The synthetic polymers represent the growing fraction of materials used for different parts of the car. Conducting polymers and oligomers find special applications in this automotive and electronic industry. There is the strong drive to develop and apply new conducting oligomers which can be applied as such or doped in polymers.

In this study the synthesis, spectral measurements and theoretical study of simple model oligothiophenes terminated symmetrically or a symmetrically by (10H-anthracene-9-one) methylene chromophores according the Scheme are presented¹.



Scheme 1

The electron absorption spectra of prepared molecules were measured in polymer matrices and chloroform solution. The absorption spectra of the investigated systems are represented by broad band without vibrational structure. The maxima of the compounds under investigation are given in the Table.

S ^a	$\lambda_A(\log \epsilon)^b$ [nm]	$\lambda_A(\log \epsilon)^b$ [nm]	λ_F^c [nm]	Φ_r^d	$\Delta\nu^f$ [cm ⁻¹]
Ia, AT	322(3.60)				
Ib, ATT	328(3.95)	445(3.07)	520	0.39	3241
IIa, ATA	323(3.55)	450(2.80)	467	0.97	810

^aSubstrates according to Scheme 1. ^bWavelength of the maximum of absorption band at long wavelength edge (log of decadic extinction coefficient in dm³mol⁻¹cm⁻¹). ^cWavelength of the maximum of fluorescence. ^dQuantum yield relative to anthracene in the given medium. ^fStoke's shift

Theoretical calculations of the electronic ground state structures have been performed at the density functional theory (DFT) level of the theory. The vertical excitations energies were calculated using the time dependent version of DFT and semiempirical Zerner's Intermediate Neglect of Differential Overlap (ZINDO).

The evaluated DFT HOMO orbitals are dominantly lo-

calized on the thiophene oligomers where as LUMO is spread into the anthrone chromophore. Excitation to the S₁ state corresponds exclusively to the significant promotion of an electron from HOMO to LUMO as it is clearly demonstrated on ATA.



HOMO → LUMO

In conclusion it can be stated that the studied systems exhibit interesting spectral properties namely fluorescence depending on the molecular architecture and the medium. Therefore these materials might serve as the basis for the spectroelectrochemical characterisation with respect to their potential usage in various optical devices, e.g. plastic solar cells or organic light emitting devices.

This work has been supported by Slovak Grant Agency VEGA (Projects No. 1/3036/06, 2/0097/09, 1/0774/08 and 1/4453/07).

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P-07

PYROLYSIS OF USED TYRES

IVAN HUDEC^a, JOZEF FERANČ^a, JUMA HAYDARY^b, and I. ŠURINA^a

^aSlovak University of Technology in Bratislava, Faculty of Chemical and Food Technology, Institute of Polymer Materials, Department of Plastics and Rubber, ^bInstitute of Chemical and Environmental Engineering, Radlinského 9, 812 37 Bratislava
ivan.hudec@stuba.sk

In generally, the scrap tyres recycling methods can be divided into:

- Mechanical recycling – re-processing of tyres into new rubber products,
- Feedstock recycling – processing of tyres into raw materials,
- Energy recovery – recovery of energy from waste through incineration.

A promising recycling route for used tyres is their transformation into useful products by pyrolysis¹. Pyrolysis can be defined as the thermal decomposition of organic material in the absence of air. Upon heating, shredded tyres are decomposed and converted into oils, gases and pyrolytic residue. The liquid oil product consists of a very complex mixture of organic components. The gaseous fraction is composed of non-condensable gases, such as H₂, H₂S, CO, CO₂, CH₄,

C₂H₄, C₃H₆, etc. The gas fraction can be used as fuel in the pyrolysis process. By using the gas fraction as fuel the consumption of external energy source is minimized. This is an advantage of pyrolysis compared to other recycling methods in which the consumption of energy is very high. From the ecological point of view, pyrolysis has practically no impact on the environment due to the closed pyrolysis system. The pyrolysis residue consists of the recovered carbon black filler, inorganic materials and varying proportions of carbonaceous materials formed from the rubber decomposition products.

A literature review²⁻⁴ shows a large variety of results depending on the technology and process conditions used in pyrolysis process. All parameters, temperature, heating rate, hydrodynamic conditions, catalyst and particle size are the main factors affecting the amount and composition of the pyrolysis products.

The aim of this work is presentation of some results obtained by the studying of the isothermal pyrolysis of rubber granulate of scrap tyre under nitrogen was investigated in the temperature range from 400 °C to 800 °C. The laboratory unit with screw type flow reactor for isothermal pyrolysis process of rubber granulate was used. The composition and properties of pyrolysis products were studied in relation to the temperature and time of pyrolysis process.

Rubber granulate from passenger tyres with different particle size distribution produced by V.O.D.S. Košice, Slovakia was used in all experiments. The laboratory pyrolysis unit was used in the study. The rubber granulate was fed into the system using a feeder and the particles are passed through the reactor using a rotation of screw. The residence time of pyrolysis process of the particles in the reactor was controlled by the rate of the screw rotation. Inert atmosphere in the reactor is achieved by nitrogen flowing through the reactor in the same direction as the solid material. Passing through the reactor, rubber particles are decomposed. The volatile products are removed from the reactor at high temperature and they are led to a condenser. The solid

residue is removed from the end of the reactor and collected. The volatile fraction after partial condensation is cooled in two scrubber type coolers. Composition of the gas and liquid fraction was measured by GC/MS spectroscopy.

Solid pyrolytic residues were characterized by specific surface area (measured by nitrogen adsorption method) and mercury porosimetry for pore size distribution. Table I shows comparison between basic structural properties of solid residue from laboratory screw pyrolytic reactor, pilot batch reactor and two types of industrial carbon black products.

From comparison is evident, that pyrolytic carbon black from laboratory screw reactor has the similar surface activity as that of low-surface commercial carbon black. In Table II the influence of temperature of pyrolysis in laboratory reactor on pyrolysis products content and surface area of carbon residue are shown.

From data is evident that by changing of basic technological parameters it is possible to change quantity of pyrolysis products and properties of carbon residue in wide range.

This work has been supported by APVV Grant Agency (project EURB-0013-06).

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P-08

PROPERTIES OF CONDUCTIVE NANOCOMPOSITES BASED ON EVA COPOLYMER AND EXPANDED GRAPHITE

IGOR KRUPA^{a*}, VOLKAN CECEN^b, ABDEL BOUDENNE^c, LAURENT IBOS^c, RADHOUAN TLILI^c, IGOR NOVÁK^a, MÁRIA OMASTOVÁ^a, JAN PROKEŠ^d, JÜRGEN PIONTECK^e, ZUZANA KRIŽANOVÁ^f, and IVO VÁVRA^f

^a Polymer Institute, Slovak Academy of Sciences, Dúbravská cesta 9, 842 36 Bratislava, Slovakia; ^b Dokuz Eylul University Mechanical Eng. Department 35100 Bornova/Izmir, Turkey; ^c CERTES EA 3481 - Centre d'Etude et de Recherche en Thermique, Environnement et Systèmes, Université Paris 12 Val de Marne, 61 Av. du Général de Gaulle, 94010 Créteil cedex, France; ^d Charles University Prague, Faculty of Mathematics and Physics, V Holešovičkách 2, 182 00 Prague 8, Czech Republic; ^e Leibniz Institute of Polymer Research Dresden, Hohe Str. 6, 01069 Dresden, Germany; ^f Institute of Electrical Engineering, Slovak Academy of Sciences, Dúbravská cesta 9, 841 04 Bratislava, Slovakia
upolkrup@savba.sk

Table I
Comparison of different types of carbon black

Sample	CBp, screw flow reactor	CBp, batch reactor	CBp, batch reactor, cyclon	Carbon black N550	Carbon black N660
Specific surface area, m ² g ⁻¹	46	18	25	40	38

Table II
The influence of temperature on content and properties of pyrolysis products

Temperature, °C	500	600	700	800
CBp content, wt. %	39,3	37,4	38,9	41,9
Specific surface area, m ² g ⁻¹	58,2	71,5	68,1	57,7
Pyrolytic oils content, wt. %	25,2	13,9	7,0	4,95

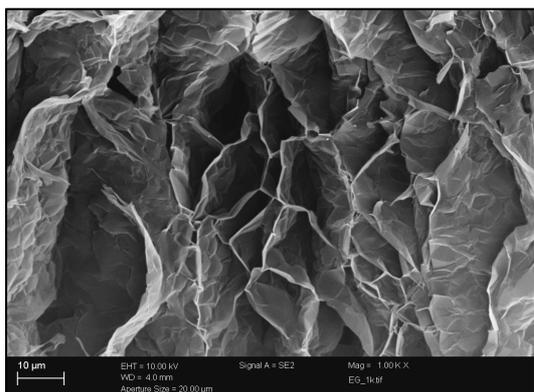


Fig. 1. SEM image of EG

Carbon additives are used in polymer composites as fillers, reinforcing agents and pigments. For some applications it is necessary that polymers exhibit a certain degree of conductivity, which can be reached by mixing conventional isolating polymers with electrically conductive fillers. One promising carbon based filler is graphite, especially in its expanded form (Fig. 1).

Polymeric nanocomposites prepared from high aspect ratio layered graphite nanofillers achieve significant improvements in mechanical, thermal, electrical and barrier properties at very low filler concentrations¹, compared to conventional composites, without a significant increase in density. This is caused by the sheet-like structure of natural graphite where the atoms are strongly bonded on a hexagonal plane but weakly bonded normal to that plane. If these graphene layers are separated down to a nanometer thickness through intercalation and exfoliation, they are able to form graphite nanosheets, which possess a huge surface area and high aspect ratio (200–1500) what results in a formation of percolating network at very low filler content. Moreover, such materials have a high strength due to a strong reinforcing effect of the nanosheets^{2,3}. The exfoliation of expanded graphite is demonstrated in Fig. 2. It is seen that the exfoliation process starts on the edges of EG grains.

Various aspects of electrical, structural, thermal and mechanical behavior of nanocomposites based on the ethylene-vinylacetate (EVA) matrix filled with nanostructuralized expanded graphite and standard, micro-sized graphite were



Fig. 2. TEM micrograph of the EVA/EG nanocomposite

investigated. The influence of micro and nano sized fillers on the final physical properties were also studied. It was found that the electrical conductivity of composites strongly depends not only on the filler content but also on the graphite structure. If micro-sized graphite was used, the percolation concentration of the filler was found to be 15–17 vol.%, whereas the percolation concentration of the filler in nanocomposites filled with expanded graphite was significantly lower – its value was at about 5–6 vol.%. Electrical conductivity of nanocomposites was also much higher than electrical conductivity of composites filled with micro-sized filler at comparable concentrations. Similarly, the strength and Young's modulus of nanocomposites filled with expanded graphite was significantly higher than the strength and Young's modulus of composites filled with micrographite.

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. 2/0063/09) and by Science and Technology Assistance Agency contract No. APVV-0478-07. This work is also a part of the research plan MSM0021620834 that is financed by the Ministry of Education, Youth and Sports of the Czech Republic. The authors appreciate the financial support by the DAAD within the program PPP Slovakia, D/07/01261. The Scientific and Technological Research Council of Turkey is acknowledged for granting of V. Cecen postdoctoral study in the framework of TUBITAK-BIDEB 2219-International Postdoctoral Research Scholarship Program. This research was also supported by the Scientific Support of the bilateral Project No. 107 M 227 of TUBITAK and Slovak Academy of Sciences.

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P-09

THERMAL STABILITY AND COMBUSTIBILITY OF CHLOROSULPHONATED POLYETHYLENE AND ITS BLENDS WITH STYRENE-BUTADIENE RUBBER

AGNIESZKA KUCHARSKA-JASTRZĄBEK,
GRAŻYNA JANOWSKA, and JAKUB KAWALEK

*Technical University of Lodz, Institute of Polymer and Dye Technology
janowska@p.lodz.pl*

Introduction

Thermodynamic miscibility of polymers, which depends greatly on their solubility parameters, is a rather rare phenomenon. Polymer blends offer a possibility for their physical modification which can result in the formation of

new polymer materials characterized by interesting and sometimes specific properties, including thermal ones with good mechanical features. This is very often a consequence of co-curing processes, i.e. an interpolymer bonding of macromolecules which form polymer blend in a common network structure¹. It follows from the literature survey that the methods of production of polymer blends and their properties are investigated in many research centers, in that number also in the Institute of Polymer and Dye Technology, Lodz Technical University². However, there has been no information on systematic studies of thermal properties and flammability of cross-linked polymer blends. The present study is dedicated to this subject.

Experimental

Studies were focused on two chlorosulphonated polyethylene with different content of chlorine: CSM24 (24 % of combined Cl) and CSM43 (43 % of combined Cl) – commercial products of Du Pont Dow Elastomers. Under investigation was also styrene-butadiene rubber, SBR, containing 23,5 % of styrene mers, product of Synthos S. A. Elastomer blends containing 85 phr of SBR and 15 phr of CSM were cross-linked by 2 phr of ZnO (product of Huta Oława) and 1 phr of nano ZnO (product of Nanostructured&Amorphous Materials Inc.).

The thermal analysis of elastomers and elastomer blends were carried out in inert gas atmosphere by means of differential scanning calorimetry (DSC) of Netzsch, DSC-204, using portions of about 5mg at heating rate of 10 °C min⁻¹ within temperature range -100 to 500 °C and in air atmosphere by means of Derivatograph; Paulik-Paulik-Erdey system (MOM, Hungary) using weighed portions of 90 mg at heating rate of 7,9 °C min⁻¹ within the temperature range from 20 to 800 °C.

The combustibility of elastomers and elastomer blends were determined by the method of oxygen index, using the

apparatus of our own construction, according to the standard PN-ISO 4589-2. The flammability was also tested on the base of combustion rate measurements in air, using the same specimens as in case of oxygen index.

Discussion

Under the inert atmosphere styrene-butadiene rubber, SBR, preserves elastic properties from the temperature -52.2 °C in which it turns from the glassy to the elastic state, to the initial temperature of thermal cross-linking process 259 °C.

In case of researched chlorosulphonated polyethylenes their glassy transition takes place at higher temperature when compared with SBR rubber (Table I). Simultaneously the chlorine content in CSM influences the increase of glass transition temperature, T_g (ref.^{3,4}). The thermal stability range of the researched CSM is much narrower when compared with SBR as a result of thermal transitions connected with the process of macromolecule dehydrochlorination at the temperature over 190 °C. The dehydrochlorination process causes thermal modification of polymer chains which results in creation of double bonds, even conjugated $\sim\text{CH}=\text{CH}-\text{CH}=\text{CH}\sim$, as in the case of polyvinyl chloride, PVC³⁻⁵.

Researched elastomer blends CSM/SBR cross-linked by zinc and nanozinc oxide are characterized by singular temperature of the transition from the glassy to the elastic state, higher than T_g of SBR and lower than T_g of CSM. It confirms good miscibility of examined elastomers³. The initial temperature of cross-linking process, T_C , of SBR is significantly higher than T_C of researched elastomer blends. As is shown in Table I, the application of nano ZnO in the cross-linking process of examined blends influences the increase of their T_C when compared with ZnO. It proves that changing zinc oxide to nanozinc oxide causes an increase of thermal stability range.

Table I
Thermal properties of elastomers and their blends

Atmosphere Sample	Nitrogen		Air				
	T_g [°C]	T_C [°C]	T_5 [°C]	T_{50} [°C]	dm/dt [mm]	Pe [%]	P_{800} [%]
SBR	-52,5	259,5	270	410	65	16,1	5,0
CSM24	-24,2	193,5*	250	420	60	15,0	5,5
CSM43	10,0	198,0*	230	375	30	21,1	2,2
CSM24/SBR _{ZnO}	-49,7	130,3	240	420	57	25,9	7,8
CSM24/SBR _{nZnO}	-48,2	149,3	240	415	50	24,0	5,5
CSM43/SBR _{ZnO}	-38,8	141,1	195	415	47	35,9	12,8
CSM43/SBR _{nZnO}	-44,1	179,1	200	415	48	29,0	7,8

* – initial temperature of dehydrochlorination process, T_g – glass transition temperature, T_C – initial temperature of cross-linking process, T_5 – temperature of elastomer/blend 5% mass loss, T_{50} – temperature of elastomer/blend 50 % mass loss, dm/dt – maximum rate of elastomer/blend thermal decomposition, Pe – residue after thermal decomposition, P_{800} – residue after heating upto 800 °C, SBR – styrene-butadiene rubber, CSM24 – chlorosulphonated polyethylen containing 24 % of combined Cl, CSM43 – chlorosulphonated polyethylen containing 43 % of combined Cl, CSM24/SBR_{ZnO} – elastomer blend of CSM24 and SBR cross-linked by ZnO, CSM24/SBR_{nZnO} – elastomer blend of CSM24 and SBR cross-linked by nZnO, CSM43/SBR_{ZnO} – elastomer blend of CSM43 and SBR cross-linked by ZnO, CSM43/SBR_{nZnO} – elastomer blend of CSM43 and SBR cross-linked by nZnO

The increase of chlorine content in CSM influences the thermal stability indicates under the air atmosphere⁵. The higher content of chlorine in CSM is, the lower is the thermal stability defined by value of T_5 of examined polymer and its blend with SBR (Table I). From among examined blends only CSM24/SBR is characterized by the highest thermal stability indicated irrespective of zinc oxide applied.

The rate of SBR thermal decomposition, dm/dt , is significantly higher than the destruction rate of examined polyethylene, because HCl which is emitted in this reaction favours ionic decomposition of polymer and its blends with SBR. Therefore higher content of chlorine in CSM causes a decrease of thermal decomposition rate in air, whereas the residue after thermal decomposition, Pe , increases.

We observed a distinct influence of the applied CSM type on the residue after thermal decomposition, Pe , of the examined blends (Table I). Higher content of chlorine and as a result higher emission of HCl, favours elastomer blend CSM43/SBR carbonization.

In case of researched chlorosulphonated polyethylenes their glassy transition takes place at higher temperature when compared with SBR rubber (Table I). Simultaneously the chlorine content in CSM influences the increase of glass transition temperature, T_g (ref.^{3,4}). The thermal stability range of the researched CSM is much narrower when compared with SBR as a result of thermal transitions connected with the process of macromolecule dehydrochlorination at the temperature over 190 °C. The dehydrochlorination process causes thermal modification of polymer chains which results in creation of double bonds, even conjugated $\sim\text{CH}=\text{CH}-\text{CH}=\text{CH}\sim$, as in the case of polyvinyl chloride, PVC³⁻⁵.

Researched elastomer blends CSM/SBR cross-linked by zinc and nanozinc oxide are characterized by singular temperature of the transition from the glassy to the elastic state, higher than T_g of SBR and lower than T_g of CSM. It confirms good comiscibility of examined elastomers³. The initial temperature of cross-linking process, T_c , of SBR is significantly higher than T_c of researched elastomer blends. As is shown in Table I, the application of nano ZnO in the cross-linking process of examined blends influences the increase of their T_c when compared with ZnO. It proves that changing zinc oxide to nanozinc oxide causes an increase of thermal stability range.

The increase of chlorine content in CSM influences the thermal stability indicates under the air atmosphere⁵. The higher content of chlorine in CSM is, the lower is the thermal stability defined by value of T_5 of examined polymer and its blend with SBR (Table I). From among examined blends only CSM24/SBR is characterized by the highest thermal stability indicated irrespective of zinc oxide applied.

The rate of SBR thermal decomposition, dm/dt , is significantly higher than the destruction rate of examined polyethylene, because HCl which is emitted in this reaction favours ionic decomposition of polymer and its blends with SBR. Therefore higher content of chlorine in CSM causes a decrease of thermal decomposition rate in air, whereas the residue after thermal decomposition, Pe , increases.

Table II
Combustibility of elastomers and their blends

Sample	t [s]	OI
SBR	206	0,293
CSM24	18*	>0,375
CSM43	incombustible	>0,375
CSM24/SBR _{Zno}	252	>0,375
CSM24/SBR _{nZno}	246	>0,375
CSM43/SBR _{Zno}	290	0,375
CSM43/SBR _{nZno}	270	0,375

* – próbka samogasnąca, **t** – time of burning in air, **OI** – oxygene index

We observed a distinct influence of the applied CSM type on the residue after thermal decomposition, Pe , of the examined blends (Table I). Higher content of chlorine and as a result higher emission of HCl, favours elastomer blend CSM43/SBR carbonization.

High-molecular components of researched blend are differentiated in respect of their flammability (Table II). SBR is a flammable polymer and flammability of CSM depends on their chlorine content, CSM belong to self-extinguishing or non-flammable polymers. So, addition of 15 phr of chlorosulphonated polyethylene to SBR causes a substantial decrease of its flammability.

The research proved that changing zinc oxide to nanozinc oxide caused inconsiderable reduction of crosslinked elastomer blend CSM/SBR burning time in air regardless of chlorine content in CSM.

Changing of CSM24 to CSM43 caused elongation of burning time of crosslinked blends, however, contrary to expectations, we did not receive samples self-extinguishing in air.

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P-10
IMPROVEMENT OF DYE ADSORPTION
ON REGENERATED CELLULOSE FIBERS BY RF
PLASMA PRE-TREATMENT

MARIÁN LEHOCKÝ^{a*}, MUSA SOWE^b,
and PETR SÁHA^b

^a Tomas Bata University in Zlín, T.G.M. Square 5555, 760 01 Zlín, ^b Polymer Centre, Faculty of Technology, Tomas Bata University in Zlín, T.G.M. Square 275, 762 72 Zlín, Czech Republic
 lehocky@post.cz

Adsorption of the dyes on the surface of the natural or synthetic polymer fibers, or weaved fabrics is created due to the effect of the intermolecular forces between fiber surface and the dye. Such forces are causing relatively strong bonding interaction between dye dipoles and the stained matrix. In the case of polymer and biopolymer materials the number of the dipoles is directly proportional to the number of polar groups in macromolecular side chains. The latter number of present dipoles is possible to be increased by several physico-chemical methods, e.g. fire treatment, chemical etching by strong acid, UV irradiation, corona discharge or low-temperature plasma treatments etc. In this communication the effect of low-temperature plasma treatment of regenerated cellulose weaved fabric on dye adsorption to the surface of the studied substrate is discussed. Obtained increased dye selectivity to the stained matrix results in improved tinctorial strength, better economical effectiveness as well as to the improved ecology of the process.

Radiofrequency (RF) plasma treatments can advantageously replace thermal, radiative or chemical processes of surface modification of fibres or weaved fabrics. In fact, these treatments can be easily controlled and are environmental-friendly. Moreover, plasma modifies the surface layer at a depth of few nanometres, depending on power and time, and leaves the bulk characteristics unaffected. Due to this fact, in some cases, plasma provides the only acceptable solution to common surface treatment problems¹⁻⁵. A cold plasma process, also referred as to as a low-temperature, low-pressure or glow discharge plasma process, is a vacuum process utilizing interactions of reactive species created in a low-temperature plasma with solid surfaces. Cold plasma is an ionized or partially ionized fluid that, as whole, is electrically neutral. The reactive species include electrons, ions, free radicals, various neutral molecules and photons of wide range of energies. The change of surface behaviour with regards to its hydrophilic modification is often useful and it allows using in different areas of temporary technologies (printing and packaging industry). It is possible to provide the necessary biocompatibility by modification of surface, for example by fixing of active organic or biopolymer thin film⁶. Fixing of metal particles for improvement especially mechanical or electromagnetic properties and design of the commercial product is also helpful^{7,8}. In this communication the measured quantity of the adsorption was the reflectance, which is directly proportional to the dye adsorption. Reflectance is the quantity characterizing ability of the materials body to reflect electromagnetic radiation falling onto it. With increasing dye adsorption, the higher

is the amount of the dye adsorbed what is reflected also in the higher sample reflectance. There was used contact angle measurement to evaluate surface hydrophilicity/hydrophobicity of the used plasma treatment. Chemical composition of viscose surface was studied by means of XPS analysis. Topography of virgin and treated fabrics was visualized using SEM.

Air plasma surface treatment was used as an effective tool to increase surface hydrophilicity and roughness of viscose surface. The level of incorporated nitrogen and oxygen was investigated to describe the kinetics of the process and to confirm wettability studies showing decrease of contact angle with treatment time. The SEM was used for surface morphology visualization observing change from relatively smooth for virgin viscose to rough one for treated substrate. Dyeing of weaved fabrics was proceeding in much better way. A new recipe for dyeing bath without any use of sodium sulphate was found with the same result of reflectance of final dyed fabrics. Thus, due to the effect of plasma treatment we could eliminate sodium sulphate in dyeing bath to obtain the same intensity of colour after dyeing what is very important from both ecological and economical point of view.

Authors would like to express their gratitude for financing of this research to the Ministry of Education, Youth and Sport of the Czech Republic (grant VZ MSM 7088352101).

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P-11
PLASMA-MODIFICATION OF THERMOPLASTIC
FOR IMPROVE BONDING PROPERTIES

ANNA MISIUN,* S. SCHMID, H. GEISLER,
and R. H. SCHUSTER

*Deutsches Institut für Kautschuktechnologie e.V., Eupener Straße 33, 30519 Hannover, Germany
 Anna.Misiun@dikautschuk.de*

In this work the influence of atmospheric pressure plasma activation and plasma polymerization processes on the

rubberthermoplastics bonding was investigated. Chemical and physical properties of the modified surfaces were confirmed through contact angle measurements, infrared spectroscopy and atomic force microscopy. It was shown, that plasma activation and polymerization affect the surface properties and were able to improve the bonding between the investigated materials.

Introduction

The industrial use of plasma processing has been known since late 1960. Most of the progress was done by the use of low pressure plasma. The disadvantage here is, that this is not suitable for the commercial technology. A new entry in this field is given by the non-thermal atmospheric pressure plasma process. From begin it was clear, that this new technique will have a favorable affect in improving material properties in the bonding technology.

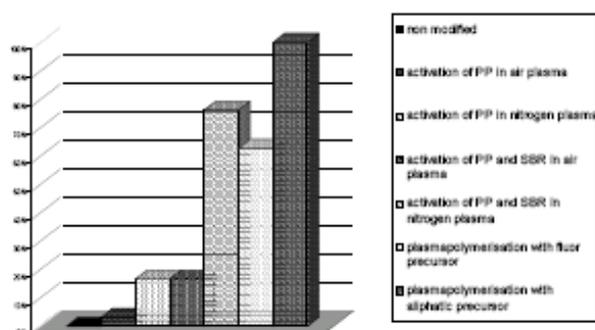
The focus of this research is the influence of atmospheric pressure plasma discharge on the properties of rubberthermoplastic bonding.

Experimental

Commercial thermoplasts like PP, PBT and PA6 were used as a substrate for plasma treatment. The materials were cleaned in acetone and modified through atmospheric pressure plasma (open air plasma reactor, model PFW 20, Plasma-Treat, Germany). The samples were treated using various process gases (nitrogen, air or argon). Plasma polymerization experiments were performed with various precursors suitable for this process. Experiment conditions like modification time, power or sample to plasma outlet distance were varied during the work.

After plasma treatment PBT and PA6 were bond with nitrile-butadiene-rubber (NBR) via vulcanization with a 1-component and 2-component adhesive system. After the treatment polypropylene was glued via an adhesive based on CR with a styrene-butadiene-rubber (SBR).

The effectiveness of experiments was measured using the contact angle method. The treated thermoplastic surfaces were also examined using atomic force microscopy (AFM) to



Scheme 1. The gluing of polypropylene with SBR with a contact adhesive based on CR



Scheme 2. Application on plasma activation and plasma polymerization as a replacement of adhesive primer

characterize the substrate topography and the thickness of the polymer films after treatment. The chemical properties of the plasma polymers were confirmed using infrared spectroscopy.

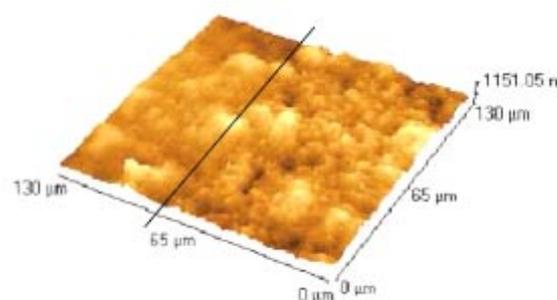
Results

The plasma processes lead to the following effects: cleaning, activation and functionalization of the thermoplastic surfaces. All this factors have a genuinely influence during the composite preparation via gluing or vulcanization.

Practical adhesion of SBR on polypropylene by use of CR adhesive equal to zero. The activation alone of the material in air or nitrogen plasma induce the adhesion forces between the bonded surfaces. However, the best effects are observed after plasma polymerization process using fluor- or aliphatic precursor (Scheme 1).

The vulcanization of NBR on thermoplastic materials can be realized by using a 2-components adhesive system, where one of the components is the primer. Without the primer the bonding can not occur. The latest experiments with various plasma polymerization precursors showed, that plasma give the opportunity to successfully replace the primer (Scheme 2) leading to a 1-component (1C) system.

The surface analysis confirms the chemical and physical changes of the treated materials. Wettability measurements are



Scheme 3. AFM picture of deposited plasmopolymer based on aliphatic precursor (right) and untreated sample (left)

showing a correlation between the experiment conditions and surface energy. This gives an ability to control the process outcome and to “adjust” the surface energies of partners, what have a relevant influence during bonding process.

Morphological images from atomic force microscopy showed a different thickness and shape of deposited layers as a function of precursor flow rate and the type of precursor itself. Scheme 3 shows the polypropylene surface with a typical layer of plasmopolymer based on an aliphatic precursor.

Conclusions

It has been confirmed, that the plasma technique can be an effective surface treatment for promoting adhesion between thermoplastic and rubber. The most successful results were obtained during the plasma polymerization process with aliphatic substances as precursors for the bonding of NBR and SBR on PP, PBT and PA6.

However, at the moment this technique can not substitute the complete adhesive system.

We thank the following companies for financial support: REMA TIP TOP GmbH, Artemis Kautschuk- und Kunststofftechnik GmbH, SKF Sealing Solution GmbH, Maschinenfabrik Herwarth Reich GmbH, Vulkan Kupplungs- und Getriebebau GmbH & Co. KG, Stromag AG, helsacom GmbH, Berleburger Schaumstoffwerke GmbH, Plasmatreat GmbH.

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P-12

STRUCTURAL EVOLUTION IN LAYERED SILICATES NANOCOMPOSITES

DANIELA JOCHEC MOŠKOVÁ^a, IVICA JANIGOVÁ, and IVAN CHODÁK

*Polymer Institute of the Slovak Academy of Sciences, Dúbravská cesta 9, 842 36 Bratislava, Slovakia
upoldamo@savba.sk*

Polymer/layered silicate nanocomposites have attracted great interest because they often exhibit remarkable improvement in materials properties when compared virgin polymer or conventional micro- and macro-composites. Nanocomposites based on biodegradable polycaprolactone (PCL) and native or organically modified layered silicates (Cloisite with different organophilisation) were prepared by melt mixing and using co-rotating twin screw extruder for comparison of the influence of mixing rate on the structure of composites. The structure and properties of prepared materials were characterized by SEM, TEM, wide-angle X-ray diffraction and

rheological measurements which provides additional information about structure.

The experiments revealed that various fillers differ in their effect and different method of homogenization strongly influenced structure. The increase of layer spacing depends on the clay concentration. Intercalation and/or exfoliation of PCL/C20A is achieved by homogenization at higher shear rate.

In the TEM images for the PCL/C20A it is clearly seen that nanoclay sheets are homogeneously dispersed in the PCL matrix. Although exfoliated individual layers can be detected by TEM, the method can not be used to draw general conclusions about the structure. TEM images for the PCL/CNa show several large dark domains and clay aggregates at a micrometer level. Exfoliated nanoclay sheets for the PCL/CNa are observed only in composites prepared via extrusion process. In order to obtain indications about the differences in composite structure in quantitative terms, SEM analysis was performed.

The melt rheological properties were analyzed using viscoelastic properties obtained from oscillatory rheological measurements. The nanocomposites showed a much higher complex viscosity than the neat PCL and significant shear-thinning behavior in the low frequency range. The storage modulus and loss modulus of the nanocomposites were also found to be less frequency dependent in the low frequency range than the virgin PCL. The reason is seen in the strong interactions between the organoclay layers and PCL molecules and in good dispersion of organoclay platelets in the polymer matrix.

Acknowledgement. APVV-51-050505.

P-13

EFFECT OF PLASMA TREATMENT ON THE PRINTABILITY OF MEDICAL GRADE PVC

MUSA SOWE^{a*}, IGOR NOVÁK^b, MARIÁN LEHOCKÝ^c, PETR SÁHA^a, and IVAN CHODÁK^b

*^aPolymer Center, Tomas Bata University in Zlin, T.G.M Square 275, 762 72 Zlin, Czech Republic, ^bDepartment of Composite Thermoplastics, Polymer Institute, Slovak Academy of Sciences, Dúbravská cesta 9, 842 36 Bratislava, Slovakia, ^cTomas Bata University in Zlin, T.G.M Square 5555, 760 01 Zlin, Czech Republic
musa_sowe2002@yahoo.com*

Introduction

Polymers are applied widely in modern industry and act in very important roles for many obvious advantages¹. However, bonding and finishing of many polymers present a problem due to the low hydrophilicity of their surfaces. Hydrophilicity affects the wettability, paintability, colorability, printability, biocompatibility, anti-electrostatic properties, adhesion, etc. Many methods have been devised and are commercially available to modify the polymer surfaces. Among them, plasma treatment has emerged as a convenient and versatile surface modification and coating technique and it is

now a common method in industry because it is a very effective way to give hydrophilicity to a polymer surface².

Poly (vinyl chloride), PVC, is a particularly important commodity polymer that accounts for an annual world-wide production of about 26 million tons. Medical grade PVC continues to be extensively used in the medical field as a biomaterial to produce catheters (intravenous and urological), blood storage bags and dialysis tubing despite public scrutiny for some of the plasticizers used in PVC³. And, in that regard extensive research on surface cross linking and surface coating have addressed some of the problems of plasticizer migration or biocompatibility of PVC⁴.

Although PVC has many applications due to its attractive characteristics such as flexibility, softness, transparency, and low production cost, the required surface properties, such as, adhesive ability, biocompatibility, antibacterial ability and printability, are often different from those of the bulk in many applications^{5,6}. For example, its surface inertness creates challenges for adhesion of ink on its surface, and therefore affects its printability⁶. In order for an ink to adhere to a substrate, it must have adhesion properties that make it capable of wetting the material. And, upon drying, it should remain adhered to the surface and not peel or chip. If this is to occur, the surface tension of the ink must be lower than the surface energy of the substrate⁷.

It has been shown that surface characteristics including surface chemistry, charge, wettability and roughness all affect biocompatibility and adhesion capability on surfaces^{8–10}. Surface plasma treatment of polymers has been shown to be a viable method in enhancing adhesion properties in that it does not affect the bulk characteristics of the material. In this regard, plasma-surface modification (PSM) is an effective and economical surface treatment technique for many materials and continues to be of growing interest in medical devices technology.

And so the purpose of this work is to investigate the effect of cold plasma treatment on the printability of medical grade PVC. The scope of the work is limited to correlating printability on PVC virgin and plasma treated samples.

Experimental method

Commercially available medical grade PVC of material RB1/T3M for extrusion, in pellet form, from Moden Plast S.P.A, Hungary, was used in this study. The additives included stabilizers and lubricants. Films of 5 cm × 5 cm × 1 cm size were produced using a hot press at 160 °C.

Experiments were performed on PVC film pieces of 4 cm × 5 cm × 1 cm. Prior to plasma treatment the samples were washed using triton and de-ionized water, sonicated, oven dried and individually stored. The coplanar discharger was used for the PVC modification. The plasma treatment was conducted in air under atmospheric pressure at room temperature for 15 seconds using 200 W power.

Wettability of the plasma treated PVC surface was evaluated by making contact angle measurements immediately after the treatment. For this purpose, 3 liquids were used, namely, deionized water, ethylene glycol, and diiodomethane. Measurement of contact angles for virgin and plasma treated PVC was made using the Surface Energy

Evaluation (See) System (Brno, Czech Republic).

Absorbance by the samples was evaluated using a FT-IR spectroscopy. Measurements were performed on a Nicolet model 730 FT-IR spectrometer.

The morphology of the surface of the virgin and plasma modified PVC was evaluated using the Tescan Vega II LMU machine at 20.0 kV and 30.00 magnifications. Samples were sliced to 1 cm x 2 cm sizes for the purpose.

After plasma treatment GPX ink series (GPX 90) from Lemmaco Ltd Company of Hungary was used for printing the PVC films at 130 °C using a Baier Gmbh & Co machine. For this purpose, samples of the virgin and plasma treated PVC were cut to 4 cm by 5 cm sizes. Printing was done on one side of the sample only.

The printed PVC films were then evaluated using the Helios Thermo Scientific spectroscopy machine. Spectral images were recorded from 400–700 nm for each set of peels of both samples with intervals of 5 peels, 10 peels, 20 peels and 40 peels until no further change was registered.

Results and discussion

Water contact angle measurements showed a decrease from 85.86 for virgin PVC to 64.85 for plasma treated, which corresponds to a higher hydrophilicity for the plasma treated. This result is consistent with SEM measurements which suggest that the plasma treatment effectively changed the surface morphology and the surface becomes rough after treatment signaling higher hydrophilicity. Also, absorbance measurements by FTIR showed higher intensity for plasma treated samples although absorbance occurred at similar locations for both virgin and treated samples. This fact again points to higher hydrophilicity after treatment correlating well with contact angle and SEM results. The “Tape test” and visible spectroscopy measurements of the printed virgin and plasma treated samples indicated that plasma modification improved adhesion of the ink to the PVC, probably because of its higher hydrophilicity. This suggests that plasma treatment has enhanced the printability of PVC.

The authors would like to express their gratitude for financing of this research to the Ministry of Education, Youth and Sport of the Czech Republic (grant VZ MSM 7088352101). Grant (MPO 2A-ITP1/126) and Scientific Grant Agency of the Ministry of Education and Slovak Academy of Science (grant VEGA 2/7103/27) is also acknowledged.

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P-14

COMPARISON OF THE EFFECT OF VARIOUS NANOFILLERS IN COMPOSITES BASED ON THERMOPLASTIC AND ELASTOMERIC MATRIX

ZUZANA NÓGELLOVÁ^a, PETER KOMADEL^b, JANA HRACHOVÁ^b, and IVAN CHODÁK^a

^a Polymer Institute, Slovak Academy of Sciences, Dúbravská cesta 9, SK-842 36 Bratislava, ^b Institute of Inorganic Chemistry, Slovak Academy of Sciences, Dúbravská cesta 9, SK-845 36 Bratislava, Slovakia
Zuzana.Nogellova@savba.sk

Layered silicates are often used as fillers for improving mechanical properties of composites based on plastics or rubbers. Their effectivity consists in their ability to create intercalated or exfoliated structures. Thus, presence of small amount of clay in plastic or rubber should result in substantial changes in properties of the composite. The effect depends significantly on the appropriate surface modification of the filler, since usually the polymer is hydrophobic while the filler is hydrophilic. The properties of composites should depend on a particle size of the filler as well.

In this work three types of unmodified fillers and one organically modified filler were used. Inorganic fillers included two types of bentonite from Jelšovský potok deposit, Slovakia, with different particle size (Ca-bentonite J10 – below 10 µm and Na-bentonite BJ40 – below 40 µm) and a Japanese Na-montmorillonite Kunipia-F (Kunimine Industries Co., Ltd.). Nanofil 15 (particle size 15 µm) (Süd-Chemie, Germany) with hydrophobic modification of surface was chosen as the organically modified filler. The fillers were added in concentration range up to 10 wt.%. The effectivity of these nanofillers were studied in three various polymeric matrices: low density polyethylene LDPE (Bralen RA 2-19, MFI = 2 g/10 min, Slovnaft, Slovakia) as an apolar thermoplastic polymer, ionomeric copolymer polyethylene-co-acrylic acid (Nucrel HC 1202, DuPont) as polar thermoplastic polymer and elastomeric polymer SBR rubber (Kralex 1500, Kaučuk Kralupy, Czech Republic).

The effect of the fillers was evaluated regarding to mechanical properties of the respective nanocomposites. Examples of the results are shown for tensile strength and for two matrices, namely LDPE and SBR rubber in Fig. 1 and 2. In both thermoplastic matrices tensile strength and elongation at

break slightly decreased with the concentration of the bentonites and Nanofil. Small differences between the fillers were observed. The addition of Kunipia-F resulted in more significant decrease of mechanical parameters considered. In elastomeric matrix (SBR rubber) tensile strength and elongation at break increased with increasing filler concentration, except for Kunipia-F, where only slight effect was observed with rising amount of the filler.

Comparison of relative values of mechanical parameters (values for composites divided by values for matrix without filler) was made. Changes of tensile strength and elongation at break were very similar for both thermoplastic polymers containing all fillers except for nanocomposites filled with Kunipia-F, where relative elongation at break for composites with ionomeric Nucrel showed higher values in comparison with apolar LDPE. Regarding the behaviour in elastomeric matrix (SBR rubber), relative mechanical properties were improved with rising concentration of nanofiller. The best

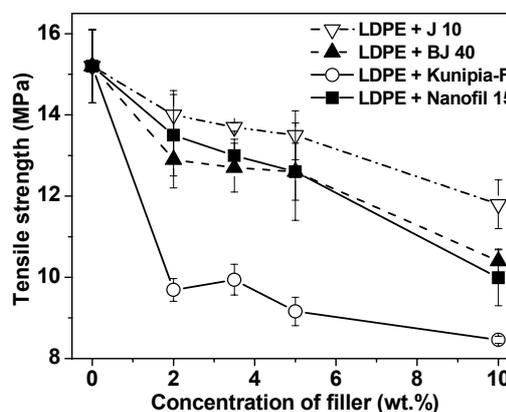


Fig. 1. Tensile strength of composites of LDPE and clay vs. concentration of the filler

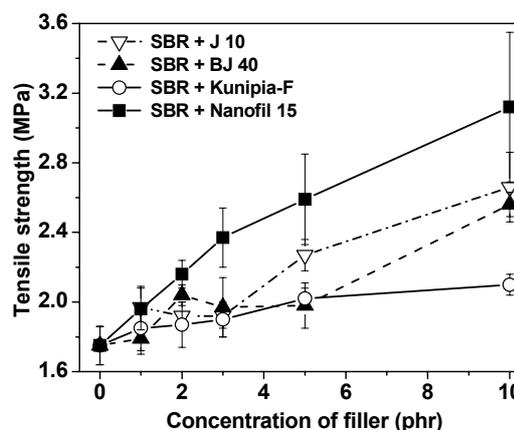


Fig. 2. Tensile strength of composites of SBR and clay vs. concentration of the filler

appeared to be the filler with smaller particle size (10 μm and 15 μm), medium increase of mechanical parameters was achieved for bentonite with particle size below 40 μm and marginal changes were observed in composites filled with Kunipia-F.

The authors acknowledge financial support of the Slovak Research and Development Agency (Grant APVV 51-050505).

P-15
POLYETHYLENE POROUS FILM
FUNCTIONALIZED BY ELECTRICAL DISCHARGE
PLASMA

IGOR NOVÁK^{a}, GALINA ELYASHEVICH^b, IVAN CHODÁK^a, and MILENA ŠPÍRKOVÁ^c**

^a Polymer Institute, Slovak Academy of Sciences, 842 36 Bratislava, Slovakia, ^b Institute of Macromolecular Compounds, Russian Academy of Sciences, 199 004 St. Petersburg, Russian Federation, ^c Institute of Macromolecular Chemistry AS CR, v. v. i., 162 06 Prague, Czech Republic
 upolnovi@savba.sk

The polyethylene porous films (PEPF) were treated by dielectric surface barrier discharge (DSBD) plasma at atmospheric pressure in oxygen (O_2), air or nitrogen (N_2) (ref.¹⁻⁴). The surface energy of films was carried out by direct measurements of contact angles of six testing liquids. The strength of adhesive joints in the system modified polyethylene porous films – polyacrylate was measured by peeling of the joints under the angle of 90° . The significant increase of the surface energy and its polar component of PEPF modified by all types of plasma were observed. The modification of PEPF was performed in static conditions by DSBD plasma in a laboratory reactor. The modification of polymer was carried out in static conditions at atmospheric pressure in N_2 or O_2 of a technical purity.

Measurement of the surface energy of polymer was carried

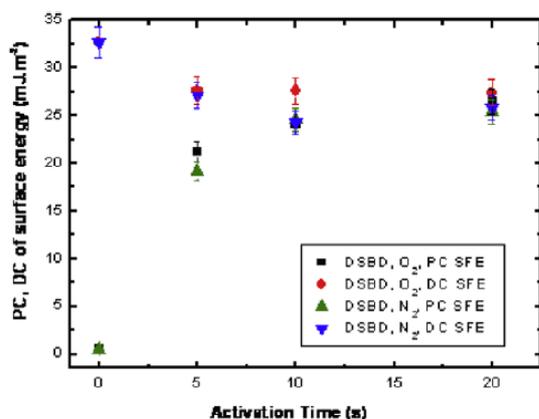


Fig. 1. Polar and dispersive component of the surface energy of PEPF modified by DSBD (50 W) plasma in O_2 , and N_2 vs. time of activation

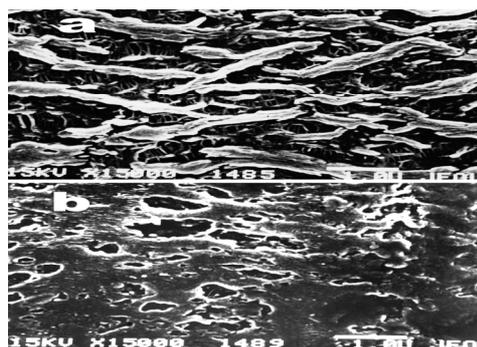


Fig. 2. SEM photographs of the untreated PEPF (a) and this sample after plasma treatment (b)

out by direct measurements of contact angles of testing liquids set⁴ (re-distilled water, ethylene glycol, thiodiglycol, formamide, methylene iodide, and 1-bromonaphthalene using SEE (Surface Energy Evaluation) system (Masaryk Univ, Czech Republik).

The surface energy and its polar component of PEPF modified by DSBD (Fig. 1) plasma increased markedly in comparison with unmodified polymer. The total surface energy of DSBD plasma modified PEPF increased from 33.2 mJ m^{-2} (unmodified sample) up to 51.8 mJ m^{-2} (DSBD, O_2 , 10s) 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.

As it is seen at Fig. 2 the morphology of the film surface is changed after plasma irradiation. First of all, the stresses ties between crystalline regions disappeared, and as a result the shape of pores became more symmetric, more close to round. The pore sizes and number of the pores sharply decreases, and the portion of dense material on the surface increases due to coalescence of crystalline regions.

The significant increase of the surface energy and its polar component of PEPF modified by DSBD plasma in O_2 , N_2 , and in air at atmospheric pressure was observed. This increase was important yet for short times of polymer modification. The morphology of the PEPF film surface was substantially changed due to plasma irradiation, and sizes and number of the pores sharply decreased.

The research was supported by the Slovak Scientific Agency project VEGA, No. 2/7103/27, by the Grant Agency of the Academy of Sciences of the Czech Republic (grant A400500505) and the Russian Foundation for Basic Research (Grant № 07-03-00177).

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