

The Effect of Silanized Bentonite on Rheological Behavior of Polymer Blends

Zuzana Mičicová*, Slavomíra Božeková, Petra Skalková, and Mariana Pajtášová

Department of Material Technologies and Environment, TnUAD of Trenčín, Faculty of Industrial Technologies, Púchov, Slovakia

*Correspondence to:

Zuzana Mičicová

Department of Material Technologies and Environment, TnUAD of Trenčín, Faculty of Industrial Technologies, Púchov, Slovakia

E-mail: zuzana.micicova@tnuni.sk

Received: October 18, 2022

Accepted: December 10, 2022

Published: December 12, 2022

Citation: Mičicová Z, Božeková S, Skalková P, Pajtášová M. 2022. The Effect of Silanized Bentonite on Rheological Behavior of Polymer Blends. *Nanoworld J* 8(3): 85-90.

Copyright: © 2022 Mičicová et al. This is an Open Access article distributed under the terms of the Creative Commons Attribution 4.0 International License (CC-BY) (<http://creativecommons.org/licenses/by/4.0/>) which permits commercial use, including reproduction, adaptation, and distribution of the article provided the original author and source are credited.

Published by United Scientific Group

Abstract

The rheological behavior of filled polymer blends is an ever-expanding field in the polymer industry today. Recently, many studies have been focused on the rheological behavior of filled polymer materials, where the filler affects not only material exploitation characteristics, but essentially determines its fabrication into a final product. The behavior of polymer materials reinforced with fillers need to be understood deeply to clarify the rubber-filler interaction and its effect on rheological behavior of filled rubber blends. Furthermore, using silane, the studies were conducted to achieve better filler dispersion and rubber-filler interaction. The rubber process analyzer stands for a rotational shear rheometer dedicated to the viscoelastic characterization of polymer materials and rubber blends at all stages of manufacturing. The work was focused on the investigation of silanized bentonite effect on rheological behavior of polymer blends. The two types of silanized bentonites were added into polymer blends as a partial replacement of the commonly used filler-carbon black. In this work, a rubber process analyzer was used to determine the changes in the curing characteristics as well as filler-filler and filler-polymer interactions by the Payne effect before and after crosslink formation.

Keywords

Rheological behavior, Bentonite, Silane, Payne effect, Polymer materials

Introduction

The rheological behavior of polymers is one of the important factors influencing the processability and properties of final products. It was reported that the rheological behavior of polymers is strongly dependent on the nature of the polymer, processing conditions and the blend components including the reinforcing filler [1, 2]. Originally, fillers were used to reduce the cost of polymer products. Over time, however, fillers have become an integral part of many applications, especially to improve the mechanical properties of the polymers [3].

In recent years, many studies have dealt with polymer composites containing fillers at the nanometer level with varying degrees of success [3-11]. Due to the size of nanofillers, a large fraction of the atoms can be found on interface, which can lead to strong interfacial interaction if homogeneous dispersion of the nanofillers in the polymer matrix is guaranteed. At higher nanofiller content, composite properties decrease indicating difficulties in dispersing the fillers. It is difficult to disperse nanofillers well in polymers because the particles are easily agglomerated. In addition, hydrophilic nanofillers and hydrophobic polymers are not compatible resulting in poor interfacial interactions [3-5]. To incorporate hydrophilic nanofillers into polymer matrix, surface treatment of the nanofillers with organosilanes is commonly recommended [6]. The final properties of

polymer composites depend on the mixing homogeneity and adhesion between phases. Surface treatment of fillers is a common method that provides practical modification to improve their compatibility with the polymer matrix [7].

For decades, nanocomposites consisting of a polymer matrix and clay minerals have inspired scientists to many potential applications [8-11]. The addition of just a small amount of clay minerals can increase stiffness and strength with minimal loss of ductility and impact resistance, improve abrasion resistance, and reduce permeability and swelling in solvents [3, 12, 13].

Bentonite is one of the most popular clay rocks with exceptional adsorption properties. The main clay mineral present in bentonite is montmorillonite which belongs to the smectite mineral group [14]. Montmorillonite is currently the most widely used clay mineral nanofiller because of its cation-exchange capacity and large active surface area. The thickness of layers is around 1 nm and it has a lateral dimensions which vary up to several microns [15-17]. The particles of montmorillonite have negative charges on their faces due to the isomorphic substitutions in its structure. This negative charge is compensated by the presence of the cations in the interlayer space, which are not fixed and have the character of so called "exchangeable cations" (i.e., Na⁺, K⁺, Li⁺, Mg²⁺, Ca²⁺). It is these special properties of smectite minerals in bentonite that give it an exceptional standing among other clays in terms of its uses [14, 18].

The rubber process analyzer (RPA) is a rheometer designed to measure the shear moduli G' , G'' and G^* of rubber blends under shear deformation. It can be operated with strain and frequency sweeps in wide ranges of strain amplitude and temperature. Rubber blends can be studied in the uncured as well as in the cured state [19]. The Payne effect is an important topic in the investigation of polymer materials viscoelasticity, featured by enormous decay of dynamic modulus with increasing strain amplitude beyond the linear viscoelastic region [20].

This work is focused on the study of the silanized bentonite effect on the rheological properties of polymer blends, where the changes in the curing characteristics as well as filler-filler and filler-polymer interactions by the Payne Effect before and after crosslink formation were evaluated.

Material and Methods

Materials

In this study, the natural bentonite was obtained from a site Stará Kremnička - Jelšový Potok with the particle size below 40 μm . Silane Bis[3-(triethoxysilyl)propyl] tetrasulfide (TESPT) and 3-(Trimethoxysilyl) propyl-methacrylate (TMSPM) used as the coupling agents were purchased from Sigma-Aldrich (Sigma-Aldrich spol. s r.o., Praha, Czech Republic). The elastomer of styrene butadiene rubber (SBR), carbon black (N339), cure activators (ZnO and stearic acid), antidegradants (N,N'-(p-Phenylene)ditoluidine, N,N'-Di-(p-tolyl)-p-phenylenediamine, N-(1,3-Dimethylbutyl)-N'-phenyl-p-phenylenediamine and wax), plasticizer (residual

aromatic extract), and cure system (N-cyclohexylbenzothiazole-2-sulphenamide, 3-Diphenylguanidine and sulfur) were obtained from CMR (CMR s.r.o., Púchov, Slovak republic).

Preparation of modified bentonites

Bentonite was modified with TESPT and TMSPM silane coupling agents. 2 ml of silane coupling agent was added to the 100 ml ethanol:water (4:1) solution. The prepared solution was heated to 60 °C with constant stirring at 450 rpm for 30 min. 5 g bentonite was added to solution and after that, the subsequent stirring process was performed for 30 min. Then it was then filtered and washed with ethanol:water in order to remove excess of silanes. Lastly, modified bentonites were being dried at temperature of 80 ± 5 °C for 180 min.

Preparation of polymer blends

The all ingredients were mixed in a Plasti-Corder Brabender®EC plus (Brabender, Duisburg, Germany) at initial temperature 80 °C and 50 rpm rotor speed, 0.75 fill factor, 20 min mixing time. The synthetic rubber SBR1723 and SBR1500 were mixed for period of 2 min, followed by cure activators addition. Stearic acid was mixed for period of 0.5 min then was followed by addition of zinc oxide for period of 0.5 min. The addition of these ingredients increased the mixing temperature to 90 °C. Subsequently, the carbon black was added and mixed for period of 4 min resulting in a mixing temperature rise to 140 °C. After that, the amine-based antioxidants were added and mixed for period of 1 min. The mixing temperature of the polymer ingredients was decreased to 130 °C. Then, plasticizer was added and mixed further for period of 3 min, resulting in a temperature reduction to 110 °C. Subsequently, cure system was mixed for period of 3 min resulting in a temperature rise to 120 °C. The bentonite (B) and prepared modified bentonites (B-TESPT, B-TMSPM) were added into the polymer blend, replacing the carbon black in an amount of 5 phr.

Characterization of rubber-filler and filler-filler interactions in polymer blends

Rheological behaviors of the polymer blends under sinusoidal shear deformation were studied on a rubber process analyzer (PRPA 2000) (Alfa Technologies, Akron, OH, USA). The cure behaviors were carried out at 160 °C, at a constant frequency of 1.67 Hz, according to ASTM D 5289. The weight of used sample was approximately 6 g. The rheometric parameters: minimum torque (M_L), maximum torque (M_H), increment of elastic torque ($\Delta M = M_H - M_L$), the optimum curing period (t_{90}), pre-curing time (t_s), were calculated on the basis of the curing curve. Cure rates (R_v) was calculated, using:

$$R_v = 100 / (t_{90} - t_s) \quad (1)$$

where t_{90} is the optimum curing period and t_s is the pre-curing time.

The silanization reaction efficiency of the polymer blends was measured, using the PRPA 2000 instrument at the test temperature of 100 °C, at the frequency of 1.67 Hz and at the strain range of (1-450)%.

The Payne effect (filler-filler interaction) of the prepared polymer blends was analyzed by using a Rubber Process Analyzer (PRPA 2000) in the range between 0.28 and 100.02% at frequency of 1 Hz before and after the curing process at 70°C. Payne effect calculated by the difference between the dynamic storage modulus at 0.28% and at 100.02% strain, using equation 2.

$$\Delta G' = G'_{0.28\%} - G'_{100.02\%} \quad (2)$$

where $G'_{0.28\%}$ is the storage modulus value determined under deformation of 0.28% and $G'_{100.02\%}$ is the storage modulus value determined under deformation of 100.02%.

Results and Discussion

Curing behaviors

Characterization of the rheometric measurements of the polymer blends reveals the impact of the studied modified bentonites on the properties of the final vulcanizates and the tendency of the nanofillers to interact (to form a network in the polymer). The curing parameters are presented in table 1 and the curing curves of polymer blends are shown in figure 1.

The values of minimum torque (M_L) decreased for all blends compared to the SBR blend. The minimum torque (M_L) corresponded to filler-filler inter agglomeration in the polymer system [21]. The lower M_L value, indicative of weaker filler-filler interaction, results in lower viscosity of the blend. In the case of maximum torque (M_H), almost all the polymer blends exhibited higher values in compared to the SBR blend, indicating higher stiffness of the polymer blends. The higher M_H values indicative good interfacial adhesion between polymer matrix and filler [13]. The increment of elastic torque ΔM (Figure 2) which indicates the extent of crosslinking, shows a similar trend to the M_H . In the case of SBR/B-TESPT polymer blend, the lower value for ΔM (cross-link density) was observed.

In the case of the pre-curing time (t_s), SBR/B-TMSPM polymer blend show the lower values, compared with the reference rubber blend, indicating the improved filler distribution and formation of three-dimensional filler networks in the polymer matrix [22]. The optimum curing period (t_{90}) of the SBR/B-TMSPM polymer blend shows lower values than that of the SBR/B-TESPT polymer blend. The cure rates (Figure 3) of the SBR/B-TESPT polymer blend show the lower values than that the SBR polymer blend.

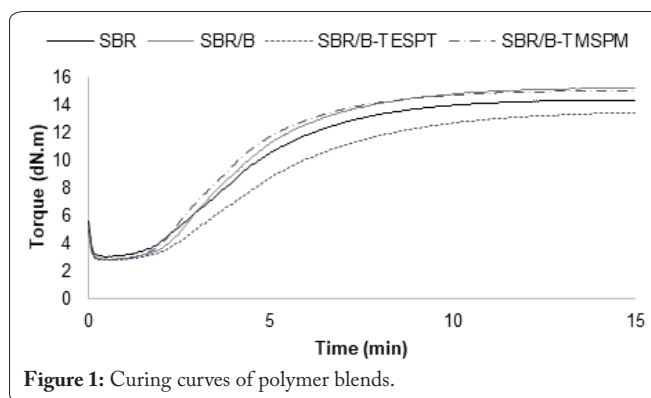


Figure 1: Curing curves of polymer blends.

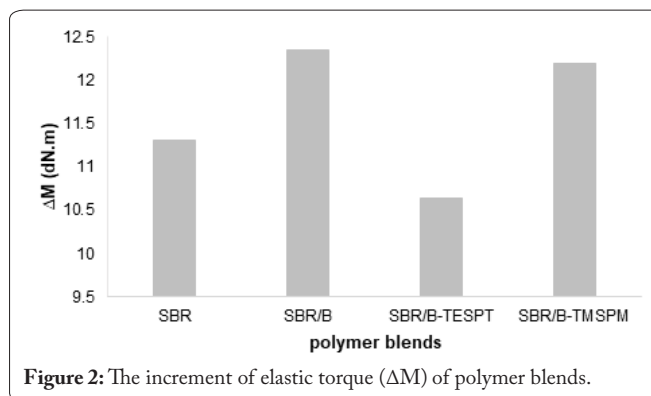


Figure 2: The increment of elastic torque (ΔM) of polymer blends.

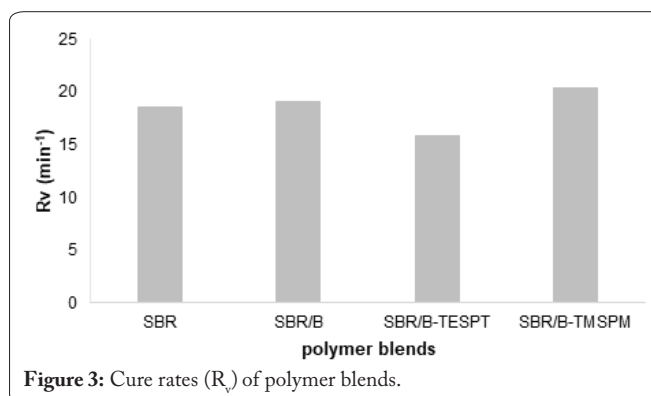


Figure 3: Cure rates (R_v) of polymer blends.

The silanization reaction efficiency

The storage shear modulus at low strain correlates with the filler-filler interaction efficiency, where elastic moment (G') was recorded. The storage shear modulus at high strain an indicator of silane degradation, where torque moment (S') was recorded [23]. The measured elastic and torque moment values of the polymer blends are shown in table 2, and the dependence of storage shear modulus on strain for the polymer blends can be seen in figure 4.

Table 1: Curing parameters of polymer blends.

Polymer blends	M_L (dN.m)	M_H (dN.m)	ΔM (dN.m)	t_s (min)	t_{90} (min)	R_v (min ⁻¹)
SBR	3.05	14.35	11.30	2.43	7.83	18.52
SBR/B	2.85	15.20	12.35	2.52	7.77	19.05
SBR/B-TESPT	2.78	13.42	10.64	2.84	9.15	15.85
SBR/B-TMSPM	2.81	15.00	12.19	2.29	7.19	20.41

Table 2: Values of G' and S' of polymer blends.

Polymer blends	G' (1%)	S' (450%)
SBR/B-TESPT	296.67	13.78
SBR/B-TMSPM	316.60	14.07

The SBR/B-TESPT polymer blend showed the lowest value of the modulus of elasticity (Figure 4) indicates good silane-filler reaction, indicating lower filler-filler interaction. But at high strains similar S' values are observed for both polymer blends.

Payne effect

The incorporation of filler into the polymer leads to an increase in the torque modulus due to the formation of a secondary structure filler in the polymer. The viscoelastic properties of polymer blends filled with nanofillers are strongly dependent on the size of the dispersed filler phase and its distribution throughout the polymer matrix. Viscoelastic properties were also used to determine the changes of filler-filler interactions in the polymer blends. The strain amplitude dependence of storage modulus (G') for prepared polymer blends is shown in figure 5.

A decrease of storage modulus with increasing strain for filler-reinforced polymer blends was due to filler network breakdown, weakening of bonding between secondary filler aggregates, and slip of the rubber chains on the filler surface [24, 25]. Comparison of the curves of the filled polymer blends displays the differences in values of torque modulus. The modification of the bentonite surface with silanes can makes the surface more hydrophobic and therefore more compatible with the rubber matrix. This reduces the filler-filler interaction strongly and results in a much lower Payne-effect [19]. As can be seen from figure 5, the SBR/B-TESPT polymer blend has a significantly lower G' value at low strains, due to the lower filler-filler interactions. In the case of the SBR/B-TMSPM rubber blend sample, there is the higher torque modulus, indicating the more powerful filler-filler interactions.

The Payne effect depends on a filler-filler interaction and on the degree of dispersion of the filler particles. The greater the strength of these interactions, the stronger the secondary structure. If the value of the Payne effect is higher, the filler has a clustered distribution of agglomerates and aggregates. At a lower value of the Payne effect, the fillers are well dispersed in

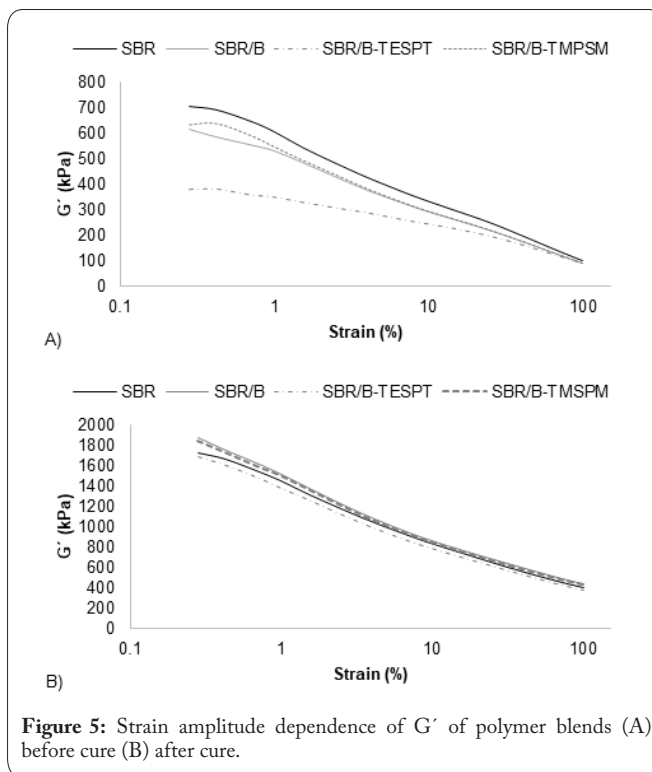


Figure 5: Strain amplitude dependence of G' of polymer blends (A) before cure (B) after cure.

the polymer matrix [26]. The calculated values of the Payne effect are shown in the table 3 and graphically shows on the figure 6.

The calculated values of the Payne effect on polymer blends before cure show the opposite behavior to that on blends after cure (Figure 6). The except for the SBR/B-TESPT which reaches the lowest of values for $\Delta G'$ in comparison with the other polymer blends. In the case of the SBR/B-TMSPM polymer blend, the value of Payne effect before cure was lower and after cure the value of Payne effect was higher compared to SBR polymer blend.

Conclusion

In this work, the effect of silanized bentonite on the rheological behavior of the polymer was investigated. Bis[3-(triethoxysilyl)propyl]tetrasulfide silane (TESPT) and 3-(trimethoxysilyl)propyl methacrylate (TMSPM) were used to modify the bentonite filler. Rubber Process Analyzer (PRPA 2000) was used to determine changes in curing char-

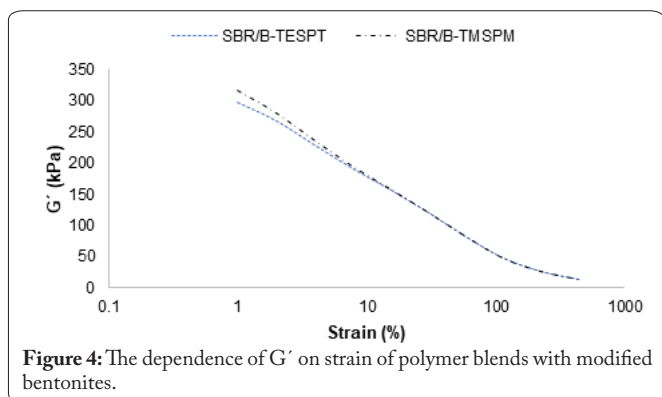


Figure 4: The dependence of G' on strain of polymer blends with modified bentonites.

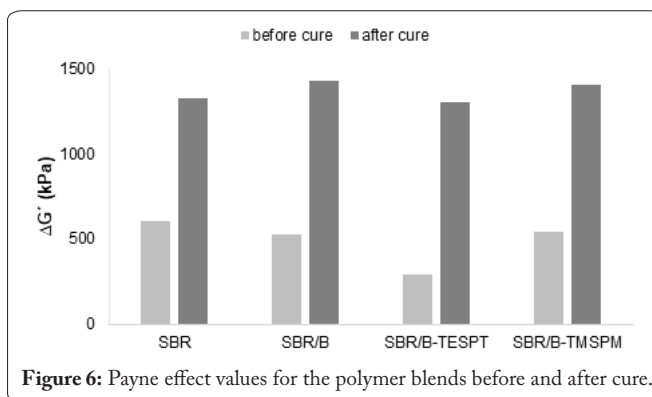


Figure 6: Payne effect values for the polymer blends before and after cure.

Table 3: Payne effect values of the polymer blends.

Polymer blends	Before cure			After cure		
	$G'_{0.28\%}$ (kPa)	$G'_{100.02\%}$ (kPa)	ΔG (kPa)	$G'_{0.28\%}$ (kPa)	$G'_{100.02\%}$ (kPa)	$\Delta G'$ (kPa)
SBR	703.97	100.92	603.05	1720.74	397.20	1323.54
SBR/B	616.69	91.30	525.39	1873.76	442.91	1430.85
SBR/B-TESPT	378.86	90.56	288.10	1680.89	379.97	1300.92
SBR/B-TMSPM	631.13	91.47	539.66	1836.69	434.67	1402.02

acteristics as well as filler-filler and filler-polymer interactions using the Payne effect. From the measured rheometric parameters it can be concluded that the SBR/B-TESPT blend is indicative of a weaker filler-filler interaction. In the case of the SBR/B-TMSPM polymer blend, the measured rheometric parameter results indicate better filler distribution and formation of three-dimensional filler networks in the polymer matrix. In the case of the silanization reaction efficiency, the SBR/B-TESPT polymer blend had the low value of the elastic modulus indicates a good silane-filler reaction, indicating a lower filler-filler interaction. For the Payne effect, the SBR/B-TESPT polymer blend exhibited a lower G' value at low strains, indicating a lower filler-filler interaction. The SBR/B-TMSPM polymer blend showed a higher G' value, indicating a stronger filler-filler interactions to contribute to their physically bound rubber. The partial replacement for the modified filler in the SBR/B-TMSPM polymer blend resulted in a significant improvement in rheological behavior.

Acknowledgements

This research work has been supported by the Operational Program Integrated Infrastructure, co-financed by the European Regional Development Fund by the project: Advancement and support of R&D for “Centre for diagnostics and quality testing of materials” in the domains of the RIS3 SK specialization, Acronym: CEDITEK II., ITMS2014+ code 313011W442.

References

- Phewthongin N, Saeoui P, Sirisinha C. 2006. Comparison of viscoelastic behaviour in silica filled cured and uncured cpe/nr blends with various mixing time. *Appl Rheol* 16(4): 182-189. <https://doi.org/10.1515/arh-2006-0012>
- Hui S, Chaki TK, Chattopadhyay S. 2008. Effect of silica-based nanofillers on the properties of a low-density polyethylene/ethylene vinyl acetate copolymer based thermoplastic elastomer. *J Appl Polym Sci* 110(2): 825-836. <https://doi.org/10.1002/app.28537>
- Bhattacharya M. 2016. Polymer nanocomposites - a comparison between carbon nanotubes, graphene, and clay as nanofillers. *Materials (Basel)* 9(4): 262. <https://doi.org/10.3390/ma9040262>
- Rong MZ, Zhang MQ, Ruan WH. 2006. Surface modification of nanoscale fillers for improving properties of polymer nanocomposites: a review. *Mater Sci and Technol* 22(7): 787-796. <https://doi.org/10.1179/174328406X101247>
- Clarizia G, Bernardo P. 2022. A review of the recent progress in the development of nanocomposites based on poly(ether-block-amide) copolymers as membranes for CO_2 separation. *Polymers* 14(1): 10. <https://doi.org/10.3390/polym14010010>
- Dolatzadeh F, Moradian S, Jalili MM. 2011. Influence of various surface treated silica nanoparticles on the electrochemical properties of SiO_2 /polyurethane nanocoatings. *Corros Sci* 53(12): 4248-4257. <https://doi.org/10.1016/j.corsci.2011.08.036>
- Elkawash H, Tirkas S, Hacıoglu F, Tayfun U. 2020. Physical and mechanical performance of bentonite and barite loaded low density polyethylene composites: influence of surface silanization of minerals. *J Compos Mater* 54(28): 4359-4368. <https://doi.org/10.1177/0021998320931906>
- Arroyo M, Lopez-Manchado MA, Herrero B. 2003. Organo-montmorillonite as substitute of carbon black in natural rubber compounds. *Polymer* 44(8): 2447-2453. [https://doi.org/10.1016/S0032-3861\(03\)00090-9](https://doi.org/10.1016/S0032-3861(03)00090-9)
- Usuki A, Tukigase A, Kato M. 2002. Preparation and properties of EPDM-clay hybrids. *Polymer* 43(8): 2185-2189. [https://doi.org/10.1016/S0032-3861\(02\)00013-7](https://doi.org/10.1016/S0032-3861(02)00013-7)
- Vu YT, Mark JE, Pham LH, Engelhardt M. 2001. Clay nanolayer reinforcement of cis-1, 4-polyisoprene and epoxidized natural rubber. *J Appl Polym Sci* 82(6): 1391-1403. <https://doi.org/10.1002/app.1976>
- Chang YW, Yang Y, Ryu S, Nah C. 2002. Preparation and properties of EPDM/organomontmorillonite hybrid nanocomposites. *Polym Int* 51(4): 319-324. <https://doi.org/10.1002/pi.831>
- Arroyo M, López-Manchado MA, Valentin JL, Carretero J. 2007. Morphology/behaviour relationship of nanocomposites based on natural rubber/epoxidized natural rubber blends. *Compos Sci Technol* 67(7-8): 1330-1339. <https://doi.org/10.1016/j.compscitech.2006.09.019>
- Ge X, Li MC, Li XX, Cho UR. 2015. Effects of silane coupling agents on the properties of bentonite/nitrile butadiene rubber nanocomposites synthesized by a novel green method. *Appl Clay Sci* 118: 265-275. <https://doi.org/10.1016/j.clay.2015.10.003>
- Schütz T, Dolinská S, Mockoviáková A. 2013. Characterization of bentonite modified by manganese oxides. *Universal Journal of Geoscience* 1(2): 114 - 119. <https://doi.org/10.13189/ujg.2013.010211>
- Hrachová J, Komadel P, Chodák I. 2009. Natural rubber nanocomposites with organo-modified bentonite. *Clays Clay Miner* 57(4): 444-451. <https://doi.org/10.1346/CCMN.2009.0570405>
- Ismail H, Mathialagan M. 2011. Curing characteristics, morphological, tensile and thermal properties of bentonite-filled ethylene-propylene-diene monomer (EPDM) composites. *Polym Plast Technol Eng* 50(14): 1421-1428. <https://doi.org/10.1080/03602559.2011.584244>
- Mittal V. 2007. Esterification reactions on the surface of layered silicate clay platelets. *J Colloid Interface Sci* 315(1): 135-141. <https://doi.org/10.1016/j.jcis.2007.06.031>
- Alexandre M, Dubois P. 2000. Polymer-layered silicate nanocomposites: preparation, properties and uses of a new class of materials. *Mater Sci Eng R Rep* 28(1-2): 1-63. [https://doi.org/10.1016/S0927-796X\(00\)00012-7](https://doi.org/10.1016/S0927-796X(00)00012-7)
- Luginsland HD, Fröhlich J, Wehmeier A. 2002. Influence of different silanes on the reinforcement of silica-filled rubber compounds. *Rubber Chemistry and Technology* 75(4): 563-579. <https://doi.org/10.5254/1.3544984>

20. Zhao A, Shi XY, Sun SH, Zhang HM, Zuo M, et al. 2020. Insights into the Payne effect of carbon black filled styrene-butadiene rubber compounds. *Chin J Polym Sci* 39: 81–90. <https://doi.org/10.1007/s10118-020-2462-2>
21. Szadkowski B, Marzec A, Rybiński P. 2020. Silane treatment as an effective way of improving the reinforcing activity of carbon nanofibers in nitrile rubber composites. *Materials (Basel)* 13(16): 3481. <https://doi.org/10.3390/ma13163481>
22. Nakamontri Y, Kummerloewe C, Vennemann N, Wisunthorn S, Pichaiyut S, et al. 2018. Effect of bis(triethoxysilylpropyl) tetrasulfide (TESPT) on properties of carbon nanotubes and conductive carbon black hybrid filler filled natural rubber nanocomposites. *Express Polym Lett* 12(10): 867–884. <https://doi.org/10.3144/expresspolymlett.2018.75>
23. Wilczynski O, Richard P. 2008. RPA 2000 - a universal tool for the rubber industry. *Plastics and Rubber* 45(11-12): 326-334.
24. Hayichelach C, Reuvekamp LAEM, Dierkes WK, Blume A, Noordermeer JWM, et al. 2018. Enhancing the silanization reaction of the silica-silane system by different amines in model and practical silica-filled natural rubber compounds. *Polymers (Basel)* 10(6): 584. <https://doi.org/10.3390/polym10060584>
25. Sarkawi SS, Dierkes WK, Noordermeer JWM. 2014. Elucidation of filler-to-filler and filler-to-rubber interactions in silica-reinforced natural rubber by TEM network visualization. *Eur Polym J* 54: 118–127. <https://doi.org/10.1016/j.eurpolymj.2014.02.015>
26. Miedzianowska J, Masłowski M, Strzelec K. 2020. Thermoplastic elastomeric composites filled with lignocellulose bioadditives. part 1: morphology, processing, thermal and rheological properties. *Materials (Basel)* 13(7): 1598. <https://doi.org/10.3390/ma13071598>