PREPARATION OF ELASTOMERIC COMPOSITES FILLED WITH MODIFIED CELLULOSE AND STUDY THEIR PROPERTIES

Petra Skalková[1*], Iveta Papučová[1], Ivan Labaj[1], Jana Pagáčová[1], Darina Ondrušová[1], Katarína Znášiková[2], Jana Dobrovská[3]

[1] Alexander Dubček University of Trenčín, Faculty of Industrial Technologies, I. Krasku 491/30, 020 01 Púchov, Slovak Republic

[2] GREENCEL, Ltd., Hencovská 2073, 093 02 Hencovce, Slovak Republic

[3] Faculty of Materials Science and Technology, Technical University of Ostrava, 17. listopadu 2172/15, 708 00, Czech Republic

Abstract

Natural polymers are one of the alternative options and are gaining more and more prominence in various fields of application. The main advantage of natural polymers is their biodegradability and the ability to obtain them from available natural sources. Research into new possibilities for the use of natural polymers in elastomeric composites is still ongoing in the rubber industry. One of the biopolymers often used as a filler in elastomeric composites is cellulose [1- 4]. This work is focused on preparing elastomeric composites filled with cellulose, which was modified chemically with SiO_2 (CEL_{sil}) and physically with plasma (CEL_{plasma}). Impact of physically modified cellulose as a filler was studied on thermal properties of elastomer composites. Natural rubber (NR) composites with different amount (30; 35; 40; 45; 50 and 55 phr) of cellulose (CEL) were prepared. On prepared composites thermal properties were studied. Physical-chemical properties were evaluated, too.

Keywords: *cellulose, thermal properties, elastomer composites, plasma, silanization, structural properties*

1. INTRODUCTION

Due to the development of biodegradable materials, blending of natural rubber with biopolymers has become very attractive. In addition to reducing the cost of the material itself, they also have generally useful properties such as biocompatibility, biodegradability and extensive use [1, 2]. To improve strength and stiffness, fibrous materials, both natural and synthetic, are added to the polymeric materials. They are added as fillers or reinforcements. Due to their high strength and stiffness, glass, carbon and talc are also often used as fillers in polymer composites. However, these are non-recyclable and non-biodegradable. Initial processing requires high costs and is also accompanied by health risks. Another problem is the high energy consumption when using them. Therefore, more attention is now being paid to the use of natural fillers [3, 4, 5].

NR is used in the manufacture of tires and in a wide range of applications in engineering, medicine, sports and households. Mainly for its excellent properties, which are better than the properties of synthetic polyisoprene. Natural rubber in its uncured form has low strength and has only limited applications. Vulcanization, a chemical process where long chains of rubber molecules are cross-linked, transforms the material into a strong elastic product with reversible deformability, good mechanical properties, excellent dynamic properties and fatigue resistance. As a result, NR has become an essential component of a number of products with a huge range of uses [6].

Natural polymers are relatively inexpensive, biodegradable, degradable and renewable. Compared to inorganic fillers, they have a lower density and more favorable mechanical properties. The disadvantage is the poor compatibility between the hydrophobic polymer particles and the hydrophilic fillers, which results in poor interfacial adhesion. In practice, chemical modification of fillers is used to improve interfacial adhesion, which directly affects their structure and composition [7]. Cellulose is a biopolymer composed of β-D-glucopyranose units linearly linked at positions 1-4. Thus, cellulose is a

homopolysaccharide, in contrast to pulp, which is formed by delignification of wood and, in addition to cellulose, also contains hemicelluloses, lignin residues and other substances [8, 9]. The cellulose macromolecule contains more than a thousand building blocks β-D-glucopyranose. Unlike starch and glycogen, there is a β-glycoside bond between them. A chain is formed which has the character of a long unbranched fiber in the natural material. Cellulose is the main building block of plant cells and, together with lignin, is involved in the construction of secondary cell walls. In some plants pure pulp (cotton) is formed, in other cases, e.g., in wood is accompanied by other substances: lignin, hemicellulose and resins. Cellulose is the most widely used biopolymer [10].

The main disadvantages of using natural fibers are their high rate of moisture absorption and poor dimensional stability. Due to the presence of hydroxyl groups and the hydrophilic nature of natural fibers, there is no effective interaction with the hydrophobic matrix. Therefore, natural fibers must be modified by chemical or physical treatments, or a combination thereof. By surface treatment of fibers, we can increase the adhesion of natural fibers to the polymer matrix. By chemical treatment we obtain dimensional stability of the composite and increase in tensile strength. The most common substances used for fiber modification are alkali metal salts, silanes, peroxide, isocyanate, stearic acid, sodium chloride and the like. The substances used are mostly toxic and have a negative impact on the environment, which complicates their actual disposal. Silanization transforms the amphiphilic cellulose to a hydrophobic/oleophilic surface with functionalization of the fibrils. Several approaches can be used, one of them being the use of silicon derivatives with vapor deposition of silanes or impregnation in silane solutions [4, 11].

In recent years, more environmentally friendly methods have been investigated, in which the surface of natural fibers (hemp, sisal, flax) is treated with plasma. We know two types of plasma, namely corona discharge at atmospheric pressure and high frequency cooled plasma. The surface energy of lignocellulosic fibers remains practically constant, even with increasing coating time, with the exception of fiber abaca. Examination of the plasma-treated cellulose surface revealed that the hydrophobic character of the cellulose had completely disappeared [12, 13].

The work deals with the study of the thermal and structural properties of elastomeric composites. To prepare the elastomer composite, natural rubber was used, into which the selected type of filler was mixed. Cellulose in modified (CEL_{sil}, CEL_{plasma}) form was used as filler. The selected type of filler and its amount in the composite significantly affects the properties of the composite.

2. MATERIALS AND METHODS

2.1. Materials

Natural rubber SMR 10 (NR) was purchased from Kuala Lumphur Malaizia. Greencel GW 70, cellulose fibres – Cellulose (CEL) 99.5 %, bulk density 90-110 $g.cm^{-3}$ and Greencel GW 70/5 cellulose fibres – Cellulose (CEL_{sil}) 99.0 %, bulk density 90-110 $g.cm^{-3}$ were supplied from Bukóza Invest, Ltd. Slovak Republic.

2.2. Methods

2.2.1. Plasma modification of cellulose

The plasma modification was performed on a flat electrode of a KPR 200 mm plasma reactor. The reactor power was set at 350 W, the plasma exposure time was 4 minutes/sample surface. The surface of the sample was approximately distant from the surface of the electrode 0.25 mm. During the modification, gentle shifts were made with the sample in order to homogeneously strike the surface generated by the plasma. From the observation with a thermal imager, the temperature of the cellulose during the modification was found to be approximately 75 °C. The modification was performed under laboratory conditions at a temperature of 19 °C and an air humidity of 25%.

2.2.2. Preparation of NR composites

Two types of cellulose were melt-blended with NR in Brabender Plasti – Corder PLE 331 (Brabender GmbH&Co. KG, Germany). Mixing was performed at 80 and 90 °C and 50 rpm. The contents of CEL_{plasma} or CEL_{sil} were from 0 to 55 parts per hundred rubbers (phr), respectively. Composites were vulcanized with the following formula: stearic acid, ZnO, Flavex, N-tert-Butyl-2-benzothiazolesulfenamide and sulphur. The temperature of vulcanization was 150 °C.

2.2.3. FT-IR measurements

FT-IR spectra were acquired in NICOLET iS 50 FT-IR spectrometer (ThermoFisher Scientific, USA) using ATR technique with 4 cm^{-1} resolutions, and an OMNIC 3.2 software. After being placed in the instrument, a diamond crystal was pressed onto the surface of the sample, by means of which the FTIR spectra were measured.

2.2.4. Thermal characterization

The thermal stability of the composites was studied using a TGA/DSC2 STARe System from METTLER TOLEDO. The weight of the samples ranged from 10 to 30 mg. The test temperature range ranged from 30 °C to 600 °C and the heating rate was 10 °C.min^{-1}. Nitrogen was used as a protective atmosphere in the test.

3. RESULTS AND DISCUSSION

3.1. FTIR spectral analysis

The Fig. 1 shows the IR spectra of cellulose fillers modified with silanization (CEL_{sil}) and plasma (CEL_{plasma}) as well as the unmodified (pure) cellulose (CEL). The spectra of all celluloses exhibit the broad band in the range of 3500–3200 cm^{-1} (with maximum around 3338 cm^{-1}) which corresponds to the stretching vibration of the O–H groups in cellulose [14, 15, 16, 17, 18]. For silanized cellulose as well as cellulose modified with plasma, the relative intensity of mentioned band is the higher in comparison with pure cellulose. The similar founding was observed in [19] for cellulose silanized with methyltrimethoxysilane. In the spectra region from 3000 to 2800 cm^{-1}, the bands around 2895 and 2870 cm^{-1} correspond to the methylene C–H asymmetric and symmetric stretching vibration, respectively [14, 16, 17, 18]. In comparison with pure cellulose, the relative intensities of given two bands are higher for silanized cellulose as well as cellulose modified with plasma. The band between 1800 and 1600 cm^{-1} may be associated with stretching vibration of C=O from carbonyl group [18] or corresponds to the O–H bending of the adsorbed water in cellulose (peak at 1637 cm^{-1}) [14, 17, 18]. The band at 1428 cm^{-1} is attributed to in-plane O–H bending in cellulose.

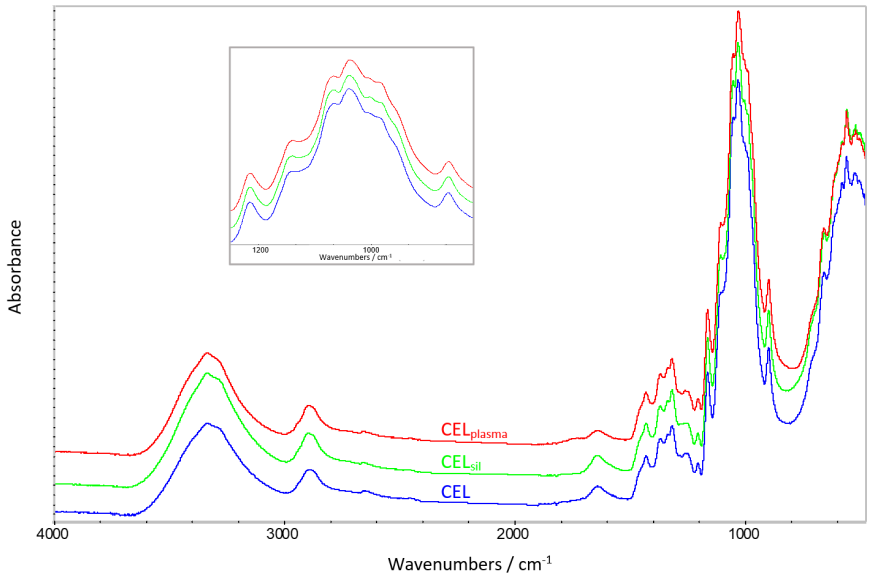

Fig. 1. IR spectra of unmodified (pure) cellulose (CEL), silanized cellulose (CEL$_{sil}$) and cellulose modified with plasma (CEL$_{plasma}$).

The bands at 1335 and 1315 cm^{-1} are assigned to the bending of hydroxyl group –OH in cellulose [16, 20]. The peaks observed at 1160, 1105 and 1027 cm^{-1} are due to the C–C ring stretching, the C–O–C glycosidic ether and the C–O–C stretching vibration in the pyranose ring, respectively [14, 17, 18]. In spectral range of 1200–800 cm^{-1}, the relative intensities of bands (mainly at 1005, 1050, 1001, 985 and 896 cm^{-1}) are the higher for silanized cellulose in comparison with pure cellulose (the zoomed area in the Fig. 1). Mentioned fact confirms that the cellulose was modified by silanes because the bands at 1050 cm^{-1} corresponds to the asymmetric stretching vibration of the Si–O–Si silane group (overlapping with C–O vibrations) [19]. The silanization of cellulose can be also confirmed by the higher relative intensity of the broad shoulder of around 950 cm^{-1} which corresponds to the Si–OH vibration [21]. In spectrum of cellulose modified with plasma, the new broad band around 1727 cm^{-1} was observed in comparison with pure cellulose or silanized cellulose. According the [22, 23], this band appears after plasma treating of cellulose and corresponds to the asymmetric stretching vibration of the C=O groups (aldehydes and ketones).

FTIR spectra of NR composites filled with different amount of modified celluloses are shown in the Fig. 2 for NR/CEL$_{plasma}$ composites and Fig. 3 for NR/CEL$_{sil}$ composites. In both spectra of NR/CEL composites, there are the characteristic peaks for NR. The peak at 2960 cm^{-1} attributes to the stretching vibrations of CH_3. The peaks at 2923 and 2850 cm^{-1} correspond to asymmetric and symmetric stretching vibrations of CH_2 [14, 24]. The absorption band at 1662 cm^{-1} attributes to the C=C stretching vibration [24, 25]. The absorption peak at 1447 cm^{-1} is feature of CH_2 deformation [14, 24, 25]. The bands at 1375 and 1360 cm^{-1} correspond to the CH_3 asymmetric deformation [24], but some authors [26] assigned the band at 1360 cm^{-1} to the group of cis –C(CH_3)=CH–. The vibration peaks observed at 1310 and 890 cm^{-1} are due to the CH_2 and CH_3 wagging vibrations, respectively. The peaks detected at 1038 and 740 cm^{-1} are attributed to the CH_3 and CH_2 rocking vibrations, respectively. Others peaks can be attributed by the following: the peak detected at 1662 cm^{-1} is due to the C=C stretching, the peak at 1127 cm^{-1} is due to the C–C stretching, the peak at 1083 cm^{-1} is due to the CH_2 twisting, the peak at 835 cm^{-1} is due to the =CH out-of-plane bending, and the peak at 570 cm^{-1} is related to the C–C–C deformation [24]. Natural rubber cis-isomer configurations can be observed at 765–744 cm^{-1}. The bands in the range of 1485–1340 cm^{-1} are attributed to the amide (–NH_2) groups produced by the accelerated sulphur curing systems due to the use of TBBS as the accelerator [25].

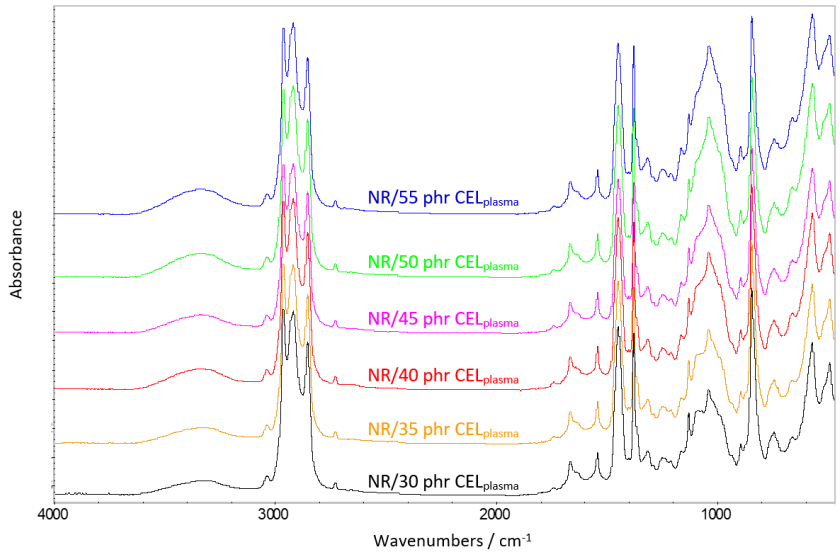

Fig. 2. IR spectra of NR composites filled with different amount of cellulose modified with plasma (CEL_{plasma}).

For NR/CEL_{plasma} composites, there is the gradual increase in the relative intensity of peaks of the composites with the increase in amount of plasma modified cellulose (Fig. 2). The intensity of peaks, which are characteristic for cellulose, was increased mainly in the ranges of 3500–3200 cm^{-1} as well as 1100–950 cm^{-1}, and below of 700 cm^{-1}. Besides mentioned spectral ranges, the intensity of some peaks was also increased for peak at 1315, 1160 and 890 cm^{-1}. With increasing amount of CEL_{plasma} filler in composite, there was observed the little decrease in the intensity of some peaks for NR, e.g., at 2960, 1125, 739 cm^{-1} which was expected. For NR/CEL_{sil} composites, there is also the increase in the relative intensity of peaks of the composites with the increase in amount of silanized cellulose (Fig. 3) but the mentioned increase is not so gradual as it was in the case of composites filled with plasma modified cellulose. When the amount of CEL_{sil} was increased, the intensity of the broad band in the range of 3500–3200 cm^{-1} increased as well as the intensity of peaks at 1160, 1104 and 897 cm^{-1} increased. According to the spectra behaviour as well as the increase of peak intensity, the spectra of NR/CEL_{sil} composites can be divided into three groups. The first group consists of the NR/30 phr CEL_{sil} and NR/35 phr CEL_{sil} composites, the second group contains the NR/40 phr CEL_{sil} and NR/55 phr CEL_{sil} composites, and the third group consists of the NR/45 phr CEL_{sil} and NR/50 phr CEL_{sil} composites. When the amount of CEL_{sil} increases, the intensity of given peaks increases from the first group to the third group.

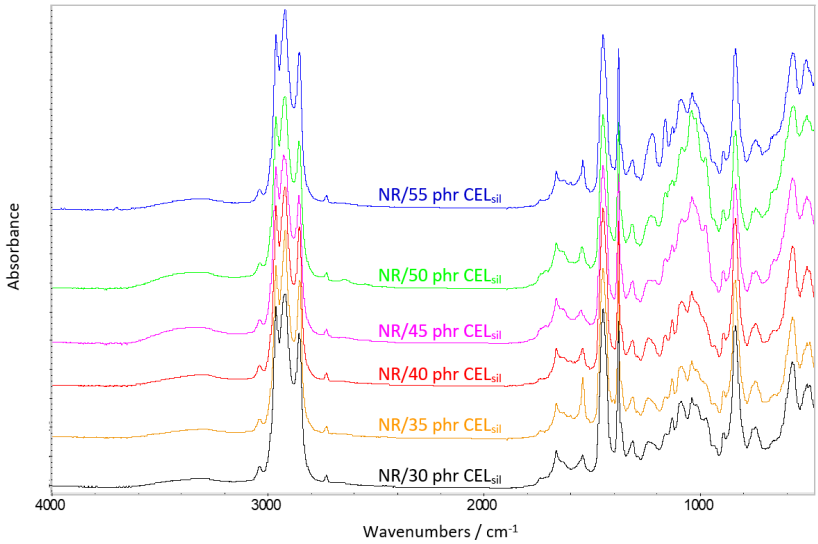

Fig. 3. IR spectra of NR composites filled with different amount of silanized cellulose (CEL_{sil}).

3.2. Thermal stability

Thermal properties were studied on NR/CEL_{plasma} and NR/CEL_{sil} composites. The difference between the TG curves of NR/CEL_{plasma} composites is negligible (Fig. 4). The thermal decomposition of the samples started at 300 °C, which roughly corresponds to the thermal decomposition of the cellulose. Cellulose decomposition is characterized by a two-step reaction presented by DTG peaks. The initial weight loss occurs from 30 °C to 120 °C, and it is associated with water loss weight. This loss presenting a negligible moisture content. Weight loss below 120 °C corresponds to the evaporation of adsorbed water (moisture) [27]. Weight loss is observed at 300 °C, which corresponds to the initial decomposition temperature of the CEL_{plasma} filler. The polymer chain depolymerization causes weight loss in this stage [27]. In good agreement with previous findings [28, 29], cellulose begin to degrade at lower temperatures than the polymer (NR). At a temperature of about 350 °C, the decomposition of natural rubber began. The decomposition of the double bonds of the methylene groups in the polyisoprene molecule occurs at a temperature of 380 °C. The last weight loss is observed at a temperature of 410 °C, which corresponds to the carbonization of natural rubber. The composites reached the maximum weight loss at a temperature of approximately 380 ° C.

For NR CEL_{sil} composites (Fig. 5) we observe the initial decomposition temperature at 300 °C. The weight loss and the overall course of thermal decomposition are almost the same for all samples. In the sample of silanized cellulose CEL_{sil} we can see a slightly lower weight loss in the dehydration of cellulose on the curve of cellulose treated by plasma. This indicates the effect of plasma modification on the binding of water by cellulose. Both types of cellulose reached an initial decomposition temperature of 290 °C.

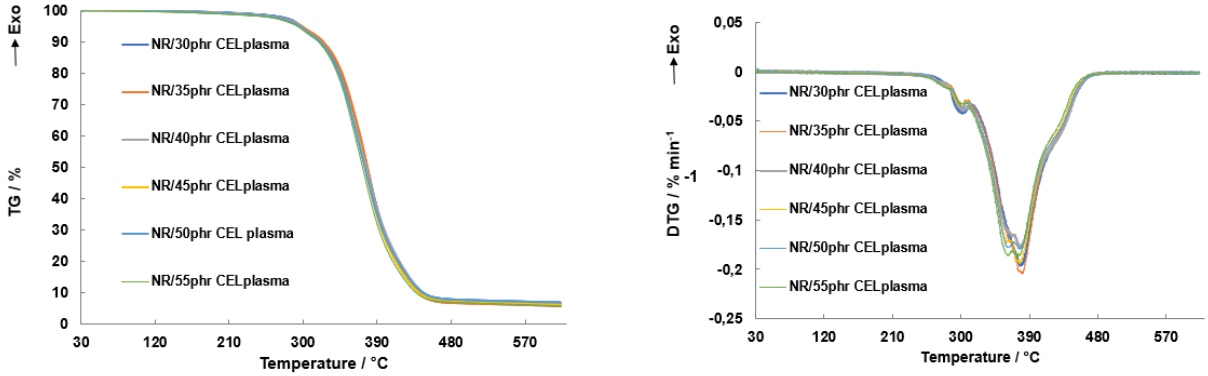

Fig. 4. TG and DTG curves of NR composites filled with various amounts of plasma treated cellulose

The analysis of DTG curves serves to distinguish the thermal decomposition of the sample more accurately. Thermal decomposition took place in the temperature range 300 to 440 °C. On the DTG curve of NR CEL_{sil} composites (Fig. 5) we can see the difference in the area of thermal decomposition of cellulose compared to the DTG curve of NR/CEL_{plasma} composites. The initial decomposition temperature of CEL_{sil} is approximately the same, but the course of weight loss is more gradual and less pronounced. At the maximum filled composite NR/55 phr CEL_{sil} we can see a slightly different course of the DTG curve. The initial decomposition of the rubber occurred earlier than in the other samples and the weight loss was higher at 350 °C. During the decomposition of the double bonds of the methylene groups, carbonation of the natural rubber took place at 380 °C and 410 °C.

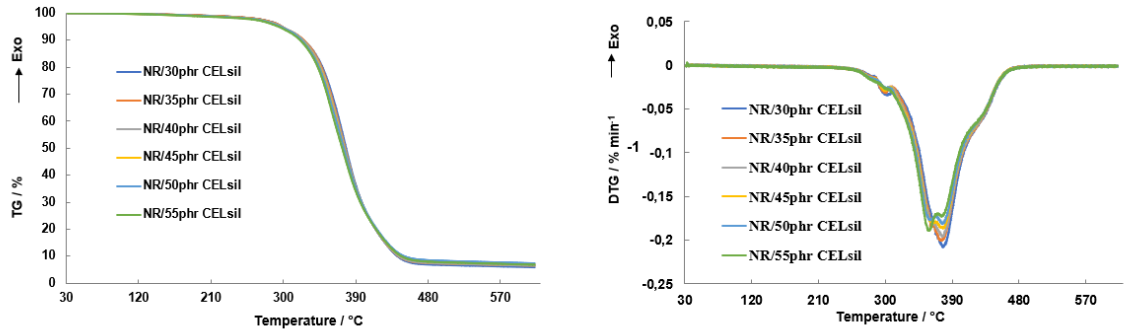

Fig. 5. TG and DTG curves of NR composites filled with various amounts of silanized cellulose

The thermal behavior of cellulose, plasma modified cellulose and silanized cellulose were monitored by DSC analysis. Peak maximum and enthalpy temperatures corresponding to the cellulose decomposition process were evaluated from the DSC curves (Tab. 1). Thermal decomposition of cellulose in N_2 atmosphere is an endothermic process [30]. From the obtained values of peak maximum temperature and enthalpy (Tab. 1) it can be seen that the treatment of cellulose with plasma has very little effect on these observed characteristics. Compared to pure (unmodified) cellulose, the peak maximum temperature for silanized cellulose has not changed, but the enthalpy value for silanized cellulose has a higher value.

	T_m /°C	ΔH /J g^{-1}
CEL	354.9	-198.7
CEL_{plasma}	354.3	-200.1
CEL_{sil}	355.2	-164.9

Table 1. Characteristics of processes obtained from DSC curves (T_m –maximum peak and ΔH – enthalpy)

Peak maximum and enthalpy temperatures were evaluated from the DSC curves of elastomeric composites filled with cellulose modified plasma (Tab. 2). DSC curves of elastomeric composites are multi peak curves as composites were prepared from natural rubber, cellulose and vulcanizing agents (stearic acid, ZnO, Flavex, N-tert-Butyl-2-benzothiazolesulfenamide and sulfur). In DSC curves, the first endothermic peak corresponds to the decomposition of cellulose [30]. The maximum temperature of this endothermic peak in the case of mixtures with plasma-treated cellulose is at temperatures from 300 ° C to 303.6 ° C (Tab. 2). The enthalpy value of the decomposition of the modified cellulose increases with increasing filler content in the mixture.

	T_{m1} /°C	ΔH_1 /J g^{-1}	T_{m2} /°C	ΔH_2 /J g^{-1}	T_{m3} /°C	ΔH_3 /J g^{-1}
Unfilled sample	-	-	370.7	21.0	467.8	5.8
NR/30 phr CEL_{plasma}	303.6	-56.6	368.3	9.5	458.3	14.3
NR/35 phr CEL_{plasma}	301.9	-41.7	369.7	9.7	458.9	3.8
NR/40 phr CEL_{plasma}	300.7	-33.5	371.2	9.3	456.8	6.4
NR/45 phr CEL_{plasma}	300.0	-37.7	369.0	9.5	457.1	3.9
NR/50 phr CEL_{plasma}	302.9	-41.2	371.4	11.9	456.5	3.1
NR/55 phr CEL_{plasma}	301.3	-37.1	369.1	5.4	461.3	7.7

Table 2. Characteristics of processes obtained from DSC curves (T_m - maximum peak and ΔH - enthalpy) for NR composites filled with plasma-treated cellulose

The other bands on the DSC curves represent exothermic processes and correspond to the decomposition of NR and the carbonization of rubber [30, 31, 32]. According to [31], the decomposition temperature of the vulcanized NR is 378 ° C (determined by DSC analysis in an N_2 atmosphere at a heating rate of 10 °C/min). The decomposition temperature (T_{m2}) of the vulcanized NR as well as the carbonization temperature of the rubber (T_{m3}) were lower in our case (Tab. 2) which may be due to the influence of vulcanizing agents. No effect of filler content on the maximum temperature of the first (T_{m2}) and second (T_{m3}) exothermic peaks was observed for the filled composites. Compared to the unfilled sample, the enthalpy (ΔH_2) values of the NR decomposition of the plasma-modified cellulose-filled composites decreased. No significant effect of filler content was found on the value of ΔH_2 and ΔH_3 of composites filled with plasma-modified cellulose.

Peak maximum and enthalpy temperatures were evaluated from the DSC curves of elastomeric composites filled with silanized cellulose (Tab. 3). In DSC curves, the first endothermic peak corresponds to the decomposition of cellulose. The maximum temperature of this endothermic peak in the case of composites with silanized cellulose is at temperatures from 300.3 °C to 301.6 °C (Tab. 3). The enthalpy value of the decomposition of the modified cellulose increases with increasing filler content in the composite. No effect of filler content on the maximum temperature of the first (T_{m2}) and second (T_{m3}) exothermic peaks was observed for the filled composites. Compared to the unfilled

samples, the enthalpy (ΔH_2) values of the NR decomposition of the composites filled with silanized cellulose decreased. No significant effect of filler content was found on the ΔH_2 and ΔH_3 value of composites filled with silanized cellulose.

	T_{m1} /°C	ΔH_1 /J g^{-1}	T_{m2} /°C	ΔH_2 /J g^{-1}	Tm_3 /°C	ΔH_3 /J g^{-1}
Unfilled sample	-	-	370.7	21.0	467.8	5.8
NR/30 phr CEL_{sil}	300.3	-52.2	369.6	6.9	460.2	2.4
NR/35 phr CEL_{sil}	300.8	-58.6	370.1	5.9	461.4	2.7
NR/40 phr CEL_{sil}	301.6	-48.8	368.6	14.8	460.3	5.2
NR/45 phr CEL_{sil}	300.9	-46.8	371.3	19.5	459.7	2.7
NR/50 phr CEL_{sil}	301.1	-26.5	369.7	15.5	460.8	2.7
NR/55 phr CEL_{sil}	300.9	-18.6	370.5	14.2	458.9	2.5

Table 3. Characteristics of processes obtained from DSC curves (T_m - maximum peak and ΔH - enthalpy) for NR composites filled with silanized cellulose

4. CONCLUSIONS

The work was focused on the preparation of elastomeric composites of natural rubber with biopolymer - cellulose and monitoring the influence of chemically and physically modified cellulose as a filler on the structural and thermal properties of elastomeric composites. Cellulose is an economically advantageous source of raw materials. The main disadvantages of cellulose include its hydrophilic character, which must be treated by modification. Cellulose filled natural rubber has great potentials for engineering applications due to their environmental suitability and economic and technical feasibility. This work investigates the relationship between chemical structure, hydrogen bond interaction, and the influence of these parameters on the thermal stability and decomposition of cellulose modified by two different ways and NR composites filled with modified cellulose. The thermal properties of silanized cellulose and plasma modified cellulose as well as the thermal properties of the individual prepared elastomer composites were determined using TG and DSC methods. The prepared composites were also studied by infrared spectroscopy using the ATR method. The thermal properties of the composites showed slight changes due to the increase in the filler content of the composites. The main difference in thermal properties was noted between the composites with plasma modified cellulose and silanized cellulose used. The effect of plasma modification on the hydrophilic character of cellulose was confirmed by TG analysis.

ACKNOWLEDGEMENTS

This research work has been supported by the Operational Programme 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

1. Skalková P, Čížová A, Sroková I. Mechanical and thermal properties of LDPE/glucuronoxylan blends. *Vlákna a Textil*. 2010;17(1): 3-11.
2. Skalková P, Csomorová K, Brezina M, Kapusnak M. Application of biopolymer in natural rubber blends. I*nter. Multidisc. Sci. GeoConference Surveyin Geology and Mining Ecology Management, SGEM*. 2014;1(6):253-260.
3. Van de Velde K, Kiekens P. Biopolymers: overview of several properties and consequences on their applications. *Polymer Testing*. 2002;21: 433 – 442.
4. Santos D, Iulianellig FA, Tavares CV. The Use of Cellulose Nanofillers in Obtaining Polymer Nanocomposites: Properties, Processing and Applications. *Mat. Sci. and Appl*. 2016;7: 257-294.
5. Mark JE, Erman B. Elastomers and rubber-like elasticity. *Performance of Plastics.* Hanser. 2001; 401-428.
6. Mark JE, Erman B, Eirich FR. *The Science and technology of rubber*. 3th Edition. Elsevier. 2005; ISBN: 9780080516677.
7. Kim J, Yun S, Ounaizies Z. Discovery of cellulose as a smart material. *Macromolecules*. 2006; 39:4202-4206.
8. Meyers MA. Biological Materials: Structure and Mechanical Properties. *Progress in Materials Science.* 2008; 53:1 – 206.
9. Van de Velde K, Kiekens P. Biopolymers: overview of several properties and consequences on their applications*. Polymer Testing*. 2002; 21:433 – 442.
10. Nair LS, Laurencin CT. Biodegradable polymers as biomaterials. *Progress in Polymer Science*. 2007; 32:762 – 798.
11. Mekki A, Boufi S, Ben Salah A. Interaction of silane coupling agents with cellulose. *Langmuir.* 2002; 18 (8):3203 – 3208.
12. Vesel A, Mozetic M, Strnad S, Peršin Z, Stana-Kleinschek K, Hauptman N. Plasma modification of viscose textile. *Vacuum.* 2009; 84 (1):79-82. DOI: 10.1016/j.vacuum.2009.04.028.
13. Temmerman E, Leys Ch. Surface modification of cotton yarn with a DC glow discharge in ambient air. *Surface & Coatings Technology*. 2005; 200: 686-689.
14. Aiswarya RN, Sambhudevan S, Shankar B. Synthesis, characterization and dye removal properties of cellulose nanocrystals embedded natural rubber latex composite. *Cellulose Chem. Technol*. 2019; 53:263–70.
15. Abraham E, Deepa B, Pothan LA, John M, Narine SS, Thomas S, Anandjiwala R. Physicomechanical properties of nanocomposites based on cellulose nanofibre and natural rubber latex. *Cellulose.* 2013; 20:417–27.
16. Agrebi F, Ghorbel N, Bresson S, Abbas O, Kallel A. Study of nanocomposites based on cellulose nanoparticles and natural rubber latex by ATR/FTIR spectroscopy: The impact of reinforcement. *Polym Compos*. 2019; 40:2076–87.
17. Kord SM, Brown RJ, Tsuzuki T, Rainey TJ. A comparison of cellulose nanocrystals and cellulose nano fibres extracted from bagasse using acid and ball milling methods. *Adv Nat Sci: Nanosci Nanotechnol*. 2016; 7:035004.
18. Siuda J, Perdoch W, Mazela B, Zborowska M. Catalyzed reaction of cellulose and lignin with methyltrimethoxysilane – FT-IR, ^{13}C NMR and ^{29}Si NMR studies. *Materials*. 2019; 12:2006.
19. Abdelmouleh M, Boufi S, Belgacem MN, Duarte AP, Ben Salah A, Gandini A. Modification of cellulosic fibers with functionalized silanes: development of surface properties. *Int. J. Adhes. Adhes.* 2004; 24:43–54.

20. Colom X, Carrasco F, Pagès P, Cañavate J. Effects of different treatments on the interface of HDPE/lignocellulosic fiber composites. *Compos Sci Technol*. 2003; 63:161–9.

21. Launer PJ. Infrared analysis of organosilicon compounds: spectra-structure correlations. *Silicon Compounds: Silanes & Silicones*. 3rd ed. Morrisville: Gelest; 2013; 175–178.

22. Korobko AP, Krasheninnikov SV, Levakova IV, Drozd SN. The interaction of a low-temperature oxidizing plasma with modified cellulose. *Russ J Phys Chem* A. 2010; 84:277–84.

23. Sinha E, Panigrahi S. Effect of plasma treatment on structure, wettability of jute fiber and flexural strength of its composite. *J Compos Mater*. 2009; 43:1791-802.

24. Nallasamy P, Mohan S. Vibrational spectra of cis-1.4-polyisoprene. *Arab J Sci Eng*. 2004; 29:17–26.

25. Yu H, Zeng Z, Lu G, Wang Q. Processing characteristics and thermal stabilities of gel and sol of epoxidized natural rubber. *Eur Polym J*. 2008; 44:453–64.

26. Barth A. Infrared spectroscopy of proteins. *Biochim Biophys Acta*. 2007; 1767:1073–1101.

27. Bonardd S, Robles E, Barabdiaran I, Saldias C, Leiva A, Kortaberria G. Biocomposites with increased dielectric constant based on chitosan and nitrile- modified cellulose nanocrystals. *Carbohydr. Polym*. 2018; 199: 20–30.

28. Bouafif H, Koubaa A, Perré P, Cloutier A, Riedl B. Wood particle/high- density polyethylene composites: thermal sensitivity and nucleating ability of wood particles. *J. Appl. Polym. Sci*. 2009; 113 (1):593–600.

29. Migneault S, Koubaa A., Perré P. Effect of fiber origin, proportion, and chemical composition on the mechanical and physical properties of wood-plastic composites. *J. Wood Chem. Technol*. 2014; 34 (4):241–261.

30. Yang H, Yan R, Chen H, Lee DH, Zheng C. Characteristics of hemicellulose, cellulose and lignin pyrolysis. *Fuel.* 2007; 86(12-13):1781–1788.

31. De PP, Choudhury R, Dutta NK. Thermal Analysis of Rubbers and Rubbery Materials, (Eds.). iSmithers, UK. 2010; 543. ISBN: 978-1-84735-103-6.

32. Medeiros ES, Galiani PD, Moreno RMB, Mattoso LHC, Malmonge JA. A comparative study of the non-isothermal degradation of natural rubber from Mangabeira (Hancornia speciosa Gomes) and Seringueira (Hevea brasiliensis). *J Therm Anal Calorim*. 2010;1 00:1045–50.

33. Silva MJ, Sanches AO, Medeiros ES. Nanocomposites of natural rubber and polyaniline-modified cellulose nanofibrils. *J Therm Anal Calorim*. 2014; 117:387–392.