Properties of Natural Rubber Biocomposities Filled with Alkaline Modified Oat Straw

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ABSTRACT: Novel elastomer biocomposites based on straw fibers (raw or chemically modified) as reinforcing elements of natural rubber (NR) were reported and studied. Oat straw fibres with different average lengths were used. Lignocellulose materials were incorporated into the elastomer, before and after chemical surface modification involving sodium hydroxide. Fourier transform infrared spectroscopy (FTIR) and microscopy techniques were employed for characterization of fillers. The kinetics of rubber mixtures, as well as rheometric properties of compounds were determined. The cross-linking density was executed on the basis of equilibrium solvent-swelling measurements applying the modified Flory–Rehner equation. The morphology of biocomposites samples was analyzed by a scanning electron microscopy. Mechanical characteristic: the values of hardness, tensile strength and attenuation coefficient were also determined. The physical and chemical investigations have proved the reinforcing effect of treated oat straw on natural rubber vulcanizates.

KEYWORDS: Alkalization, biocomposites; natural fibres, natural rubber, straw

1 INTRODUCTION

Research and engineering interest in cellulose fibers such as flax, hemp, sisal, cotton, kenaf, jute, bamboo, coconut and date palm, which has developed over the last decades, was dictated primarily by their several economic, technical and environmental concerns [1, 2]. Lignocellulosic materials are abundant, based on renewable source, have less density and low cost [3]. They can also be easily disposed of at the end of their life cycle by recovery of their calorific value in a furnace or by composting. Due to their unique properties natural fillers can replace the reinforcement of synthetic fibers such as glass, carbon, aluminum oxide in composites [4]. Notwithstanding natural fibers also exhibit some disadvantages, these are mainly: High moisture absorption, low thermal resistance and high anisotropic properties [5]. Typical natural fiber consist of: Cellulose, hemicellulose, lignin, pectin, waxes and water soluble substances. However the biocomposition may differ from each other through the growing condition and test methods even for the same kind of fiber [6]. Hemicellulose is amorphous polysaccharide, partially soluble in alkaline solution, while cellulose is semi crystalline and responsible for the hydrophilic nature of the plant fiber [7]. Lignins are amorphous, highly complex, mainly aromatic, polymers of phenylpropane units [8] but have the least water sorption of the natural fiber components [9]. Many problems occur at the interface of natural fibers used as reinforcement in biocomposite materials due to their incompatibility [5].

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As a result the full capabilities of the biocomposite cannot be exploited. Poor adhesion at the interface causes susceptibility to environmental attacks, which weaken biomaterial, thus reducing its lifespan. Insufficient adhesion between hydrophobic polymers and hydrophilic fibers result in poor mechanical properties of the natural fiber reinforced polymer biocomposites [10]. Therefore one of the largest areas of current research to improve compatibility and interfacial bond strength surface are modifications of the natural fibers [1, 11].

The straw and other agricultural residues existing in the waste streams from commercial crop processing plants have little inherent value and have traditionally constituted a disposal problem. Actually, these residues represent an abundant, inexpensive, and readily available source of renewable lignocellulosic biomass. The straw constitutes the residual structure of the plant after grain harvesting. Since roots are not harvested, straw is composed of stem structures (internodes and nodes), leaves and earstructures (chaffs and rachis). The literature indicates that straw is mainly composed of internodes (50-60%), leaves (15-30%) and nodes (≈10%). The cellulose, hemicellulose, and lignin contents of straw are 34-40%, 30-35%, and 14-15%, respectively. Hemicelluloses and lignin can be extracted effectively and completely. Cellulose in straw comprises the cellulose I allomorph with low crystallinity and only the stable cellulose I polymorphic crystal structure exists in the straw.

 Natural fibers are chemically treated to remove lignin, pectin, waxy substances, and natural oils covering the external surface of the fiber cell wall. Sodium hydroxide (NaOH) is the most commonly used chemical for bleaching and/or cleaning the surface of

plant fibers. It also changes the fine structure of the native cellulose I to cellulose II by a process known as alkalization. The increase in the percentage of crystallinity index of alkalitreated fiber occurs because of the removal of the cementing materials, which leads to better packing of the cellulose chains. In addition, treatment with NaOH leads to a decrease in the spiral angle and an increase in molecular orientation. The elastic moduli of fibers, for instance, are expected to increase with increasing degree of molecular orientation.

Recently, there has been a rapid growth in research and innovation in the natural fibre biocomposite. Commonly, geography relating to fibre availability plays a major role in fibre selection [12]. The focus, for example in Europe has been on flax fibre, whereas hemp, jute, ramie, kenaf and sisal have been of greater interest in Asia. In whole Europe is the enormous quantity of straw, utilization of straw to the utmost extent is now demanding attention in the major cereal-growing areas of the world. Researches on the use of straw in biocomposites focus mainly on thermoplastic polymers consisting of rapeseed and rice straw as fibres. Unfortunately, the problem of utilization of straw is still not fully resolved and requires search for new opportunities and technologies of its use.

The objective of this study is to develop a new type of composite material straw reinforced natural rubber composite. In polymer technology, the use of an appropriate medium is a key issue and forms the basis of its subsequent, relevant properties. Natural rubber (NR) is a possible natural polymer matrix material. NR is obtained from the rubber tree (Hevea brasiliensis) in the form of field latex. NR is produced by plant which means it is renewable and inexpensive. Natural rubber is one of the most important elastomers in terms of versatility and application volume owing it to its superior strength, elasticity, flexibility, resilience, and abrasion resistance [13]. In comparison with thermoplastics, natural rubber belongs to the group of elastomers, which involves various methods of processing, sample preparation and selection of conditions for the production of bicomposites. The use of the new matrix is undoubtedly a scientific novelty, both from a cognitive and application point of view.

One of the most important aspects of biocomposite manufacture is to achieve adequate adhesion between fibres and the rubber matrix. In this work we report studies on the effects of alkaline modification of oat straw on the curing characteristics, mechanical and damping properties of rubber biocomposites.

2 EXPERIMENTAL

2.1 Materials

Natural rubber-RSSI, cis-1,4-polyisoprene, density 0,93-0,988 g/cm^3 was provided by Torimex Chemicals. Conventional sulfur curing system: sulphur (Siarkopol, Tarnobrzeg), micro-sized zinc oxide (Huta Będzin), mercaptobenzothiazole (Aldrich) and stearin (POCH). Oat straw was collected from local farms (Poland) and have been cut in order to achieve the mean length of 4 mm. Part of pre-prepared straw was alkalized. For alkali treatment, the dried straw was soaked in an aqueous solution of sodium hydroxide (10 wt. % solution of NaOH) for 48 h at room temperature. Afterwards, the fibres were rinsed with distilled water until the straw reached pH=7. Next, the fibres were dried again at 70°C, until a constant mass was reached. Dried straw was crushed using a mixer (Blixer 4)- grinding time 15 min. Then the straw was separated into fractions using a vibratory shaker and set of sieves with 4,0; 2,0; 1,0; 0,5; 0,25; mm. The morphology of straws was examined from the structure images of the fillers, which were taken using an optical stereomicroscope Leica MZ6 (Figure 1).

Composition of typical elastomer mixture: NR rubber (100 phr-per hundred parts of rubber), sulfur (2 phr), mercaptobenzothiazole (2 phr), zinc oxide (5 phr), stearic acid (1 phr) and fillers -10phr.

2.2 Methods

Rubber mixtures, based on natural rubber filled with oat straw were prepared by a Brabender measuring mixer N50 (temp. 50°C, rotor speed range 40 min^{-1}, time of the process 15 min). Then, two-roll mill was used to addition vulcanization system and obtain blends sheets. The condition of mixing: roll dimensions of D=140 mm and L=300 mm, the rotational speed of the front roll was Vp=16 min^{-1}, the friction was and the width of the gap between rollers was 1-1.2, 1.5-3 mm, the average temperature of the rolls was of about 30°C. The rheology of rubber mixtures, as well as curing properties of compounds were studied using MDR rheometer from Alpha (ISO 6502) at 160°C. Then the mixtures were cured (steel vulcanization molds) at 160°C, at 15 MPa pressure for time corresponding with curing properties (t_{90}). Rubber mixtures were placed into molds previously heated to 160°C.
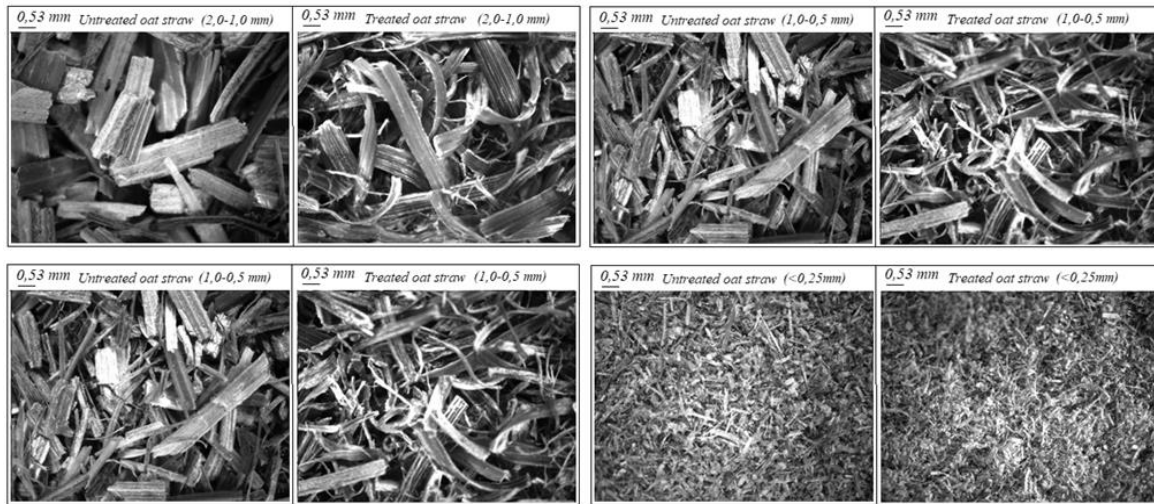
Figure 1 Microscope images of raw and treated oat straw in different size fractions.
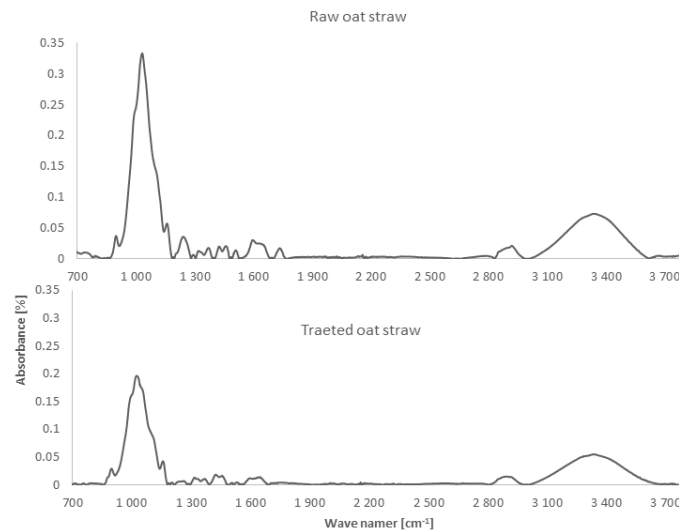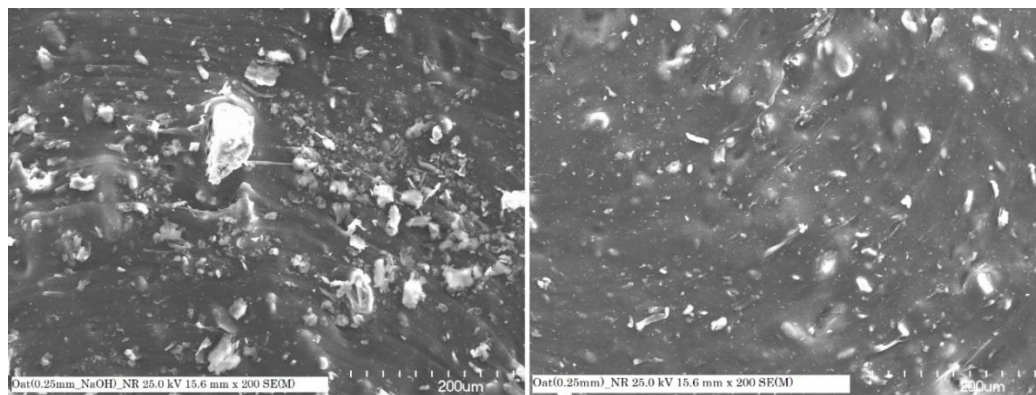

Figure 2 FTIR spectra of raw and treated oat straw.

Figure 3 SEM images of vulcanizates containing 10 phr of pure oat straw <0.25 mm (left) and NaOH treated oat straw <0.25 mm (right).
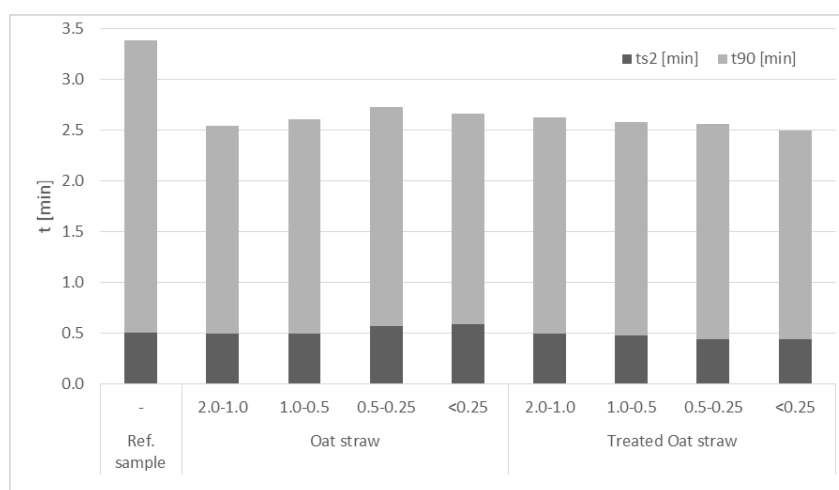
Figure 4 Curing and scorch times of NR mixtures containing raw and treated oat straw in different size fractions.
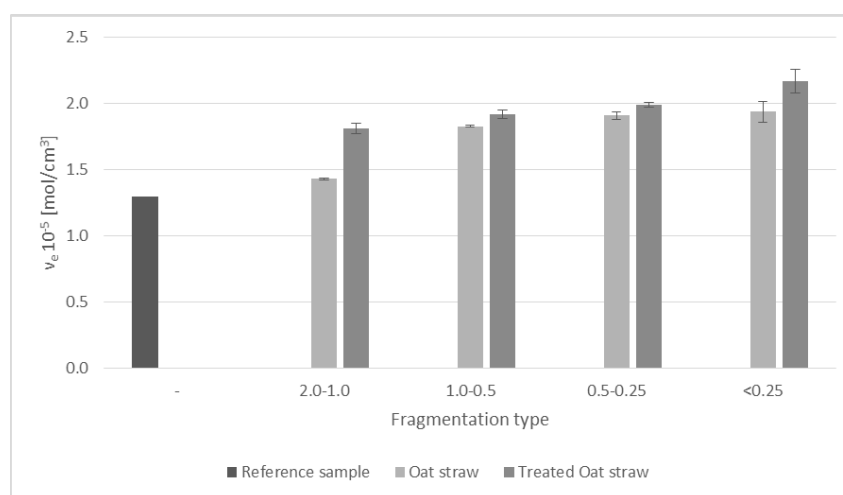

Figure 5 Crosslinking density of NR vulcanizates containing raw and treated oat straw in different size fractions.

Fourier transform infrared (FTIR) spectra were recorded on a FTIR Nicolet 6700 spectrophotometer and OMNIC 3.2 software (Thermo Scientific Products: Riviera Beach, FL, USA) at room temperature. The tensile properties were conducted according to the standard procedures in ISO 37 on the universal testing machine Zwick (RoellGroup, Ulm, Germany). The tensile test was carried out for 5 dumbbell (W-3) samples, the result given is an average value. The cross-linking density of the vulcanizates was determined by equilibrium swelling in toluene, based on the Flory-Rehner method [14].

Hardness was performed according to ISO 868 standard using a Shore type A Durometer (Zwick/Roell). Damping properties of biocomposites were executed under the influence of compressive stress using a ZWICK 1435 (Zwick/Roell), according to polish standard PN-C-04289. The method is used for testing rubber with a hardness of 30-85 °ShA with the exception of porous rubber. The test consists in cyclically compressing the sample (cylindrical shape, D=35mm, H=17.8mm) from 0-0.7 MPa stress value, registering the hysteresis loop, integrating the fields formed by the compression and relaxation curves and calculating the relative attenuation according to the equation:

$$T_{\tau w} = \frac{\Delta W_i}{\Delta W_{ibel}} \cdot 100\%$$

where: $T_{\tau w}$-relative damping, ΔW_i-the difference between the compression work and the work during reducing the compressive stresses, W_{ibel}-compression work.

The morphology of composites samples (10 phr straw <0.25 mm) was analyzed by means of the SEM, a

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scanning electron microscopy with field emission S-4700 Hitachi (Japan). The accelerating voltage was 25 kV.

3 RESULTS AND DISCUSSION

The influence of alkali treatment on oat straw was studied by infrared spectrometry. All the results show that the treatment with sodium hydroxide resulted in a dissolution of amorphous parts of the straw fiber. Figure 2 showed the infrared spectra obtained.

The spectra of raw and treated fibers showed a broad band observed at 3000-3500 cm^{-1} in the spectra indicating the presence of OH bond which found to decreased by the sodium hydroxide treatment. This could be explained by the fact that the hydroxyl groups are involved in hydrogen bonding with the carboxyl groups of the fatty acids available on the fiber surface [1]. The absorbance at 2850 cm^{-1} was related to symmetric C-H vibrations [15]. The band for 1745 cm^{-1} is attributed to the C=O stretching of the acetyl groups of hemicellulose and lignin [16]. This peak was not presented in the alkali treated samples. According to the literature [10], the removal of hemicellulose from the straw surfaces makes this disappear. This disappearance was due to the hydrolysis of hemicellulose in alkaline medium characterized by breaking the C-O-C bonds between two monomers [17]. The peaks detected at 1650 cm^{-1} and 1620 cm^{-1} is correlated with the carbonyl group of the acetyl ester in hemicellulose and the carbonyl aldehyde in lignin. Those peaks can be visible prior and after alkali treatment. Even whole hemicellulose is removed, lignin residue is still present in the fiber structure, what is confirmed by the small peak at about 1240-1250 cm^{-1}, that correspond to C-O vibration was also attributed of lignin [18]. Samples presented little absorptions between 1500 cm^{-1} and

1400 cm^{-1}, which correspond to unsaturation (C=C) in the molecules, which may be related to the waxes, extractives and lignin, and is in agreement with the lignocellulosic natural fibers [19]. This region could be also characterized by the aromatic ring vibrations and ring breathing with C-O stretching in lignin. The regions: from 1360 cm^{-1} to 1375 cm^{-1} is represented by the C–H bending vibration and in the 1317-1320 cm^{-1} occurred peak corresponds to the C-O at the groups of the aromatic ring in cellulose. The intense peak near 1028 cm^{-1} correlated with C-O-C bonds.

In order to illustrate the morphology of the composites, scanning electron microscopy measurements were performed. Microscopy images of selected vulcanizates were given in Figure 3.

The filler particles exhibit inhomogeneities in size and shape. Mostly they resemble fibers with the size range from several dozen to several hundred microns. Vulcanizates containing pure and NaOH treated straw indicated that, modification increased dispersion of the fillers. More homogenous structure of alkalized straw particles can be clearly seen, what might influence on the properties of final products.

The rheometric study performed with a rheometer measures the torque response over time of elastomers during the curing process. The measured torque is related to the modulus of the biocomposite. Table 1 showed the rheometric properties of rubber mixtures cured at 160°C. The kinetic characteristic of rubber vulcanization studied in this work was presented in Figure 4.

Table 1 Rheological properties of NR mixtures containing raw and treated oat straw in different size fractions.

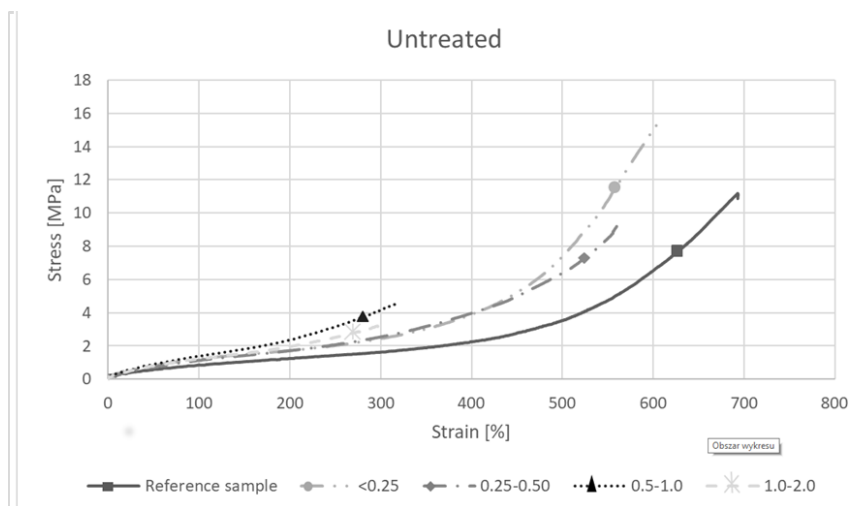| Filler type	Filler content	Size fractions	M_L	M_H	ΔM
	[phr]	[mm]	[dNm]	[dNm]	[dNm]
Reference sample	**-**	-	0.76	5.71	4.95
Oat straw	**10**	2.0-1.0	1.68	6.86	5.18
		1.0-0.5	1.62	6.98	5.36
		0.5-0.25	1.32	6.93	5.61
		<0.25	1.61	7.33	5.72
Treated Oat straw	**10**	2.0-1.0	1.80	7.04	5.24
		1.0-0.5	1.82	7.47	5.65
		0.5-0.25	1.87	7.54	5.67
		<0.25	1.96	7.88	5.92

Figure 6 Stress-strain plots of NR vulcanizates containing untreated oat straw in different size fractions.
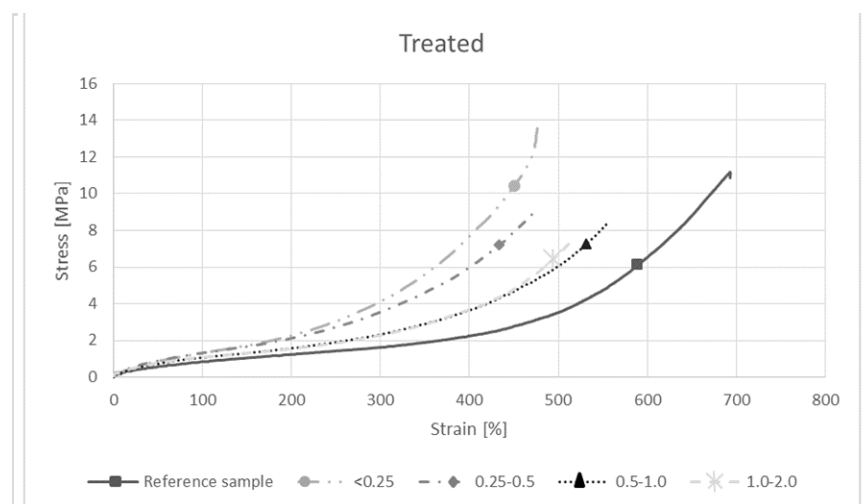

Figure 7 Stress-strain plots of NR vulcanizates containing treated oat straw in different size fractions.
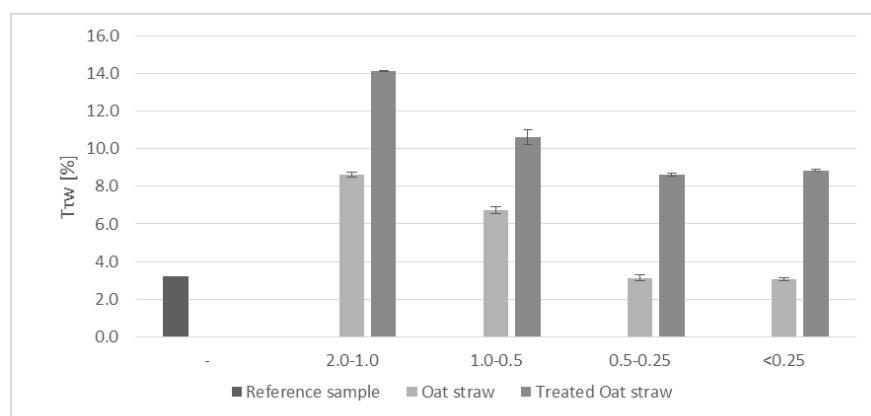

Figure 8 Relative damping values of NR vulcanizates containing raw and treated oat straw in different size fractions.

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Table 2 Mechanical properties and hardness of NR vulcanizates containing raw and treated oat straw in different size fractions.

Filler type	Filler content	Size fractions	SE$_{100}$	TS	Eb	H
	[phr]	[mm]	[MPa]	[MPa]	[%]	[°ShA]
Reference sample	-	-	0.80±0.02	11.5±0.4	591±11	26.0±0.3
Oat straw	10	2.0-1.0	1.15±0.01	3,2±0.5	296±15	37.1±0.1
		1.0-0.5	1.32±0.04	4.4±0.2	328±11	36.5±0.2
		0.5-0.25	1.15±0.05	9.3±0.6	560±14	37.5±0.1
		<0.25	1.20±0.05	15.3±0.6	503±22	38.6±0.3
Treated Oat straw	10	2.0-1.0	1.08±0.08	7.6±0.3	516±9	39.1±0.2
		1.0-0.5	1.04±0.04	8.3±0.7	551±21	38.7±0.3
		0.5-0.25	1.14±0.07	9.2±0.6	502±16	41.0±0.3
		<0.25	1.34±0.11	13.9±0.4	473±17	40.4±0.3

Where: SE$_{100}$ -Stress at 100% elongation, TS-Tensile strength, Eb-elongation at break, H-hardness.

Fillers with their reinforcing potential influence on the rheometric properties. These properties considered in this work were characterized by the minimum torque (M_L), maximum torque (M_H), difference between M_H and M_L(ΔM), the scorch time (t_{s2}), the time for reaching the 90% of the curing (t_{90}). The minimum torque M_L in a rheograph is related to the viscosity of the biocomposites, and the maximum torque M_H is generally correlated to the stiffness and crosslink density. It is well known that the difference between maximum and minimum torque (ΔM) is a rough measure of the crosslink density of the samples. In the case of conventional cross-linking systems, the vulcanization speed and the rheological properties depend predominantly on the groups on the surface of the filler as well as on its specific surface. The introduction of straw into natural rubber has increased its viscosity and stiffness. The effect on M_H and M_L was the size of the filler. The decrease in the size of the straw fibers most likely resulted in an increase in the filler's specific surface, contributing to the increase in minimum and maximum torque and consequently to the increase in the ΔM value. Comparing the rheological properties of the rubber mixtures containing NaOH modified and unmodified, the alkalization process resulted in an increase in the torque values during vulcanisation, regardless of the filler size. Surface modification could increase the impact on the rubber-filler boundary, affecting the rheological characteristics of the biocomposites tested. The rate of vulcanisation was mainly affected by the addition of straw, which shortened the curing process by approximately one minute.

Confirmation of the obtained rheological properties was the equilibrium swelling measurements, on the basis of which the cross-linking density of natural rubber vulcanizates was evaluated (Figure 5). The degree of fragmentation of the filler had a significant effect on the increase of the network nodes in the biocomposites. Vulcanizates containing smaller particles of straw were characterized by higher values of v_e. The modification of the straw with sodium hydroxide resulted in an increase in the cross-linking density of the vulcanizates as compared to the use of the unmodified filler. Alkalization has probably resulted in improved adhesion at interfacial interfaces, resulting in better dispersion in the elastomer and thus increased filler activity and its ability to create its own spatial network. Rubber products are often exposed to deformation. The use of modified rubber materials or their constituents is intended to improve the properties, and at least not to deter them from being made in a conventional manner. It was investigated how the alkalization of straw and its degree of fragmentation affected the mechanical properties of the filled vulcanizates. The results of the mechanical properties are presented in Table 2.

The tensile strength of the tested biocomposites depended on the size of the applied filler and its modification. Compared to the reference sample, the TS value improved only for biocomposites containing the smallest straw (less than 0.25 mm). Large straw fibers can cause stress concentration, leading to premature destruction of the sample. The effect of the modification on the mechanical properties was observed for a larger filler. Biocomposites containing 2.0-1.0 mm and 1.0-0.5 mm modified straw showed a 2-fold increase in tensile strength, while samples filled with smaller particles showed no significant change. The straw fibers were surface modified and then crushed and separated into fractions. As a result of grinding, the modified surface was fragmented, so the

smaller particles were characterized by a lower degree of coverage by the modifier, which was reflected in the results of the strength properties. It was previously reported that with decreased size of the filler, higher tensile strength of composites was obtained [13].

The introduction of the natural filler, as expected, reduced the elasticity of the biocomposites, which can be measured by the relative elongation of the sample at break. The lowest Eb values were obtained for biocomposites containing a large size filler where premature breakage of the sample occurred. The remaining samples were highly elastic, the Eb values were about 500%. Stress-strain curves are presented in Figures 6 and 7. The addition of straw regardless of size and modification performed resulted in an increase in hardness of approximately 11-15 °ShA.

Vibration suppression occurs in the elastic medium, its size is determined by the hysteresis loop. By measuring the relationship between stress and deformation in one full cycle, the hysteresis loop is obtained, which determines the relative damping coefficient.

Vibration constitute a major problem in the general use of composites materials and their applications, where fiber-reinforced composites are employed. Vibration control of composite materials is therefore also an important issue to be studied.

The damping properties of the composites are closely related to their ability to dissipate energy during deformation. Therefore, the relative attenuation values obtained were higher, so the composite dissipates the energy more strongly, and therefore shows better performance. The relative damping coefficient values for the test biocomposites are shown in Figure 8.

Vulcanizates containing straw fractions of size 2-1 and 1-0.5 mm exhibited higher compression attenuation capacity compared to the reference system. Biocomposites filled with smaller fractions are characterized by a damping factor at the level of the reference sample. Large size fibers acted as reinforcement elements, allowing the reduction of vibration transmitted to the system. Moreover fine particles of the filler less effectively absorb the kinetic energy generated by the compressive force. Alkalization in each case almost doubled the ability to suppress compressive stresses.

Natural fibers are a non-deformable solid phase, the additional advantage of which is the transfer of loads and thus the greater damping potential. The modification applied resulted in improvement of rubber-filler interactions, which allowed for more efficient energy transfer during compressive stress.

4 CONCLUSIONS

Oat straw found to be an active filler of natural rubber composites, which improves a number of properties: Rheometric, crosslinking density, mechanical and damping characteristic. It can potentially provide benefits for commercial applications in various industries such as the automotive or construction.

The chemical modification applied affected the changes in the fiber structure and the morphology of the composites filled with them. Moreover the reduction of the amount of waxes, lignin and hemicellulose on the fiber surface, was observed by the FTIR analysis.

The rubber mixtures containing pure and alkalized lignocellulosic materials demonstrate a favorable characteristic kinetics of crosslinking. The application of chemical modification and especially alkali treatment can be very beneficial for getting good bonding at the interface between a polymer matrix and the modified straw fibres. The addition of filler (in an appropriate amount, degree of fragmentation and treated) modified natural rubber vulcanizates, improving mechanical and physic properties of biocomposites or the ability to damp under the influence of compression stress. This was due to the removal of some non-cellulose compounds of the straw fibres.

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