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# Effect of Surface Treated Biopolymer on Curing Behavior and Tensile Properties of Natural Rubber Composites

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## Abstract

The growing demand for environmentally friendly materials has prompted several researchers to explore naturally occurring biopolymers for potential applications in a variety of fields. Cellulose is a biopolymer formed by the repeated joining of D-glucose building blocks and is characterized by its hydrophilicity, broad chemical modification capacity, biodegradability, and the formation of versatile morphologies of semicrystalline fibers. However, the interactions between the cellulose and the polymer matrix are limited due to the fact that the cellulose is hydrophilic while the matrix is hydrophobic. The surfaces are thus not sufficiently compatible, leading to a reduction in mechanical properties. In this study, cellulose was surface treated with two types of silanes. Modified cellulose was used as filler in natural rubber composites. The influence of treated and untreated cellulose on the curing characteristics, rheological properties, mechanical properties and crosslinking density of natural rubber composites was examined. The curing characteristics of the natural rubber composites, the scorch time and cure times, decreased for natural rubber composites filled with modified cellulose compared with natural rubber composite filled with unmodified cellulose. The measured values of tensile strength and crosslinking density showed higher values for natural rubber composites filled with modified cellulose compared with natural rubber composite filled with unmodified cellulose.

**Keywords:** cellulose, natural rubber composites, surface treatment, curing behavior, tensile properties, biomaterials, silane, biopolymers

## 1. Introduction

Biopolymers are referred to as materials that are synthesised or produced from natural sources. The use of these materials has increased significantly in recent years as the industry has moved away from unsustainable fossil fuel supplies and toward a more environmentally sustainable approach [1, 2]. The surface of cellulose can be modified and altered by physical interactions or by adsorption of molecules or macromolecules on its surface, or by a chemical approach to achieve covalent bonds between the cellulose and the grafting agent [3]. One of these methods is silanization, which modifies the surface of the filler with a silane agent, resulting in a reduction in the number of hydroxyl groups of the filler at the filler-matrix interface.

## 2. Experimental

Natural rubber was mixed with fillers on cellulose treated on a surface as well as other chemicals necessary for curing via the sulphur system. All ingredients were mixed using an internal Plasti-Corder Brabender®EC mixer plus (Brabender, Duisburg, Germany) at initial temperature 100 °C with a rotor speed of 50 rpm and a fill factor of 0.70.

The rheological behaviors of natural rubber composites were studied using a rubber process analyser (PRPA 2000) (Alfa Technologies, Akron, OH, USA) in accordance with ASTM 5289. About 6 g of sample was placed between a pair of rotating disks and cure behaviors were set at a temperature of 150 °C, at a constant frequency of 1.67 Hz. Selected curing parameters such as minimum torque ( $M_L$ ), maximum torque ( $M_H$ ), cure time ( $t_{90}$ ) and scorch time ( $t_s$ ), were measured from the cure curve (torque vs. time). The curing rate index ( $R_v$ ) was calculated according to Eq. (1).

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

Mechanical properties of the composites that were tested such as tensile strength, elongation and hardness. The tensile test of the prepared rubber composites was measured using a universal testing machine – Shimadzu Autograph AG-X plus – 5kN operation (Shimadzu, Tokyo, Japan) with a cross head speed of 100 mm/min according to the ASTM D412 87 standard. Five samples were prepared for each rubber composites. The hardness test was determined according to ASTM D 2240 86. Specimens with a thickness of 6 mm were determined using a Shore A Durometer hardness tester (Wallace LTD, Croydon, UK). Swelling experiments were performed on small square (approximately 20 x 20 x 2 mm) samples in toluene at room temperature for 72 hours After swelling, the sample was removed, quickly dried with filter paper and weighed to obtain the swollen weight of the sample. Based on the Flory-Rehner equation, the crosslinking density was determined using Eq. (2):

$$-\ln[(1 - v_r) + v_r + \chi v_r^2] = \rho v_s M_c^{-1} (v_r^{1/3} - v_r/2) \quad (2)$$

The Payne effect of natural rubber composites was studied using a rubber process analyser (PRPA 2000) (Alfa Technologies, Akron, OH, USA) according to ASTM The magnitude of the Payne effect was measured by the difference between the dynamic storage modulus at 0.28% and at 100.02% strain using Eq. (2).

$$\Delta G' = G'_{0.28\%} \cdot G'_{100.02\%} \quad (3)$$

### 3. Results and discussion

#### 3.1. Curing behavior

The measured cure parameters of the natural rubber composites are in Table 1.

Table 1: Curing characteristics of natural rubber composites.

Composites	M <sub>L</sub> (dN.m)	M <sub>H</sub> (dN.m)	ΔM (dN.m)	t <sub>s</sub> (min)	T <sub>90</sub> (min)	R <sub>v</sub> (min <sup>-1</sup> )
NR	1.49	12.65	11.16	5.55	9.98	22.57
NR/CEL	0.64	25.56	24.91	7.94	13.27	18.76
NR/CEL_Si69	0.60	25.65	25.05	7.58	12.68	19.61
NR/CEL_APTES	0.63	26.07	25.44	7.27	12.58	18.83

The minimum torque values of the natural rubber composites filled with fillers decreased compared to the natural rubber composite without filler, resulting in a lower blend viscosity or stiffness of the natural rubber composite compound prior to the crosslinking reaction [4, 5]. M<sub>H</sub> values were significantly higher compared to pure natural rubber composite. The results of the measured delta torque showed a trend similar trend to the maximum torque. In the case of the NR/CEL\_APTES composite, the highest delta torque value is observed. The scotch time curing parameter refers to the time during which the rubber composite can be processed at a given temperature before curing [6]. It can be clearly seen that the addition of surface treated and untreated cellulose increased the cure time, indicating sufficient scotch safety of the blends [7]. The natural rubber composites filled with surface treated cellulose showed a slight decrease T<sub>c(90)</sub> compared to NR/CEL. Filled NR composites showed lower R<sub>v</sub> values in the presence of surface treated cellulose treated with silane compared to untreated cellulose.

#### 3.2. Mechanical properties

The tensile strength, elongation, shore A hardness and crosslinking density for sample NR, NR/CEL, NR/CEL\_Si69 and NR/CEL\_APTES rubber composites are showed in Table 2.

Table 2: Curing characteristics of natural rubber composites.

Composites	Tensile strength (MPa)	Elongation (%)	Shore Hardness A	Crosslinking density ( $\cdot 10^{-4} \text{ mol.cm}^{-3}$ )
NR	$17.17 \pm 1.58$	$795 \pm 33.72$	$36.33 \pm 0.41$	$5.27932 \pm 0.45$
NR/CEL	$5.47 \pm 0.87$	$334 \pm 44.24$	$73.59 \pm 0.17$	$8.08643 \pm 0.21$
NR/CEL_Si69	$5.73 \pm 0.39$	$358 \pm 33.36$	$72.82 \pm 0.29$	$8.39166 \pm 1.28$
NR/CEL_APTES	$6.45 \pm 0.49$	$365 \pm 31.79$	$72.97 \pm 0.70$	$8.82627 \pm 0.61$

From the measured tensile properties, it can be seen that the introduction of cellulose into the polymer matrix resulted in a significant decrease in the properties of the pure natural rubber composite (NR). CEL\_Si69 and CEL-APTES filled natural rubber composites exhibited higher tensile strength and elongation values than CEL filled natural rubber composites. This behavior can be attributed to the surface treatment of the cellulose with silane coupling agents and is indicative of good dispersion of the treated cellulose in the polymer matrix.

### 3.3. Payne effect

The curve of dependence of the storage modulus ( $G'$ ) on the different strain amplitude of the prepared natural rubber composites before and after cure is shown in Fig. 1

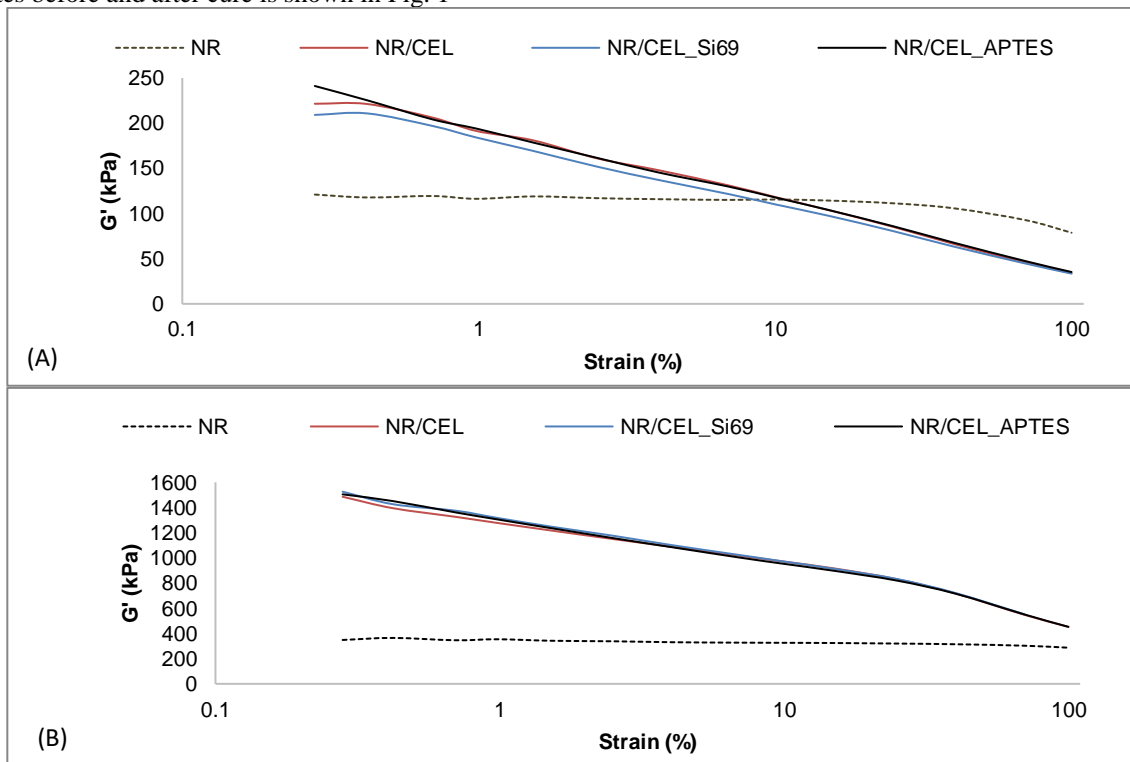


Fig. 1 Strain amplitude dependence of  $G'$  of natural rubber composites (A) before cure (B) after cure

From the figure, it can be seen that the NR/CEL\_Si69 composite before cure has a significantly lower  $G'$  value at low strains, which is due to lower filler-filler interactions. In the case of the NR/CEL\_APTES, there is a higher torque modulus, indicating higher filler-filler interactions. The difference between  $G'$  at very low and high strains is always used as an indicator of the Payne effect. The calculated higher values of the Payne effect in the case of NR/CEL\_APTES can be attributed to the poor dispersion of the filler particles in the rubber matrix. Here a strong agglomeration occurs between filler particles even in the presence of a silane agent. From Fig. 2 it can be seen that the NR/CEL\_Si69 composite shows a lower Payne effect than the NR/CEL composite. This is evidenced by the

reduction in the agglomeration of treated cellulose by the adding of silane reagent, resulting in a reduction in filler-filler interactions [8].

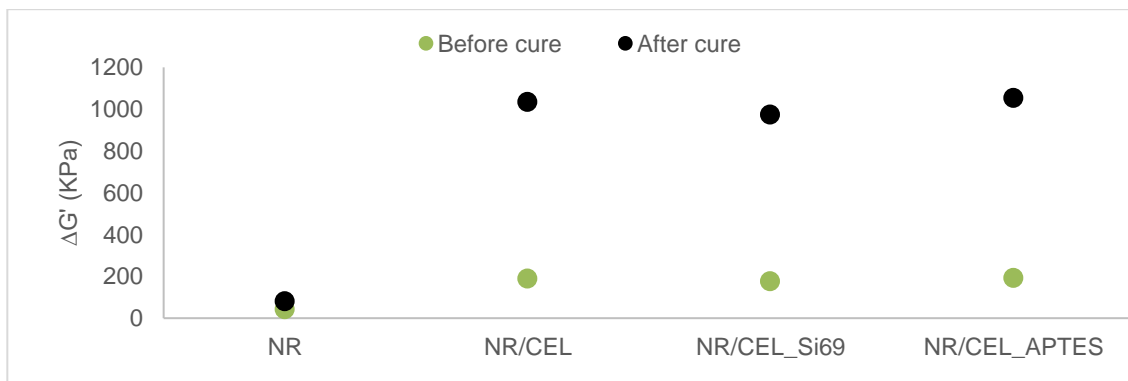


Fig. 2 Payne effect of natural rubber composites

#### 4. Conclusion

The results show that the composites containing surface treated celluloses are characterized by higher tensile strength and ductility compared to the composites containing untreated cellulose. Indicates it a good dispersion of the treated cellulose in the polymer matrix. This is also confirmed by the crosslinking density results, where the composites containing surface treated celluloses showed a higher value of the crosslinking density, which indicates a good filler-matrix interaction and may be due to the reduced hydrophilic nature of the surface treated cellulose.

#### Acknowledgements

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# Characterization and Thermal Stability of Surface Modified Cellulose in Polymer Composites

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## Abstract

This work deals with the characterization and thermal stability of surface modified cellulose as filler in polymer composites. Two different silanes have been used for surface modification of cellulose due to their ability to react with the low number of free hydroxyl groups on the cellulose surface. The natural rubber (NR) composite filled with surface modified cellulose were characterized by TG/DSC, IR spectroscopy and scanning electron microscopy.

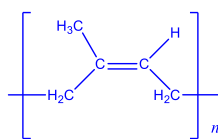
**Keywords:** thermal stability, cellulose, polymer composites, surface modification, silane, scanning electron microscopy

## 1. Introduction

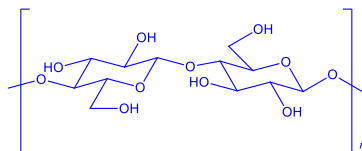
In recent years, cellulose has taken center stage of an increasing number of research papers devoted to understanding this material and its applications. Cellulose is an effective and environmental alternative material, which reduces the dependence on the conventional materials and protect our environment. From a chemical point of view, cellulose is biopolymer, which composed of polymer chains consisting of un-branched  $\beta$ -(1,4)-glycosidic linked D-glucofuranosyl building blocks, characterized by its hydrophilicity, biodegradability, and its formation of versatile semicrystalline fiber morphologies [1, 2]. The main disadvantage of this biopolymer is poor water resistance, compatibility within the hydrophobic matrix and low mechanical strength. The free of hydroxyl groups on the cellulose surface allows for a wide range of surface modifications [3].

## 2. Starting Materials

Natural rubber SMR 10 (NR) - Kuala Lumpur Malaizia.



Cellulose (CEL) - Greencel GW 70, cellulose fibres –99.5 %, bulk density 90-110 g.cm<sup>-3</sup> - Bukóza Invest, Ltd. Slovak Republic.



## 3. Methods

**FT-IR:** NICOLET iS 50 FT-IR spectrometer (ThermoFisher Scientific, USA) using ATR technique with 4 cm<sup>-1</sup> resolutions, and an OMNIC 3.2 software.

**TGA/DSC2:** STARe System Mettler Toledo; dynamic heating from 30–600°C at 10 °C/min in N<sub>2</sub>.

**Preparing of composites:** Plasti – Corder PLE 331 (80 and 90°C, at 50 rpm). The temperature of vulcanization was 150 °C.

**SEM microscopy:** TESCAN VEGA3 scanning electron microscope in the mode of secondary electrons. Au-Pd mixture was used for plating the samples.

XRD: Panalytical Empyrean (Netherlands), CuK $\alpha$  radiation,  $\lambda = 1.5405 \text{ \AA}$ , and a High Score Plus 3.0.4 software.

Surface modification of CEL:

Activation of CEL in ethanol, followed by reaction with (3-aminopropyl)triethoxysilane (APTES) or Si69 (bis(3-triethoxysilyl)propyl)tetrasulfide (5:1) at 60 °C for 2 h as described in [4].

#### 4. Results and Discussion

After modification of cellulose with both silanes, there were small changes in the intensities of some peaks. For cellulose modified with both silanes, the intensity was increased for peaks about at 1315, 1161, 1104 and 1050  $\text{cm}^{-1}$  in comparison to unmodified cellulose, and for peak about 896  $\text{cm}^{-1}$ , it was only for modification with APTES.

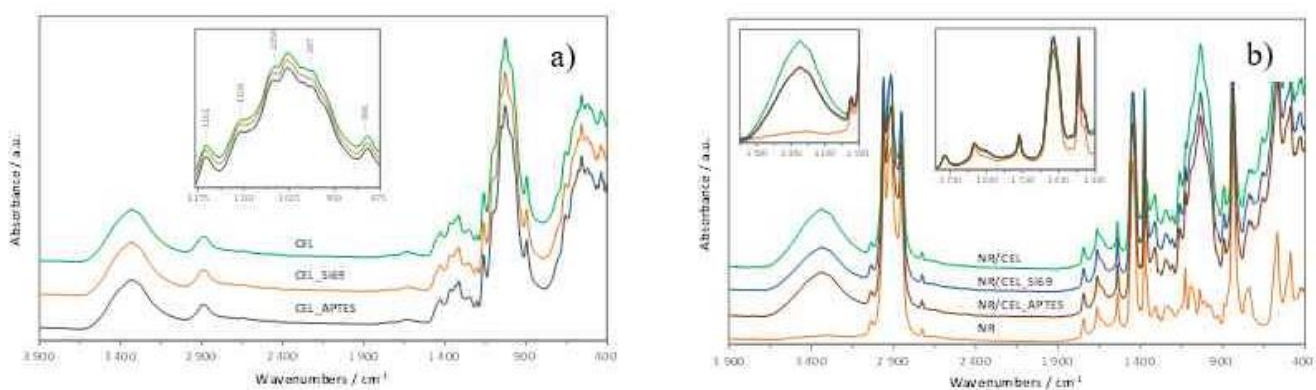


Fig. 1: ATR-IR spectra of modified and unmodified cellulose (a) and of NR, NR/45phr CEL and NR filled with 45 phr of modified cellulose (b).

The TG and DTG curves obtained at heating rate of  $10^\circ\text{C}\cdot\text{min}^{-1}$  for the unmodified cellulose and cellulose modified with APTES and Si69 are shown in Fig. 2. The degradation profile of unmodified and modified cellulose is the same, and it means that the silanization did not affect the thermal degradation process of studied cellulose.

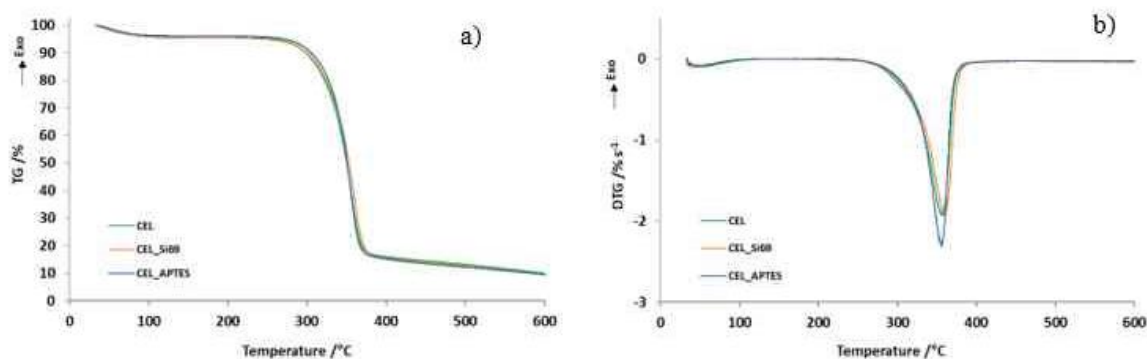


Fig. 2: TG (a) and DTG curves (b) of the unmodified cellulose (CEL) and the modified cellulose (CEL\_Si69, CEL\_APTES).

The temperature of peak maximum and the enthalpy change value of processes were evaluated from DSC curves of the NR and composites filled with unmodified and modified celluloses, and the obtained characteristics are summarised in Table 1. DSC curves of NR composites represent "multi-peak" curves due to the composites were prepared from natural rubber, filler (cellulose) and vulcanizing agents.

In DSC curves, the first endothermic peak corresponds to the decomposition of cellulose. The temperature of peak maximum for this endothermic peak is 296 °C in the case of NR/CEL and NR/CEL\_Si69 composites and 295°C for NR/CEL\_APTES composite.

Table 1: Characteristics of processes obtained from DSC curves of NR and NR composites.

Sample	Effect I		Effect II		Effect III	
	T <sub>m</sub> /°C	ΔH <sub>I</sub> / J.g <sup>-1</sup>	T <sub>m</sub> /°C	ΔH <sub>II</sub> / J.g <sup>-1</sup>	T <sub>m</sub> /°C	ΔH <sub>III</sub> / J.g <sup>-1</sup>
NR	-	-	369.5	14.3	467.8	17.2
NR/CEL	295.9	-3.7	370.4	9.9	459.1	3.4
NR/CEL_Si69	296.3	-2.1	371.7	3.1	458.8	4.4
NR/CEL_APTES	294.9	-4.7	372.3	2.5	459.8	3.4

The X-ray diffractograms for studied celluloses are shown in Fig. 3. Modified and unmodified cellulose showed typical cellulose of I structure with peaks around 15.9°, 22.4° and 34.5° of 2Theta. After modification with silanes, the intensity of diffraction peaks at 15.9° (110 plane) and 22.4° (200 plane) was enhanced. The crystallinity index value of CEL, CEL\_Si69 and CEL\_APTES was calculated to be 58.9%, 65.4% and 65.7%, respectively. These results indicate that unmodified cellulose was less crystalline than silanes modified cellulose.

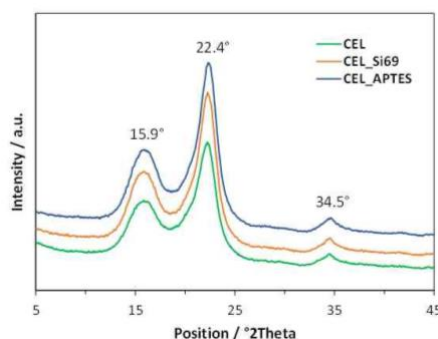


Fig. 3: X-ray diffractograms of unmodified cellulose (CEL) and modified cellulose (CEL\_Si69 and CEL\_APTES).

In Fig. 4 are SEM images of the surface morphology of unmodified cellulose and cellulose modified with silanes. As can be seen in Fig. 4c), the fiber diameter of APTES silane-modified cellulose (CEL\_APTES) is smaller than that of unmodified cellulose (CEL). SEM micrographs of modified cellulose fibers appear to be smoother, whereas the surface of unmodified cellulose is slightly scaly.



Fig. 4: SEM images of unmodified cellulose (a), modified cellulose CEL\_Si69 (b) and CEL\_APTES (c) 200x.

Fig. 5 presents SEM images of unfilled NR, NR composite filled with 45 phr unmodified cellulose (NR/CEL) and NR composites filled with modified cellulose NR/CEL\_Si69, respectively. NR/CEL\_APTES. The dispersed cellulose phase in the natural rubber matrix indicates a low quality of interface adhesion. Adhesion of filler and matrix is based on intermolecular interactions at the interface. The strain at the interface can be explained by the hydrophilic nature of cellulose and the hydrophobic nature of the natural rubber matrix. The cellulose fibers present in the prepared NR composites are randomly oriented and distributed throughout the rubber matrix.



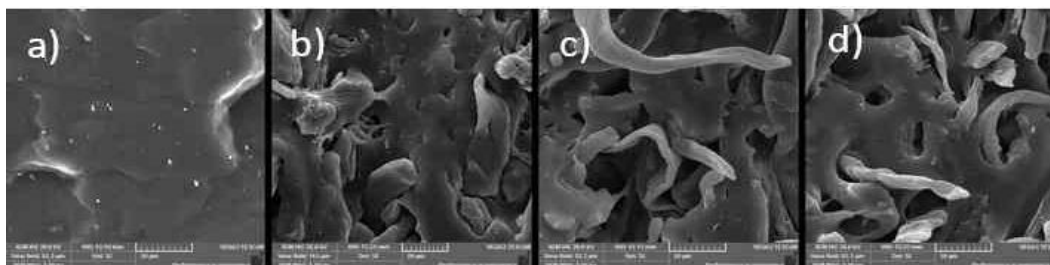


Fig. 5: SEM images of unfilled NR (a) and NR/45 phr CEL (b), NR/45 phr CEL\_Si69 (c), NR/45 phr CEL\_APTES (d) composites 200x.

## 5. Conclusion

Structure and chemical analyses of the modified cellulose were performed using advanced characterization techniques. The results show that the crystalline structure of the modified cellulose by two silanes was preserved, and modification occurred mainly on the CEL surface, which confirms the recorded crystallinity index of 58.9 % and 65.7 % for pure and modified CEL. TG analysis showed a decrease in the thermal stability of modified CEL and NR composites filled with 45 phr of modified cellulose by silanes, too.

## 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.

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# Integration of Circular Economy Thinking for Sustainable Production: Bio-based Hybrid Composites from Waste Materials

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## Abstract

The circular economy is an economic model which fosters resource efficiency, waste minimization, and innovative manufacturing. Bio-based hybrid composite materials play an essential role in the transition to a circular economy which can be a feasible option for the sustainable production of polymeric composite materials by reducing their virgin plastic content and increasing the product life cycles. This research aims to explore recycled glass waste powder and date palm leaf fiber (DPF) as a reinforcement for polymeric composite materials. To this end, material-reinforced composites were fabricated by adding predetermined mixtures from 0 to 70% of waste date palm fibers and glass waste powder to epoxy and then mechanically characterized by conducting tensile and hardness tests. The results showed that the FG/E mixture was much more homogeneous than the CG/E and DPF/E mixtures, which resulted in a more consistent tensile behavior. It is also demonstrated that the CG/E and the DPF+CG/E specimens had the lowest strains at failure. In addition, the DPF/E Specimens had the highest energy densities, up to around 50% higher than the CG/E. It was also revealed that the waste material reinforced composites are softer than the pure epoxy specimens, where DPF/E specimens were the weakest among the tested specimens. However, the hybridization increased the hardness value, where adding fine and coarse glass particles to the DPF/E mixture increased the hardness values by 38.6% and 56.4%, respectively. The authors believe that the proposed analysis can be applied to other hybrid composites produced from waste materials and reveal their mechanical and environmental performance toward ensuring dematerialization, resource efficiency, and sustainability in advanced manufacturing systems.

**Keywords:** Bio-Composites; Date Palm fibers; Glass waste; Circular Economy; Sustainable Manufacturing.

## 1. Introduction

United Nations Sustainable Development Goals (SDGs) aim to support social, economic, and environmental development at a global level. A transition to a sustainable and resource-efficient economy can be achieved by ensuring sustainable production and consumption patterns, as defined in goal 12 of UN SDGs [1]. The concept of circular economy can be considered an innovative economic model which can substantially reduce the use of nonrenewable resources and waste generation through recycling, reuse, and remanufacturing [2], [3]. This model supports sustainable product development while minimizing resource use with efficient waste management and prevention for valuable materials, including the earth's scarce metals and minerals. Using innovative manufacturing technologies such as composites from various waste materials, it can be possible to minimize the excessive use of natural resources, dependence on scarce materials and fossil fuels, and reduce the life cycle environmental impacts of production [4]. Hybrid systems are well-known in engineering design for enhanced material and structural performance [5][6]. However, nature's materials inspiration motivates the path toward advanced materials and structural techniques. One of the major obstacles to long-term waste management and mitigation is the environmental impact of discarded glass [7]. According to reports, several affluent countries' landfills have been expanded to accept around 200 million tons of waste glass each year, despite a low recycling rate [8]. Glass waste recycling is of great interest to many researchers

[9]–[14]. Auspicious results were found when integrating fine glass particles in cement-based materials due to the favorable pozzolanic reaction, which benefits the mechanical properties.

In addition, using natural plant fibers for engineering applications caught the attention of engineers for quite a while [15]–[18]. As the world demands alternative renewable materials, the interest in natural plant fibers also increases. The drive to establish more sustainable, strong materials in natural bio-composites has arisen [19]–[22]. The main advantages are that these fibers require less energy, are renewable, and are bio-degradable [23]. Additionally, they are light and have excellent acoustic and thermal insulation properties [24]. Bio-composites are now actively being explored in different technical aspects, mainly due to their ability to resist moisture, low costs, strength, and discarded natural materials [25], [26]. Most publications focus on a selected fiber and matrix and report the results of empirical fiber treatment and fiber-fraction trials [27]–[30]. Overall, the results show that the composite strength and modulus increase to a peak value by increasing the fiber content. Moisture resistance and biodegradability can also be enhanced with a high fiber volume fraction.

Phoenix dactylifera, or the date palm trees' fiber (DPF), is considered one of the common waste leaves. They are considered a renewable resource because many date palm trees are in the region, and their leaves need to be removed annually [31]. However, bio-composites face environmental instability issues, as being early attacked by natural factors that allow bio-degradability [32]–[34]. Thus, it appears necessary to conduct fundamental investigations to develop a functional green composite. Selecting effective matrix material while keeping specific fiber characteristics in mind is one of the main issues in developing bio-composites [35], [36]. Natural fibers have some limitations, including low thermal resistance, high moisture absorption, and a lack of good interfacial adhesion with plastics.

On the other hand, natural hydrophilic fibers can strengthen biopolymers and attain ultimate moisture absorption resistance at the fiber-matrix interface because of their high compatibility [37]–[39]. On the other hand, biopolymers are several times more expensive than their synthetic counterparts, limiting their use in various industries. Furthermore, synthetic resins are routinely reinforced with hydrophilic fibers to make commercially viable natural composites, which increases incompatibility difficulties such as void formation and delamination at fiber-matrix interfaces [40]–[42]. Therefore, modifications of the surface of natural cellulosic fiber by physical or chemical treatment are of primary importance to produce a rough surface topography that will enhance the fiber and matrix adhesion and mechanical properties.

Although many researchers have enumerated the process of using alkali to refine natural date palm fibers [43], more information needs to be provided regarding the type of palm to be used or the exact location of the fiber. Date palms generally have a fibrous structure, with three different types of fibers present in the peduncle: baste fibers (stem) and wood fibers (trunk) surface fibers (around the trunk) [44]. In some research, HCl was used to treat the natural fibers, and it was found to have reduced the tensile and surface distortions to a greater extent because of the acidic attack on the fibers' surface [45]. At the same time, it was also observed that increasing the NaOH concentration enhances the removal of the waxy layer covering the natural fibers [46]. The main drive behind this research is to introduce a new material utilizing waste materials as filler addition to a commercially available polymeric matrix (epoxy), where plant-based. Waste-based materials can be a viable choice for the sustainable manufacturing of polymeric composite materials by reducing their overall plastic content and increasing product life cycles, which can be a realistic option for the sustainable production of polymeric composite materials. [4]. Waste material-reinforced composites were mechanically characterized. These composite materials were fabricated by adding predetermined mixtures from 0-70% of waste date palm fibers and waste glass powder to the epoxy matrix. Mechanical tests were carried out to determine their tensile behavior and hardness.

Various studies also analyzed the applications of circular economy models in sustainable production. Hao et al. (2020) [53] analyzed the circular economy approach to green energy and investigated carbon fiber material recirculation for wind turbines at the highest possible quality. Shanmugam et al. (2020) [54] investigated the role of additive manufacturing (AM) and circular economy applications and analyzed polymer reuse and recycling for AM technologies. Naqvi et al. (2020) [55] critically reviewed recycling carbon/glass fiber reinforced composite using the pyrolysis method. The study identified a strong connection between recycling and threads' re-usability, which can foster the circular economy

and cradle-to-cradle life cycle design approach. Balaji et al. (2020) [56] discussed the importance of carbon fiber recycling technologies and reusing carbon fibers and reverting them to the circular economy. Mahdi et al. [4] investigated the Khalasa date palm leaf fiber (KDPLF) as a reinforcement for polymeric composite materials. They discussed the role of bio-based polymeric composite materials in achieving circular economy and material efficiency in manufacturing. Overall, the findings of these studies proved the benefits of composite materials from mechanical and environmental performance perspectives. However, in recent empirical studies, the sustainability impact of circular economy practices in composite material production is typically addressed only through the environmental dimension, neglecting the social and economic pillars of sustainable development [57]. These necessitate a holistic and integrated life cycle sustainability assessment of emerging manufacturing technologies necessary [58], [59].

## 2. Materials and Methods

### 2.1. Materials

The polymeric matrix comprises 100 parts mass of the epoxy resin (EL2) with a density of  $1.1 \text{ g/cm}^3$  and 30 parts mass of curing agent hardener (AT30) with a density of  $0.9 \text{ g/cm}^3$ . The collected waste glass was crushed in the PM100CM planetary ball mill machine. The delicate glass was crushed as a powder with a particle width of  $425 \mu\text{m}$  on average, while the coarse glass was crushed as particles of  $850 \mu\text{m}$  on average (Figure 1). And it was revealed from the microscopic imaging that the fine and coarse glass particles had non-uniform shapes and sizes.

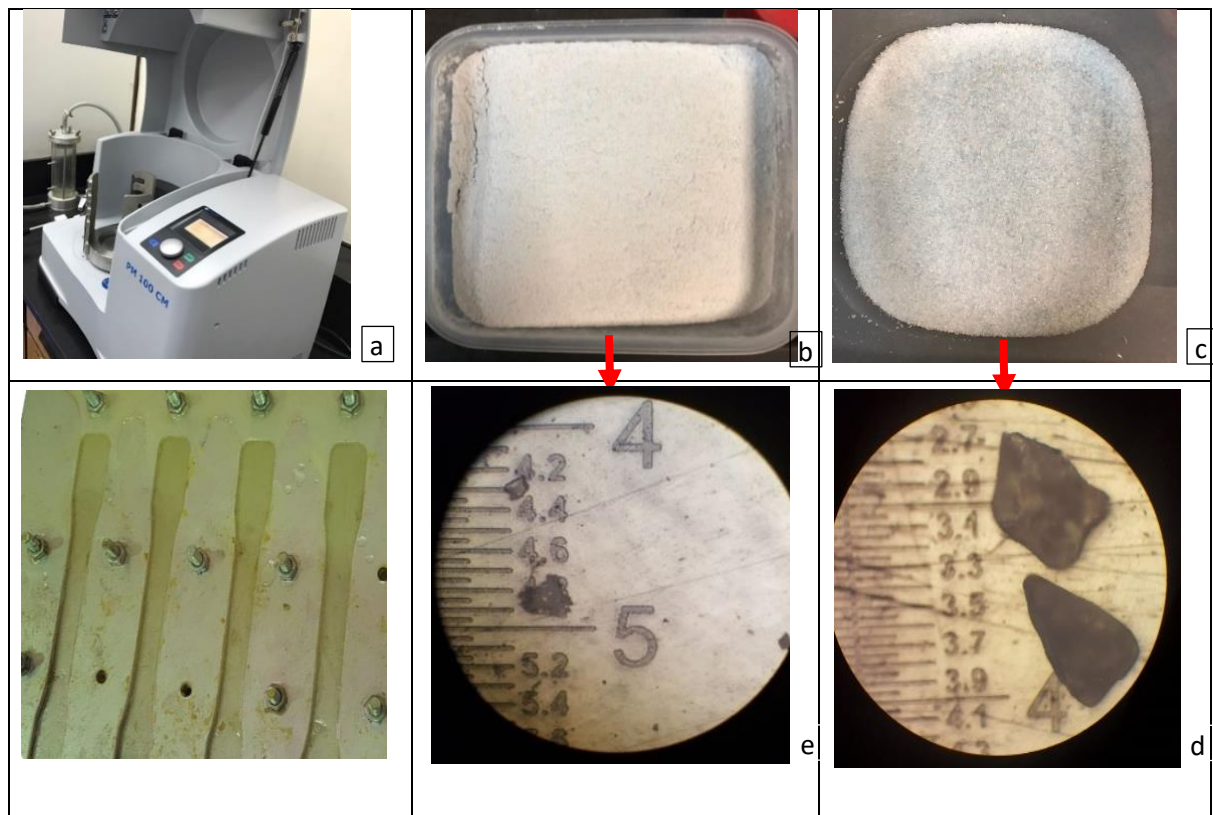


Figure 1. a- PM100CM planetary ball mill machine, b- fine glass particles, c- coarse glass particles, d- microscopic image for the fine glass particles, E- microscopic image for the coarse glass particles.

The collected DPF from local sources were washed with fresh water and dismantled into virgin bundles of fibers. They were dried at room temperature, treated with several alkaline solutions, such as calcium hydroxide ( $\text{Ca}(\text{OH})_2$ ), sodium hydroxide ( $\text{NaOH}$ ), and Lawrence solution (calcium, potassium, and sodium hydroxides mixture), and cut into smaller pieces of the desired length (0.8–1mm). Cellulose represents about (46%) of DPF weight, lignin (20%), hemicellulose (18%), water (5%), and impurities

make up the rest. The DPF has diameters larger than most natural fibers, ranging from 0.1 to 1 mm. DPF has a density of 0.917 g/cm<sup>3</sup>, thermal stability until 250°C, a tensile strength of 60 to 275 MPa, and Young's Modulus of 2 to 12 GPa. The reinforced polymer composites' mechanical properties greatly depend on their components' individual properties and the interfacial interaction (adhesion) between the polymeric matrix and reinforcements [54]. Thus, seven different filler volume fractions (10%-20%-30%-40%-50%-60%-70%) were used to fabricate the waste material/epoxy specimens for tensile testing for each filler type (fine glass powder, coarse glass powder, and date palm fibers). In addition, hybrid DPF-glass/epoxy specimens were prepared using the optimized filler volume fractions based on the specimens' tensile results (DPF/epoxy alone and glass waste/epoxy alone). And again, the same seven different filler volume fractions were used to fabricate the hybrid DPF-glass/epoxy specimens. Table 1 lists the abbreviations and descriptions for all the tested specimens in this study.

Table 1. Abbreviations and descriptions for the tested specimens

<b>ABBREVIATION</b>	<b>DESCRIPTION</b>	<b>ABBREVIATION</b>	<b>DESCRIPTION</b>
<b>FG/E-70/30</b>	Fine Glass 70% to Epoxy 30%	<b>DPF/E-30/70</b>	Date palm fiber 30% to Epoxy 70%
<b>FG/E-60/40</b>	Fine Glass 60% to Epoxy 40%	<b>DPF/E-20/80</b>	Date palm fiber 20% to Epoxy 80%
<b>FG/E-50/50</b>	Fine Glass 50% to Epoxy 50%	<b>DPF/E-10/90</b>	Date palm fiber 10% to Epoxy 90%
<b>FG/E-40/60</b>	Fine Glass 40% to Epoxy 60%	<b>DPF+FG/E-70/30</b>	Date palm fiber/epoxy 70% to Fine glass/epoxy 30%
<b>FG/E-30/70</b>	Fine Glass 30% to Epoxy 70%	<b>DPF+FG/E-60/40</b>	Date palm fiber/epoxy 60% to Fine glass/epoxy 40%
<b>FG/E-20/80</b>	Fine Glass 20% to Epoxy 80%	<b>DPF+FG/E-50/50</b>	Date palm fiber/epoxy 50% to Fine glass/epoxy 50%
<b>FG/E-10/90</b>	Fine Glass 10% to Epoxy 90%	<b>DPF+FG/E-40/60</b>	Date palm fiber/epoxy 40% to Fine glass/epoxy 60%
<b>CG/E-70/30</b>	Coarse Glass 70% to Epoxy 30%	<b>DPF+FG/E-30/70</b>	Date palm fiber/epoxy 30% to Fine glass/epoxy 70%
<b>CG/E-60/40</b>	Coarse Glass 60% to Epoxy 40%	<b>DPF+FG/E-20/80</b>	Date palm fiber/epoxy 20% to Fine glass/epoxy 80%
<b>CG/E-50/50</b>	Coarse Glass 50% to Epoxy 50%	<b>DPF+FG/E-10/90</b>	Date palm fiber/epoxy 10% to Fine glass/epoxy 90%
<b>CG/E-40/60</b>	Coarse Glass 40% to Epoxy 60%	<b>DPF+CG/E-70/30</b>	Date palm fiber/epoxy 70% to Coarse glass/epoxy 30%
<b>CG/E-30/70</b>	Coarse Glass 30% to Epoxy 70%	<b>DPF+CG/E-60/40</b>	Date palm fiber/epoxy 60% to Coarse glass/epoxy 40%
<b>CG/E-20/80</b>	Coarse Glass 20% to Epoxy 80%	<b>DPF+CG/E-50/50</b>	Date palm fiber/epoxy 50% to Coarse glass/epoxy 50%
<b>CG/E-10/90</b>	Coarse Glass 10% to Epoxy 90%	<b>DPF+CG/E-40/60</b>	Date palm fiber/epoxy 40% to Coarse glass/epoxy 60%
<b>DPF/E-70/30</b>	Date palm fiber 70% to Epoxy 30%	<b>DPF+CG/E-30/70</b>	Date palm fiber/epoxy 30% to Coarse glass/epoxy 70%
<b>DPF/E-60/40</b>	Date palm fiber 60% to Epoxy 40%	<b>DPF+CG/E-20/80</b>	Date palm fiber/epoxy 20% to Coarse glass/epoxy 80%
<b>DPF/E-50/50</b>	Date palm fiber 50% to Epoxy 50%	<b>DPF+CG/E-10/90</b>	Date palm fiber/epoxy 10% to Coarse glass/epoxy 90%
<b>DPF/E-40/60</b>	Date palm fiber 40% to Epoxy 60%		

## 2.2. Specimens preparation

Using a CNC milling machine, a mold was designed to prepare the specimens (Figure 2). First, fabricated composites were cut and characterized as per ASTM D638 standards. Next, a DMU 50 DECKEL MAHO model CNC machine made 3 mm thick aluminum plates molds. Finally, the plates and molds were coated with one layer of wax to ensure that the specimens were not stuck to the molds.

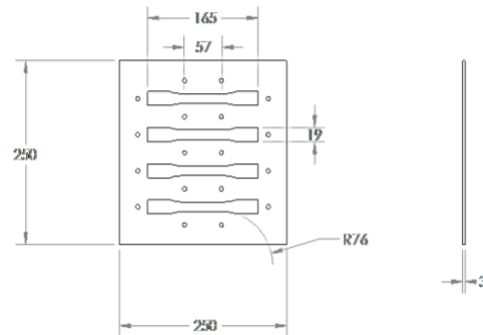
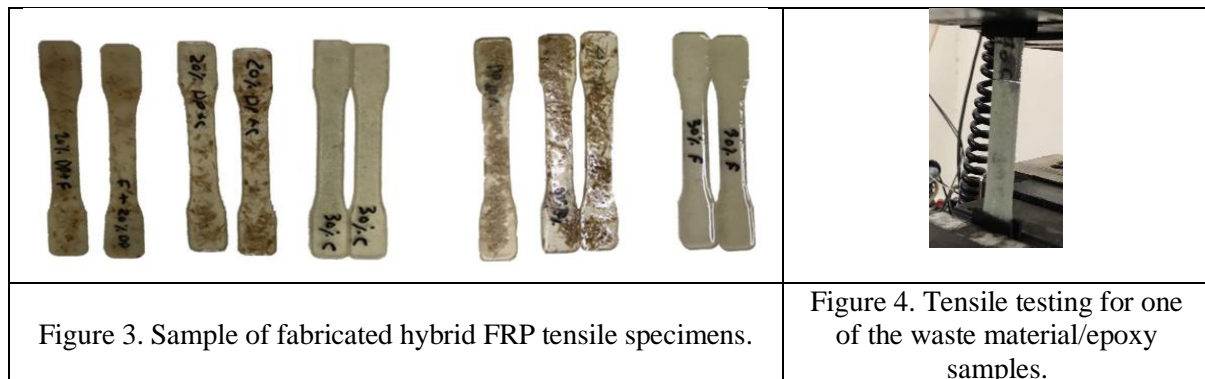


Figure 2. Designing and fabrication for tensile specimens' mold.

The appropriate fillers and epoxy resin were prepared and mixed based on the filler volume fractions presented in Table 1. Then poured into the molds and left to cure in an oven for 8 hours at a temperature of 80°C. Figure 3 presents an image of some fabricated waste material/epoxy samples.

### 2.3. Tensile testing

Universal Testing Machine INSTRON 5585H was used to conduct the tensile testing for the fabricated specimens based on ASTM D3039 standard with a crosshead speed of 1mm/min. In addition, tests were carried out for three identical specimens to guarantee the reliability of the results.



### 2.4 Hardness test

Surface hardness is considered one of the most critical factors in composites to determine wear rate. The filler volume fraction significantly affects the hardness and density of prepared composites. Thus, three identical cylindrical specimens were prepared for each waste material/epoxy composite (FG/E, CG/E, DPF/E, DPF+FG/E, and DPF+CG/E) by molding method. The fabricated composites were subjected to a Brinell Hardness test to evaluate their hardness property. Brinell hardness was measured for each specimen, where the measurements were done using a load of 7.5 kN.

## 3. Results and Discussion

### 3.1. Tensile Behavior

Typical stress/strain curves obtained from tensile testing of FG/E, CG/E, DPF/E, DPF+FG/E, and DPF+CG/E composite samples with different filler volumes fractions are shown in Figures 5-9. For all the cases, stress increased linearly with increasing strain up to a knee point, which occurred at different strain levels. In the case of FG/E, the highest ultimate tensile strength is demonstrated by the FG/E-70/30 specimen. In contrast, for both CG/E and DPF/E specimens, the highest strength level was achieved by

specimens with a filler volume fraction of 60/40. In the case of hybridization (DPF+FG/E and DPF+CG/E), the highest stress levels were detected at a filler volume fraction of 10/90 and 30/7, respectively. The stress-strain curve nonlinearity was associated with deformation, matrix cracking, and microfracture. The cracks observed that grew through the resin-rich areas for the CG/E and DPF/E specimens were attributed to the non-uniform resin distribution. The CG/E and the DPF+CG/E specimens had the lowest strains at failure. In addition, the DPF/E Specimens had the highest energy densities, up to around 50% higher than the CG/E. The correlation of these results highlights the importance of having a homogeneous combination of glass and date palm in an epoxy matrix.

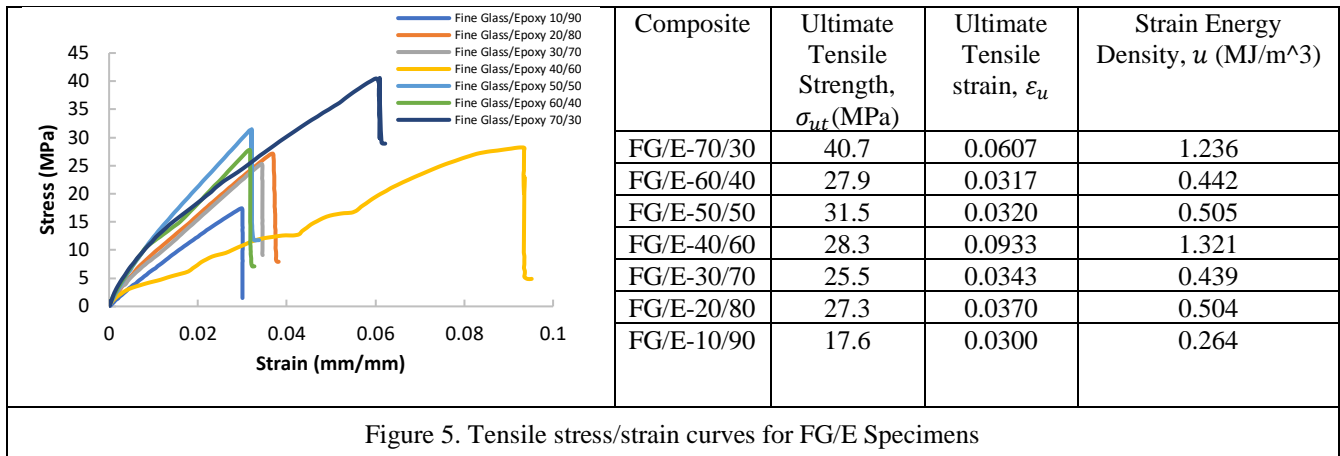


Figure 5. Tensile stress/strain curves for FG/E Specimens

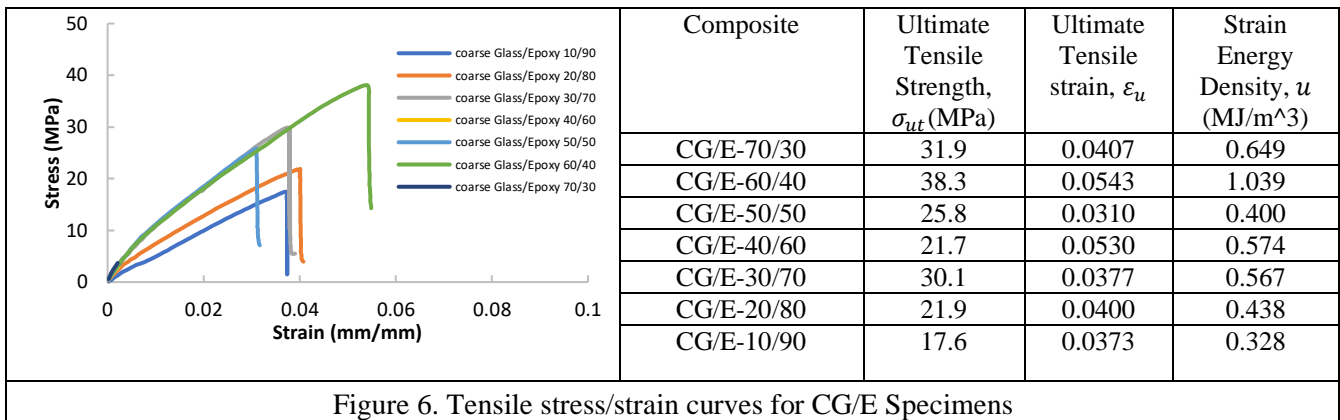


Figure 6. Tensile stress/strain curves for CG/E Specimens

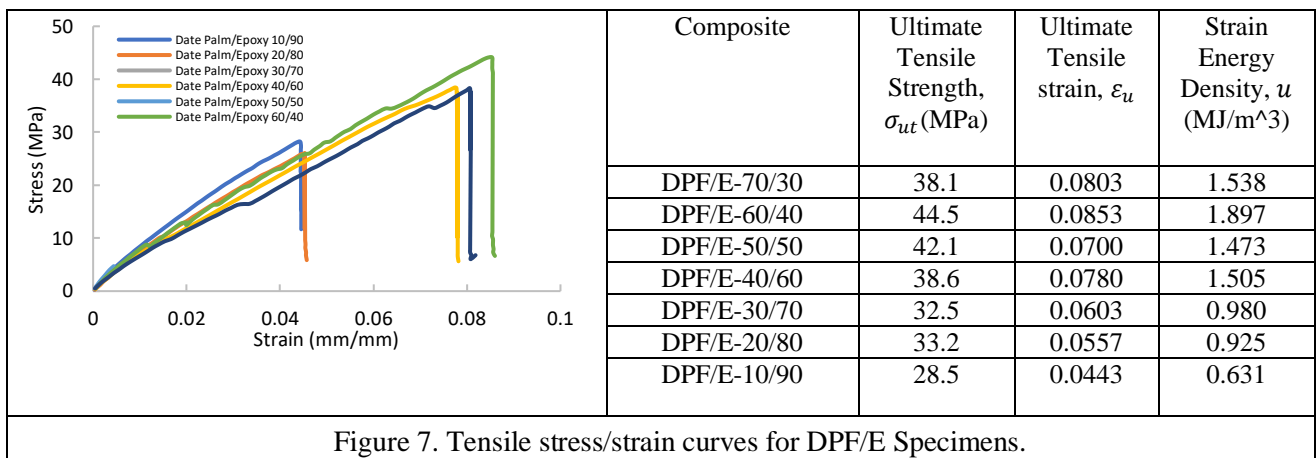


Figure 7. Tensile stress/strain curves for DPF/E Specimens.

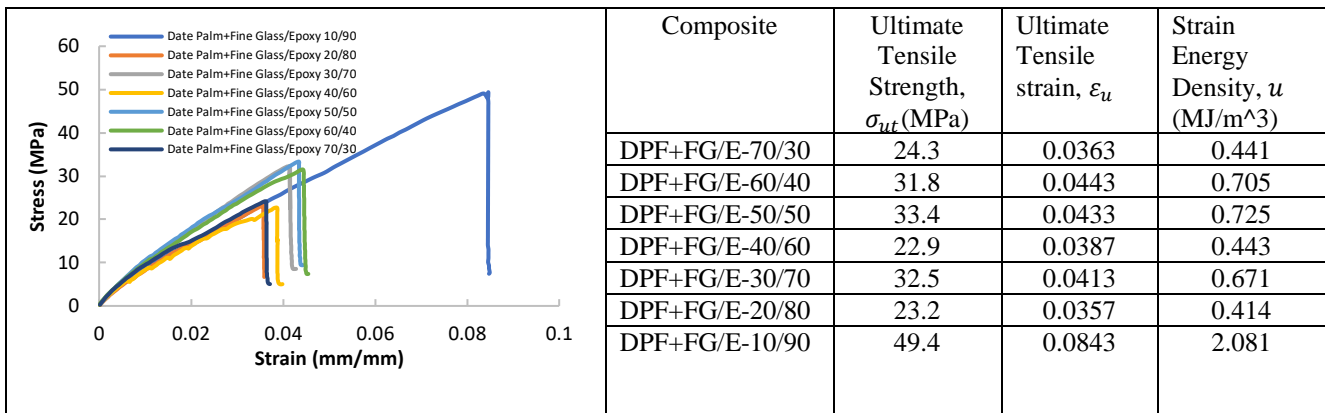


Figure 8. Tensile stress/strain curves for DPF+FG/E Specimens

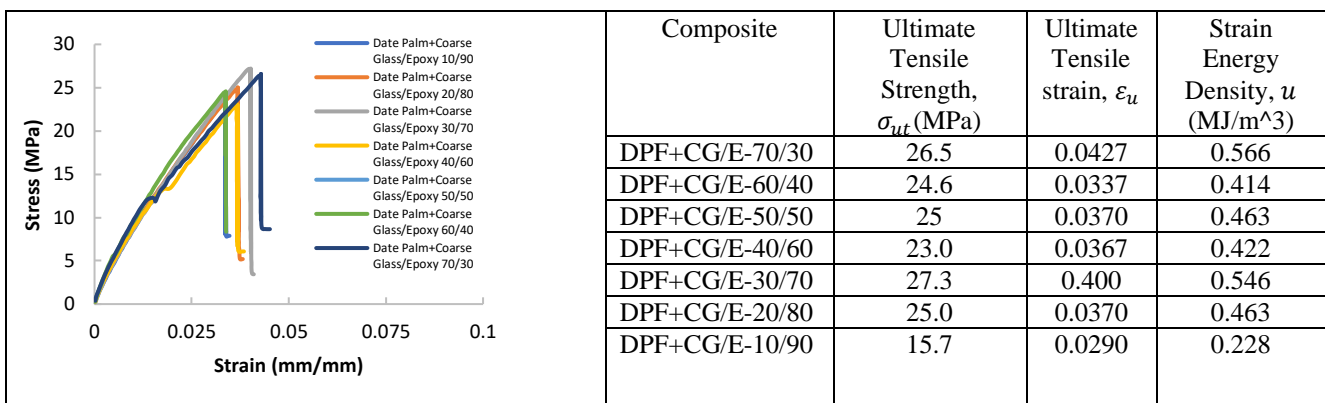


Figure 9. Tensile stress/strain curves for DPF+CG/E Specimens.

### 3.2. Hardness

Table 2 presents the Brinell hardness values for the tested specimens. It is well noticed that the waste material reinforced composites were softer than the pure epoxy specimens, where DPF/E specimens were the softest among the tested specimens. However, the hybridization increased the hardness value, where adding fine and coarse glass particles to the DPF/E mixture increased the hardness values by 38.6% and 56.4%, respectively.

Table 1. Brinell hardness values for the different tested samples.

Material	Hardness (BHN)	Fabricated Specimens
Resin	79.11	
70% Fine	47.78	
70% Coarse	60.85	
60% Date Palm	35.3	
70% DP +Fine glass	48.94	
30% DP + Coarse glass	55.22	

### 3.3. Carbon emissions

To compare the environmental performance of different designs, we conducted a carbon footprint analysis. Using the Ecoinvent v. eight databases, the total carbon footprint analysis is performed. The



study considered the amount of glass, epoxy, and electricity (see Fig. 10a). The results showed that FG/E-70/3 is found to have the most significant carbon emissions to relatively higher electricity consumption to produce fine glass powder. It is followed by FG/E-60/30, whereas the DPF specimens have the lowest carbon footprint compared to fine and coarse glass powder mixed epoxy specimens. Fig. 10b also presented the total carbon footprint versus tensile strength to present the environmental performance against the mechanical performance. The results showed that DPF/E-60-40 is found to have the lowest carbon footprint per tensile strength and is followed by DPF/E-50/50 and FG/E-70/30. In contrast, FG/E-10/90 and CG/E-10/90 have higher carbon emissions against their mechanical performance in terms of tensile strength. Overall, DPF specimens showed a better performance in terms of total emissions per tensile strength.

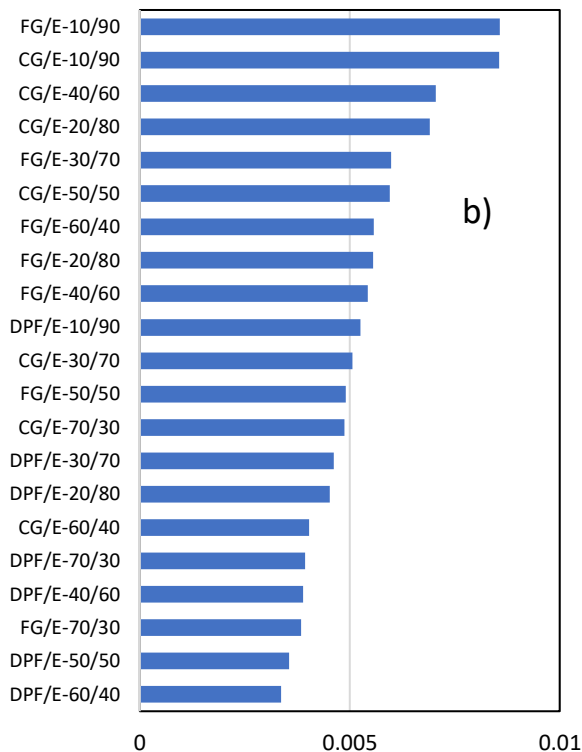
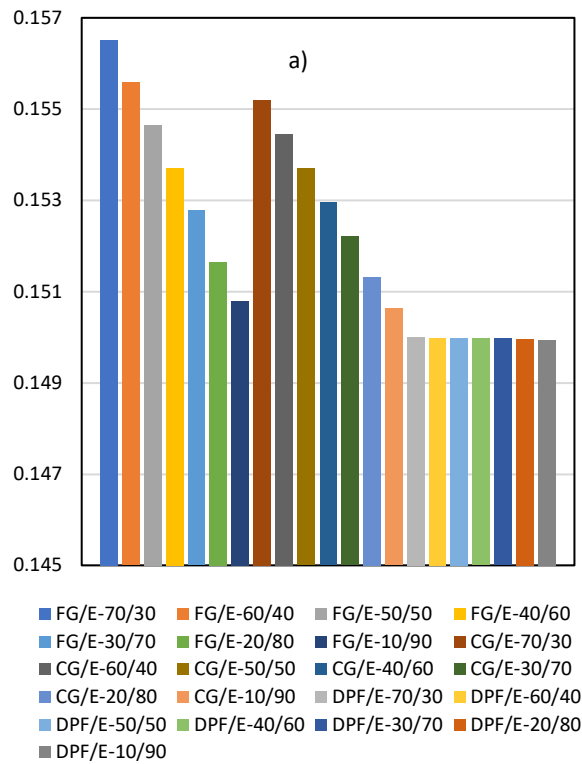


Figure 10. Carbon footprint analysis a) total carbon footprint (kg CO<sub>2</sub> eq); b) total carbon footprint /tensile strength (kg CO<sub>2</sub> eq/ MPa)

#### 4. Conclusion and Future work

This paper explores glass waste and date palm leaf fiber (DPF) as a reinforcement for polymeric composite materials. To this end, waste material reinforced composites were fabricated by adding

predetermined mixtures from 0-70% of waste date palm and glass to epoxy and then mechanically characterized by conducting tensile and hardness tests. The FG/E mixture was much more homogeneous than the CG/E and DPF/E mixtures, which resulted in a more consistent tensile behavior. The CG/E and the DPF+CG/E specimens had the lowest strains at failure. In addition, the DPF/E Specimens had the highest energy densities, up to around 50% higher than the CG/E. The correlation of these results highlights the importance of having a homogeneous combination of glass and date palm in an epoxy matrix. In addition, it was revealed that the waste material reinforced composites are softer than the pure epoxy specimens, where DPF/E specimens were the softest among the tested specimens. However, the hybridization increased the hardness value, where adding fine and coarse glass particles to the DPF/E mixture increased the hardness values by 38.6% and 56.4%, respectively. In addition, this paper presented a novel approach to using waste materials to reinforce composites, and mechanical tests was then performed. Carbon footprint analysis compares the environmental performance of different weight compositions of recycled date palm and glass powder waste in bio-based hybrid composite materials. For future research, the authors propose developing a full life-cycle-sustainability-assessment model to compare waste material-reinforced composites' social, economic, and environmental impacts. Furthermore, various metrics such as eco-efficiency, energy intensity, resource intensity, and renewability ratio can be developed to investigate the sustainability performance of each composite material alternative. Using multi-criteria decision-making methods such as Analytic Hierarchy Process (AHP), Weighted Sum Model (WSM), Weighted product model (WPM), Technique for Order Preference by Similarity to Ideal Solution (TOPSIS), VIKOR, PROMETHEE, ELECTRE, and Multi-Attribute Utility Analysis (MAUA), the current research can be extended with expert-based decision making considering the trade-offs between indicators of sustainability towards the selection of the most sustainable composite materials.

### **Declaration of Competing Interest**

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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# Influence of Physical Modified Biopolymer by Ultrasound and its Application in NR Composites

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## Abstract

In this work, cellulose was physically treated by means of ultrasound in an aqueous environment. The time and temperature of the aqueous solution of cellulose under the influence of ultrasound were monitored, which could increase the possibility of the reaction of cellulose with microbubbles generated by the ultrasound process. Cellulose treated in this way was mixed with a matrix of natural rubber. Morphology, curing characteristics and physical-mechanical properties were studied on the prepared composites. The use of ultrasound could lead to a reduction in the costs associated with the chemical treatment of cellulose (solvent, modifying agent).

**Keywords:** physical treatment, cellulose, elastomeric composites, morphology, ultrasound

## 1. Introduction

Currently, a great deal of research is devoted to polymer composites with satisfactory properties. Among the fillers used in the elastomeric matrix, biopolymers such as starch and cellulose can be used [1]. Cellulose is a high molecular weight biopolymer containing glucose units connected to each other by  $\beta$ -1,4-glycosidic bonds, as well as intra- and intermolecular hydrogen bonds. The high percentage of crystallinity in cellulose makes it difficult for cellulose to dissolve or hydrolysis [2, 3]. To achieve better solubility, hydrolysis and miscibility with the polymer matrix, it is advisable to adjust the cellulose structure, particle size, and crystallinity. Ultrasound can be an ecological method for the physical treatment of cellulose. In this way, it would be possible to obtain cellulose with lower crystallinity and larger aspect ratio with a diameter in the nanometre range, which is the basis for choosing the optimal cellulose treatment process with a focus on its use as a reinforcing filler in elastomeric composites of great industrial importance.

## 2. Experimental

### 2.1. Material

Cellulose GW 70 used in this work was provided by Grencel Ltd. company (Hencovce, Slovakia), and distilled water by TnUAD. Natural rubber SMR 10 purchased from Kuala Lumpur Malaizia. Zinc oxide purchased from SlovZink a.s. (Košeca, Slovakia). Stearic acid purchased from Setuza a.s. (Ústí nad Labem, Czech Republic), linseed oil purchased from Novochema (Levice, Slovak Republic). Sulphur type Crystex OT33 purchased from Eastman Chemical company (Kingsport, TN, USA). N-tert-butyl-2-benzothiazole sulphonamide (TBBS) purchased from Duslo a.s. (Šaľa, Slovakia).

Before ultrasonic treatment, cellulose was soaked in distilled water for 24 hours. The cellulose suspensions (1 and 4 wt. %) were treated 4 hours by ultrasonication using a Bandelin electronic DT 106 sonifier at frequency of 35 kHz. The ultrasonically treated cellulose was filtered and dried at 105°C for 48 hours.

The changes in cellulose suspension after ultrasonic treatment were observed visually using the sedimentation experiment under various time (0 and 24 hours).

For physically ultrasonically treated cellulose and raw cellulose, microstructural analysis was observed using a Tescan VEGA3 thermoemission scanning electron microscope (Tescan, Brno) in the solar electron (SE) mode with the applied accelerating voltage (HV) set at 20 to 30 kV.

The cellulose samples were analysed via X-ray diffraction (XRD) in a PANalytical Empyrean X-ray diffractometer (PAN Analytical, the Netherlands) with CuK $\alpha$  radiation ( $\lambda = 1.5405 \text{ \AA}$ ). The intensities were measured in the 5–45° 2Theta range.

Natural rubber was mixed with fillers on cellulose treated on a surface as well as other chemicals necessary for curing via the sulphur system. All ingredients were mixed using an internal Plasti-Corder Brabender®EC mixer plus (Brabender, Duisburg, Germany) at initial temperature 100 °C with a rotor speed of 50 rpm and a fill factor of 0.70.

The rheological properties of the unvulcanized elastomeric composites were measured by using a rubber process analyser (PRPA 2000) (Alfa Technologies, Akron, OH, USA) in accordance with ASTM 5289. The curing characteristics were determined at an oscillating frequency 1.67 Hz and set at a temperature of 150 °C.

Mechanical properties of elastomeric composites were measured by using a universal testing machine – Shimadzu Autograph AG-X plus – 5kN operation (Shimadzu, Tokyo, Japan). Tensile strength and elongation were determined according to the ASTM D412 87 standard. The dumbbell-shaped samples of elastomeric composites were subjected to a stress–strain test with a cross head speed of 100 mm/min. Hardness of elastomeric composites was determined to ASTM D 2240 86 using a Shore A Durometer hardness tester (Wallace LTD, Croydon, UK).

The crosslinking density of the elastomeric composites was determined by its equilibrium swelling in solution. Based on the Flory-Rehner equation, the crosslinking density was determined using Eq. (1):

$$-\ln[(1 - v_r) + v_r + \chi v_r^2] = \rho v_s M_c^{-1} (v_r^{1/3} - v_r/2) \quad (1)$$

### 3. Results and discussion

In 1% solution of untreated cellulose, the cellulose fibres were settled at the bottom of the glass container. After ultrasonic treatment, a substantial increase in the dispersion of cellulose suspension was observed, and a more colloidal solution was obtained above the sedimented cellulose. For 4% solution of cellulose, the result of sedimentation experiment is not clearly visible.

#### 3.1. SEM microstructure analyses

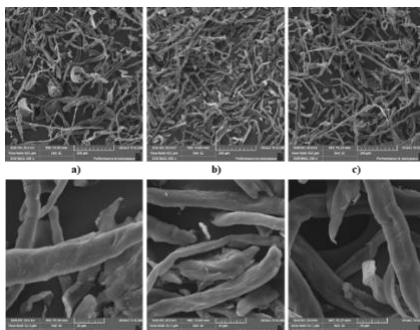


Fig. 1 SEM images of cellulose a), CEL\_1%U b), CEL\_4%U c), at 200x and 1500x magnification

Significant changes in surface micromorphology are observed on the CEL\_1%U cellulose microfibrils (Fig. 1b), which are due to the presence of non-uniformities in the surface microstructure of the fibrils. The micro-mechanism of degradation on the fibre surface may be due to the effect of ultrasonic waves in combination with the prepared 1% solution that was applied to the sample. It can be seen from Fig. 1c that no significant change in the surface micromorphology of microfibrils was observed with this treatment of the sample, compared to untreated cellulose. For cellulose treated sample CEL\_4%U at 200x magnification, longitudinal fibrils are observed whose length is visibly greater compared to untreated cellulose and CEL\_1%U cellulose.

#### 3.2. XRD of the ultrasonic ultrasonically treated cellulose

The major peaks observed in all celluloses are at 2Theta diffraction angles of 15.9° (110 plane), 22.4° (200 plane) and 34.5° (004 plane) indicating the typical cellulose. After ultrasonic treatment, there is no significant difference in crystallinity between CEL\_1%U and CEL\_4%U samples (Fig. 2), suggesting that the cellulose concentration during ultrasonication had not an influence on the crystalline parts of the cellulose.



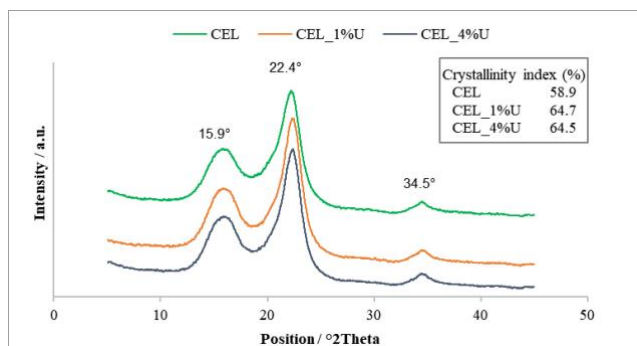


Fig. 2 X-ray diffraction patterns of untreated CEL, treated CEL\_1%U and CEL\_4%U

### 3.3. Thermal properties of the ultrasonically treated cellulose

The TG and DTG curves of the untreated and ultrasonically treated cellulose are shown in Fig. 3. All untreated and ultrasonically treated celluloses show the same degradation profile, which indicates that the ultrasonication process does not affect the thermal degradation process of studied samples.

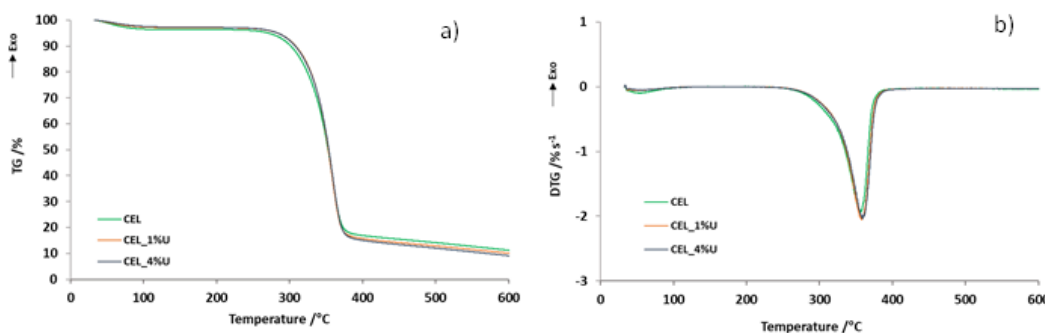


Fig. 3 G (a) and DTG curves (b) of the untreated cellulose (CEL) and the ultrasonic treated celluloses (CEL\_1%U, CEL\_4%U)

### 3.4. Infrared spectroscopy of the ultrasonically treated cellulose

After ultrasonic treatment, the spectra of celluloses were fairly close to that of the untreated cellulose, and it suggests that the original structure of cellulose was maintained after ultrasonication. In the spectra after ultrasonic treatment, there was only a little reduction in the intensities of peaks at  $\sim 3331$  and  $\sim 2894$   $\text{cm}^{-1}$  for CEL\_1%U sample in comparison with the untreated cellulose. For CEL\_4%U, there was only a little intensity reduction of the shoulder near of  $3420$   $\text{cm}^{-1}$ . For both celluloses after ultrasonic treatment, the intensity was slightly increased for peaks about at  $1315$ ,  $1161$ ,  $1104$ ,  $1050$  and  $896$   $\text{cm}^{-1}$  in comparison with untreated cellulose, however, for peaks at  $\sim 1000$  and  $\sim 987$   $\text{cm}^{-1}$ , the intensity was slightly reduced.

### 3.5. Curing Characteristics of the Elastomeric Composites

The values of minimum torque ( $M_L$ ), maximum torque ( $M_H$ ), scorch time ( $t_s$ ) optimum curing time ( $t_{90}$ ) were determined from the cure curves of elastomeric composites with untreated and ultrasonically treated cellulose (Table 1).

Table 1: Curing characteristics of natural rubber composites.

Composites	$M_L$ (dN.m)	$M_H$ (dN.m)	$t_s$ (min)	$T_{90}$ (min)
NR	1.53	12.80	4.75	9.03
NR/CEL	1.39	23.71	4.57	9.16
NR/CEL_1%U	1.48	22.83	4.94	9.68
NR/CEL_4%U	1.41	24.29	4.75	9.43

For the NR composites filled with ultrasonically treated cellulose, there was an increase in the minimum torque values compared to the NR composite filled with untreated cellulose. The results showed that there was an increase in the maximum torque values for the filled composites compared to the unfilled NR. The  $t_s$  values of the filled composites were lower compared to the unfilled NR, which may be related to the fact that the hydroxyl

groups present on the cellulose surface limit the movement of free radicals generated during vulcanization, which reduces the curing rate [4,5]. In the case of filled composites, the values of the optimum curing time  $t_{90}$  increased compared to the unfilled NR.

### 3.6. Mechanical Properties of the Elastomeric Composites

The tensile strength, elongation, shore A hardness and crosslinking density for sample NR, NR/CEL, NR/CEL\_Si69 and NR/CEL\_APTES rubber composites are showed in Table 2.

Table 2: Curing characteristics of natural rubber composites.

Composites	Tensile strength (MPa)	Elongation (%)	Shore A Hardness	Crosslinking density ( $\cdot 10^{-4} \text{ mol}\cdot\text{cm}^{-3}$ )
NR	$17.17 \pm 1.58$	$795 \pm 33.72$	$36.33 \pm 0.41$	$5.27932 \pm 0.45$
NR/CEL	$5.47 \pm 0.87$	$334 \pm 44.24$	$73.59 \pm 0.17$	$8.08643 \pm 0.21$
NR/CEL_Si69	$5.73 \pm 0.39$	$358 \pm 33.36$	$72.82 \pm 0.29$	$8.39166 \pm 1.28$
NR/CEL_APTES	$6.45 \pm 0.49$	$365 \pm 31.79$	$72.97 \pm 0.70$	$8.82627 \pm 0.61$

The filled NR composites exhibit significantly lower tensile properties compared to the unfilled NR. The reduction in these properties may be related to the presence of a high number of hydroxyl groups in the cellulose, which causes agglomerations in the rubber matrix [6]. The elongation at break for the NR/CEL\_4%U composite showed higher values compared to the NR/CEL composite. The increase in elongation may be due to the fact that we observed longitudinal fibres whose length was visibly greater compared to the untreated cellulose and CEL1%U cellulose (Fig. 2c). The NR/CEL and NR/CEL\_4%U composites exhibited lower crosslinking density compared to the unfilled NR. In the case of CEL\_1%U untreated cellulose composite, there was an increase in the value of crosslinking density compared to NR composite. In the NR composite with cellulose CEL\_1%U, there is a slight increase in the crosslinking density. For NR composite filled with CEL\_4%U, the crosslinking density decreases. The increase in the crosslinking density can be attributed to the presence of hydroxyl functional groups and the three-dimensional network structure of cellulose, which help in the formation of additional crosslinks with NR through the deprotonation of cellulose in the presence of  $\text{Zn}^{2+}$  from the used ZnO [7].

### 3.7. XRD of the elastomeric composites

In the case of the NR composite, a diffuse peak for amorphous NR was observed at 2Theta diffraction angles of  $18,22^\circ$  and several sharp peaks to the right at 2Theta diffraction angles of  $30^\circ$ , which are characteristic of ZnO and stearic acid. In the case of NR composites filled with untreated and ultrasonically treated cellulose, changes in intensity and angle ( $2\theta$ ) of the broad region and an added peak that is characteristic of cellulose can be observed at 2Theta diffraction angles of  $18,22^\circ$ .

### 3.8. Thermal properties of the elastomeric composites

After the thermal treatment of NR composites filled with cellulose, there is the higher residue, which represents the products of thermal decomposition of cellulose. All filled composites show a lower initial temperature of degradation in comparison to the NR.

### 3.9. FTIR of the Elastomeric Composites

There is no significant difference between spectra of NR/CEL and NR/CEL\_1%U composites. In the spectra of the composites, the characteristic peaks originate from cellulose are present in the spectral range of  $1350\text{--}850 \text{ cm}^{-1}$ . In comparison with NR/CEL\_1%U composite, the intensities of peaks at  $1446$ , and  $1375 \text{ cm}^{-1}$ , which correspond to the  $\delta(\text{CH}_2)$  and  $\delta(\text{CH}_3)$  vibrations, respectively, was decreased for the NR/CEL\_4%U composite. Similarly, there was observed the decrease in intensity of peaks in the spectral range of  $1200\text{--}900 \text{ cm}^{-1}$  for NR/CEL\_4%U composite in comparison with NR/CEL\_1%U composite.

## 4. Conclusion

In this work, cellulose was physically treated using ultrasound and then applied to a natural rubber matrix. In CEL\_1%U, a significant number of microfibrils were observed, which were elongated in shape, but their length

was smaller compared to cellulose fibers. In the case of the cellulose treated by ultrasound (CEL\_4%U), longitudinal fibrils were observed, the length of which was visibly longer compared to untreated cellulose and CEL1%U cellulose. The reduction of these properties could be related to the presence of a high number of hydroxyl groups in the cellulose, which causes agglomerations in the rubber matrix.

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## Pretreatment and modification of cellulose as a filler for elastomeric composites

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### Abstract

This study evaluates changes in the properties of the prepared elastomeric composites. The vulcanization characteristics (minimum and maximum torque, processing safety, vulcanization speed coefficient and optimal vulcanization time) and physico-mechanical characteristics (static tensile test - change in strength, elongation at break and dynamic tensile test – using the DMA thermal method) were studied and evaluated. The natural rubber was filled with cellulose (CEL). The study of the properties of the filler cellulose was carried out on cellulose pretreated with ozone and cellulose modified by DCSBD plasma discharge. The mentioned and modified devices are well feasible under both laboratory and industrial conditions. In addition, both represent a combination of environmentally, economically, and partly also technologically acceptable processes. The ideal setting/implementation of the pretreatment and modification of the filler, cellulose as filler, is crucial to achieve the best dispersion effect of the filler in the matrix, and thus for ensuring adequate adhesion between the filler and the matrix. At the same time, when rubber compounds are used, it is important that the elastomeric composites effectively fill the mould cavities before the vulcanisation itself begins. The increasing demand for materials with tailor-made properties, which must also meet the needs of multifunctional use, leads to the development of commercial elastomeric composites with fillers that mediate these properties.

**Keywords:** Ozone, DCSBD plasma; Cellulose; Composites; DMA analysis

### 1. Introduction

Cellulose is among the most widespread biopolymers found in nature. Today, a lot of attention is paid mainly to the use of cellulose in polymer composites. The advantage of cellulose is that it has good mechanical properties and a low coefficient of thermal expansion. However, it is hydrophilic in nature, which leads to poor compatibility with hydrophobic polymers and thus also to deteriorated mechanical properties of the resulting composites. For this reason, it is necessary to modify the cellulose surface or edit. There are many methods of fiber treatment based on mechanical, chemical, biological or physical action. However, it is important to consider whether the mentioned methods are effective, without serious cellulose degradation and do not burden the environment. Chemical methods of cellulose treatment (oxidation, hydrolyses, esterification, etherification, silanization) are used to reduce crystallinity [1]. However, most chemical methods have the disadvantage that they are toxic and burden the environment. Plasma can be used for the surface modification of polymers [2]. The composition of the working gas in plasma treatment leads to material ablation, activation or cross-linking [3]. There is a change in the physicochemical properties of the polymer surface (wettability, adhesion, refractive index, chemical resistivity, slipperiness and biocompatibility [4]. Plasma treatment results in partial decomposition and the formation of new functional groups on the polymer chain [5]. Another physical surface treatment of polymers is ionization by corona discharge [6]. Advanced modifiers include ozone. Ozone treatment is nontoxic, ozone is readily available, and no additional separation steps are required. When ozone is used to treat polymers, time, energy, and water are saved and the impact on the environment is reduced. Ozone can be created from oxygen or dry air [7]. Ozone is used to treat the surface of polyester fibres [8], to depolymerisation of cellulose [9], to improve the solubility of cellulose in alkaline solutions [10], removal of lignin from cellulose [11], etc. In our work, we focused on the surface treatment of cellulose with ozone and plasma in order to improve the interfacial adhesion between the filler (cellulose) and the hydrophobic polymer matrix (natural rubber) in the preparation of elastomeric composites.

## 2. Material and methods

The pretreatment of CEL was carried out in an ozone atmosphere using a simple ozone generator (total 45 minutes of exposition). The modification of CEL was performed by a DCSBD plasma (CEL exposed to plasma for 3 minutes/surface). The DCSBD power unit was set at 350 W. The fluorescence of the the surfaces of prepared elastomeric compounds was determined by the Recognoil ® 2W device. The relevant modules of dynamic-mechanical analysis were determined (in a selected temperature interval – 100 ° C to + 50 ° C) on the TA Instruments Q800 with a frequency of 60 Hz. Tensile strength and elongation were achieved on the Shimadzu AG-X Plus device Tensile tester. Curing characteristics were studied on an Alfa Technologies PRPA 2000.

## 3. Results and discussion

The dispersion of cellulose as a filler in the prepared elastomeric composites (ECs) was studied as the average fluorescence value of the surfaces of the upper and bottom surfaces of all ECs: ozone pretreated cellulose, plasma-modified cellulose and cellulose not treated – RAW. The measured values were then subjected to the Grubbs test to identify values that do not meet the standard criterion of Alpha = 0.05 and the values obtained are marked as outliers. Values marked as outliers were not included in the mean value or standard deviation interval. The different fluorescence values of the surfaces of the prepared composite elastomeric composites also correspond to the different visual dispersion of cellulose on the surfaces of the elastomeric composites. Cellulose pretreated with ozone can often be visually observed to aggregate. The highest average surface fluorescence value = 4,100,419 [F. U.]. Locally observed maximum fluorescence values on the fluorescence maps were evidence of cellulose aggregation. Cellulose alone (RAW) achieves a high fluorescence value (15,973,500 F.U.) on the surface of the mixture. Exactly such values have often been observed in fluorescence maps of elastomeric composites with ozone-pretreated cellulose. The dispersion of cellulose, which has been modified by plasma, cannot be visually observed or assessed. The average fluorescence value of the surfaces of the mentioned elastomeric composites is 2,230,806 [F. U.]. Therefore, the measured fluorescence values were the lowest, almost 52% less than in the cellulose mixture with ozone-pretreated cellulose. Cellulose dispersion that has not been pretreated or modified visually resembles cellulose pretreated with ozone to a lesser extent. The visually observed aggregation of RAW cellulose is less intense and is observed on a smaller surface area of the mixture. The average fluorescence value of the surfaces of elastomeric composites with RAW cellulose as filler is 3,487,554 [F. U.]. Therefore, the average value of fluorescence is lower than that of the surfaces of elastomeric composites with ozone-pretreated cellulose, but higher than that of the surfaces of elastomeric composites with plasma-modified cellulose.

The highest tensile strength (8 MPa) was measured for an EC with plasma-modified cellulose (Figure 1, left). The EC that contained cellulose in its original state (RAW) has a lower tensile strength (6.5 MPa). The EC with ozone pretreated has the lowest tensile strength (6.2 MPa).

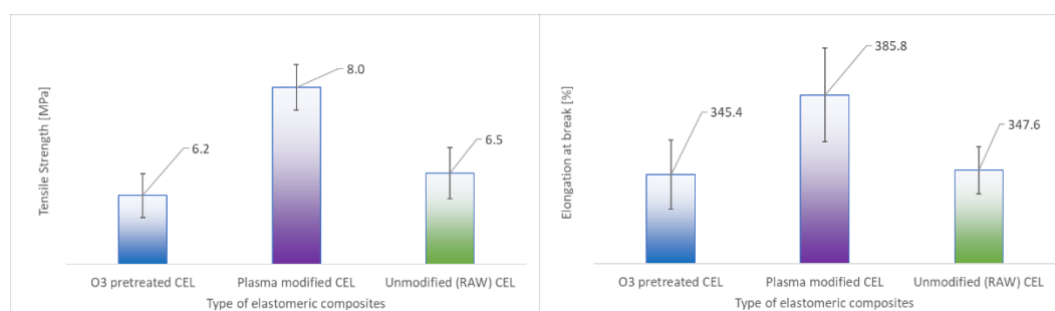


Figure 1: Tensile strength and elongation at break of prepared ECs.

The effect of cellulose on the elongation at break of elastomeric composites has the same trend as in tensile strength (Figure 1, right). The highest value of the elongation at break of the ECs was measured in a elastomeric compositite (EC) with plasma-modified cellulose (385.8 %). A slightly lower elongation at break (347.6 %) was measured in an EC that contained cellulose in its original condition (RAW) as filler. A very similar value of elongation at break (345.4 %) was measured in an EC with cellulose pretreated with ozone.

The addition of cellulose as a filler to elastomeric composites (cellulose pretreated with ozone or modified by plasma or untreated) was carried out to determine changes in the temperature of the glass transition and determine the Tan delta values. Depending on the maximum value of the Tan delta peak, there is a glassy transition of individual elastomeric composites at a temperature interval of approximately -41 to -39 °C. The lower value of the Tan Delta (0.8675) EC with plasma-modified cellulose means that the EC has a higher elasticity rate in proportion to the ability to absorb and store energy. The higher value of the Tan Delta (0.9386) EC with reference RAW cellulose at a glass transition temperature indicates that the mixture has better damping properties, higher heat dissipation, but has a lower level of elasticity. The composite mixture with ozone-pretreated cellulose is 0.9154 at the temperature of the glass transition, the properties are located in the middle of the two compounds. The curves of the storage modulus curves shows a higher level of the mixture with plasma-modified cellulose. When comparing the course of the loss Modulus it is clear that the mixture also has a higher loss modulus. The storage and loss module curves with ozone pretreated cellulose and reference cellulose are similar. The curves also show the temperature of the glassy transitions of the storage and loss modulus. In the storage modulus, the glass transition temperatures were recorded in a temperature interval of approximately -55 to -52 °C. For the loss modulus, the glass transition temperatures of the examined elastomeric composites occur in the temperature range of approximately -48 to -46 °C.

Due to the physical treatment of the cellulose filler, there was a decrease in the minimum torque  $M_{MIN}$  of the elastomeric composites. This decrease is directly caused by the treatment, as the plasma damages the cellulose fibres, which subsequently tend to break under stress (even when mixing the blend itself), and in the case of ozone, occurs aging of fibres under the influence of ozone and temperature during treatment (lignin degradation). Thus, after treatment and mixing, the fibres do not stiffening the elastomeric composites, and this is reflected in the  $M_{MIN}$  values. From the point of view of the maximum torque, it can be seen that the Ozone pretreated CEL sample reached only a slightly lower value than the Unmodified (RAW) CEL sample, and therefore ozone alone does not have a significant effect on the crosslinking network density (as well as the absence of lignin, which acts as a stiffening filler in the blend). The plasma modified CEL sample reached the highest  $M_{MAX}$  value due to the aforementioned fibre breakage, when the fibres break under tension and shorten their length, which creates more space in the matrix for the formation of crosslinking bonds. An interesting finding is that the treatment of the filler using ozone almost does not affect the vulcanization characteristics such as scorch time  $T_{S02}$  and optimum cure time  $T_{C90}$ . It is possible that ozone itself affects the surface of cellulose fibres, but subsequently it is not stable, and its effect disappears (except for the breakdown of lignin). Unlike ozone, the plasma treatment of the filler is permanent, especially from the point of view of the effect on the fibres themselves, which break and shorten due to defects. In the case of plasma processing of the filler, lignin is also preserved, which in the rubber elastomeric composites delayed the vulcanization process.

#### **4. Conclusions**

Elastomeric composites were prepared. The subject of the study was the effect of cellulose as a filler and these elastomeric composites. The influence of pretreatment and modification of cellulose with ozone and DCSBD plasma was investigated on selected parameters such as filler dispersion, changes in tensile strength, and break was investigated. Curing characteristics, glass transition temperatures, and Tan Delta values at these temperatures were also determined and evaluated. The pretreatment of cellulose with ozone and modification of cellulose with DCSBD plasma were found to have an effect on the parameters mentioned. The process of pretreatment and plasma treatment in one is similar in character; ozone is present in both. However, the process of plasma modification also involves heat and UV exposure, which is generated during plasma modification. However, the influence of heat and UV radiation during DCSBD plasma modifications is not the subject of the present work.

#### **Acknowledgements**

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# Study of properties of elastomeric composites with maleinized rubber and biofiller

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## Abstract

Cellulose as a biopolymer belongs to an effective filler for elastomeric composites. Its uniform dispersion in hydrophobic matrix of natural rubber, it is very difficult to achieve due to its hydrophilic character. Maleinized natural rubber is used to improve the interfacial adhesion between hydrophilic filler and a polymer matrix with a hydrophobic character. This work deals with the modification of the matrix of natural rubber with maleic anhydride and the preparation of elastomeric composites with partial substitution of natural rubber for maleinized rubber filled with cellulose. The influence of chemically modified natural rubber on the properties of elastomeric composite based on natural rubber (NR) filled with cellulose (CEL) was studied. Natural rubber was replaced by its modified form in contents of 2, 4, 6, 8 and 10 phr. Vulcanization characteristics, hardness, tensile strength, elongation at break, cross-linked density and degree of swelling, morphology were studied on the prepared composites.

**Keywords:** natural rubber, cellulose, modification, maleic anhydride, elastomeric composite

## 1. Introduction

Natural rubber is a high molecular weight elastomeric polymer obtained from the latex of the Brazilian tree - *Hevea brasiliensis*. Its main advantages include easy processability, excellent abrasion resistance, low density, and useful properties [1,2]. Polysaccharides are renewable sources occurring in nature in the form of plants, animals, and microorganisms. The physical properties of polysaccharides such as solubility, viscosity, surface properties depend on their differences in composition of monosaccharides, types of bonds, chain shapes, and molecular weight. In elastomeric mixtures, polysaccharides are used as fillers, which increase the volume of the mixture and improve the resulting properties. The hydrophilic nature of polysaccharides is the reason for their relatively low interaction with the hydrophobic rubber matrix [3]. Maleic anhydride (MA) can be used as a modifier of natural rubber in the preparation of elastomeric mixtures, which is capable of reacting with long isoprene chains of natural rubber to form maleinized rubber. The high reactivity of maleinized rubber ensures its binding to various surfaces, allowing for stronger bonds between the polymer matrix and polysaccharides [4,5].

## 2. Materials and Methods

### 2.1. Materials

Cellulose was purchased from Bukóza Invest, Hencovce, Slovak Republic and it was used as filler in blends. The natural rubber was used as a matrix of all prepared blend. For modification of natural rubber was used a maleic anhydride (BDH Middle East LLC, Dubai, United Arab Emirates). As activator were used zinc oxide (Bayer, Kuala Lumpur, Malaysia) and stearic acid (Setuza a.s., Ústí nad Labem, Czech Republic). Linseed oil (Novochema, Levice, Slovak Republic) was used as plasticizer. Sulphur was used as crosslinking agent (Bayer, Kuala Lumpur, Malaysia) and as curing accelerator was used N-tert-butyl-2-benzothiazole sulfonamide - TBBS (Duslo a.s., Šaľa, Slovakia).

### 2.2 Modification of natural rubber by maleic anhydride

Maleinization process of natural rubber was realised by mixing of natural rubber with maleic anhydride (MA) in internal laboratory mixer at 145 °C for 10 minutes and the rotor speed at 50 rpm under normal atmosphere. During modification of MNR, the amount of maleic anhydride was 6 g with respect to 100 g of natural rubber.

### 2.3 Preparation of elastomeric composites

Elastomeric blends were prepared at 55°C in one-step by using laboratory mixer Plastograph Brabender type with chamber volume 80 cm<sup>3</sup> and 50 rpm (Brabender, Duisburg, Germany). The filler was modified by pressing process



at 110°C with 200 kN at 4 minutes for easier manipulation and its dosage. By using laboratory twin roll VOGT LaboWalz W 80 T I (VOGT, Berlin, Germany) was obtained better homogeneity of elastomeric blends. The blends were left for 24 hours at laboratory temperature of  $25 \pm 2^\circ\text{C}$ , before another processing procedure. The specification of all prepared blends is given in Table 1.

Table 1: Specification of prepared elastomeric composites

Component	Natural Rubber (phr)	Maleinized Rubber (phr)	Cellulose (phr)	Crosslinking agent – sulphur (phr)	Plasticizer – linseed oil (phr)
Blend type					
Standard	100	0	45	2.7	4.3
MEL2	98	2	45	2.7	4.3
MEL4	96	4	45	2.7	4.3
MEL6	94	6	45	2.7	4.3
MEL8	92	8	45	2.7	4.3
MEL10	90	10	45	2.7	4.3

#### 2.4 Measurement of vulcanization characteristics

Determination of vulcanization characteristics was performed by using RPA 200 (Alfa Technologies, Akron, OH, USA). By using Cutter 2000 (Instron Ltd., HighWycombe, UK) were cut samples to the needed shape for rheological measurement from prepared slabs of elastomeric blends. Cellophane film was used for protection of testing chamber and rotor of device. All tests were performed for uncured elastomeric blend at 150°C with frequency of 1.66 Hz at 20 minutes and 5% oscillation.

#### 2.5 Determination of hardness Shore A

The hardness of the elastomeric composites was determined by using hand hardness tester with SHORE A scale (Wallace LTD, Croydon, UK). Measurement was performed 5 times according to ASTM D2240-15 [6]. All results were statistically evaluated.

#### 2.6 Measurement of mechanical properties

Elongation at break and tensile strength of the composites were measured on a tensile tester machine Shimadzu AG-X Plus (Shimadzu, Tokyo, Japan) with the two pneumatic clamping jaws. By using Instron cutter machine (Instron, Norwood, MA, USA) in shape of dumb-bell type II according to ASTM D 412 [7] were prepared samples. Speed of tensile tests was determined at  $100 \text{ mm} \cdot \text{min}^{-1}$ .

#### 2.7 Determination of cross-linked density and degree of swelling

The determination was carried out in accordance with ISO 1817 standard [8]. Samples with dimensions of 30 x 5 x 2 mm were weighed on analytical scales and placed in a container with toluene until reaching equilibrium for 72 hours at laboratory temperature. The measured values were statistically processed after measuring five samples, with a measurement error of 9% taken into account.

#### 2.8 Observation of fracture surface morphology

By using ultrasonication in isopropyl alcohol, the samples were rid of all loose particles on the surface, as well as traces of moisture and oils. After drying with nitrogen gas, a conductive layer was deposited on the surface of the samples by sputtering a gold-palladium (80:20) alloy in atomic form for 150 seconds. The micro-morphology of the sample surface was observed using a TESCAN VEGA 3 scanning electron microscope (SEM).

### 3. Results and discussion

#### 3.1 Vulcanization characteristics

Measured values of vulcanization characteristics of prepared elastomeric composites with partial substitution of natural rubber for maleinized rubber filled with cellulose are in Tab. 2.

Table 2: Rheological properties and vulcanization properties of prepared blends

Blend type	Standard	MEL2	MEL4	MEL6	MEL8	MEL10
$M_{min}$ (dN.m)	2.01	1.91	1.73	1.70	1.64	1.59
$M_{max}$ (dN.m)	26.83	21.73	21.93	21.54	21.52	20.99
$t_{s02}$ (min)	5.85	4.43	4.58	5.00	5.19	5.49
$t_{c90}$ (min)	11.15	9.46	9.66	10.14	10.72	11.27

The highest value of  $M_{min}$  was achieved by an elastomeric composite without maleinized rubber content (2.01 dN.m). As the content of maleinized rubber in the composite increased, the values of  $M_{min}$  decreased. The decrease in  $M_{min}$  values can be attributed to the presence of maleinized rubber, which reduces the viscosity of the matrix, facilitating its flow around the filler fibers under stress. This decrease is likely caused by the degradation process during the modification of natural rubber with maleic anhydride, which reduces its molecular weight [9,10,11,12]. The highest  $t_{c90}$  value was recorded for the standard composite system without any maleated rubber content. In the case of the elastomeric composite with maleinized rubber content, lower  $t_{c90}$  values were achieved compared to the standard. The exception was the composite system with maximum maleinized rubber content of 10 phr, which achieved the highest  $t_{c90}$  value among all prepared composite systems (11.27 min). With an increasing content of maleinized rubber, the  $t_{s02}$  values increased. The increasing trend of  $t_{s02}$  and  $t_{c90}$  values of composite systems with maleinized rubber can be attributed to the acidity of maleic anhydride or the opening of its anhydride groups. The acidic nature of maleic anhydride makes the rubber matrix more acidic, causing adsorption of accelerators, and thus slowing their reactivity in the vulcanization process. Therefore, with an increase in the proportion of maleinized rubber in the composite, the increase in  $t_{s02}$  and  $t_{c90}$  times is even more pronounced [13,14].

### 3.2 Hardness Shore A

In Table 3, can be seen hardness of all prepared elastomeric systems. The highest hardness value was achieved for composite without maleinized rubber content (75.16 Shore A). After adding the smallest amount of maleinized rubber to the elastomeric composite, the hardness values did not decrease significantly. However, with increasing maleinized rubber content, the hardness values decreased more and more significantly. The decreasing trend of hardness values can be attributed to maleinized rubber, which decreased the stiffness of the matrix. The reduced stiffness of elastomeric composites with maleinized rubber caused these composites to offer less resistance to the penetration of the indenter into their surface, which was reflected in lower hardness values [13,14,15].

### 3.3 Mechanical properties

In Table 3 are shown measured values of tensile strength and elongation at break of prepared elastomeric composites.

Table 3: Hardness, tensile strength and elongation at break of prepared blends

Blend type	Standard	MEL2	MEL4	MEL6	MEL8	MEL10
Hardness (Shore A)	75.16 ± 0.58	74.50 ± 0.42	71.94 ± 0.53	71.01 ± 0.52	71.12 ± 0.87	69.44 ± 1.08
Tensile Strength (MPa)	7.72 ± 0.17	7.75 ± 0.16	6.83 ± 0.44	6.11 ± 0.19	6.34 ± 0.15	5.76 ± 0.14
Elongation at break (%)	408.36±4.96	450.82±10.59	416.83±12.21	439.23±12.18	439.46±9.49	422.02±11.62

The highest value of tensile strength was recorded for the composite with the lowest content of maleinized rubber

2 phr. For all composites with higher content of maleinized rubber than 2 dsk, there was a decrease in tensile strength values. The decrease in values can be attributed to the maleinized rubber, which degraded during modification due to the acidic nature of maleic anhydride, limiting the cross-linking process. The lowest value of elongation at break was recorded for the elastomeric composite without maleinized rubber (Standard). With increasing content of maleinized rubber in the elastomeric composite, the values of elongation at break

increased. The increase in values of elongation at break can be attributed to the effect of the acidic environment of maleic anhydride, which limits the cross-linking of rubber and maintains its plastic character [13,14].

### 3.4 Crosslinking density and degree of swelling

In Table 4 can be seen values of crosslinking density and swelling of all prepared elastomeric composites.

Table 4: Crosslinking density and degree of swelling of all prepared elastomeric composites

Blend type	Standard	MEL2	MEL4	MEL6	MEL8	MEL10
Crosslinking density *10 <sup>-4</sup> (mol.cm <sup>-3</sup> )	3.60	3.49	3.09	3.26	2.78	2.97
Degree of swelling (%)	222.52	341.51	314.28	329.80	361.90	311.27

The highest value of crosslink density was recorded for the composite without maleinized rubber (Standard). After adding maleinized rubber to the composite, the values of crosslink density had a decreasing trend. The lower density of overall crosslinking of composites is largely influenced by the acidic character of maleic anhydride, which prolongs the time required for crosslinking and also affects the density of the formed network [14,16]. With decreasing values of crosslink density, the degree of swelling increased. The increasing degree of swelling can be attributed to the lower density of the network, which allowed the solvent to diffuse more freely into its open spaces, causing the rubber matrix to swell [16].

### 3.5 Surface morphology

The result from SEM measurements can be seen in Figs. 1 a), b).

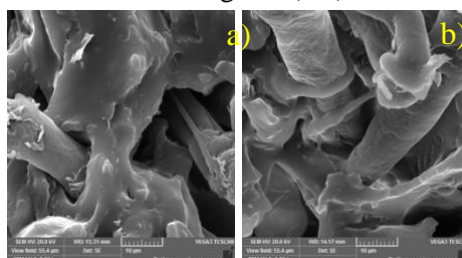


Fig. 1 a): SEM scan of Standard, 2500 x mag. ; Fig. 1 b): SEM scan of MEL2, 2500 x mag.

On the fracture surface of the Standard sample, a significant micro-area region around the cellulose fiber without matrix and only with local occurrence of interphase adhesive bonds can be seen. The adhesive bond between rubber and cellulose fiber, which remained intact even after the application of tensile stress, is also visible. In the case of the MEL2 composite, a visibly smaller free micro-area region is present compared to the Standard. In terms of interphase adhesion, this type of composite exhibits a greater number of intact adhesive bonds on the fracture surface due to the application of tensile stress. Due to the intact adhesion bonds, the cellulose fiber remains in the matrix during the fracture process of the test sample, and this has a direct correlation with the tensile strength values.

## 4. Conclusion

The influence of chemically modified natural rubber on the properties of elastomeric composite based on natural rubber (NR) filled with cellulose (CEL) was studied. It was proven that chemically modified natural rubber had an effect on the values of physical, mechanical properties as well as vulcanization characteristics and crosslinking density. By using SEM, the interfacial adhesion of the tested samples was observed after tensile stress. For the elastomeric system with minimal content of maleinized rubber (MEL2) a smaller number of deficient micro spaces around the cellulose filler were observed. From the point of interphase adhesion, this type of elastomeric composites shows a higher amount of adhesive bonds, which remained intact during the formation of the fracture surface due to the application of tensile stress. Due to the integrity of the adhesive bonds, the cellulose fibers do not pull out in the process of breaking the test sample, but remain in the matrix and are directly related to the measured tensile strength values.

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## Modification of Bio-Fillers to Improve Properties of Elastomeric Composites

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### Abstract:

Modification of fillers is used to improve the function of fillers in elastomeric composites. In the case of bio-fillers, this is often the only way to modify their properties for use in polymer blends and composites. Compared to commonly used inorganic fillers and carbon blacks, bio-fillers have several disadvantages, starting with their hydrophilic character and continuing with poor interfacial adhesion, which leads to lower values of physical-mechanical properties. With the help of modification, it is possible to affect the effect of bio-fillers in elastomeric blends or composites for the desired effect of improving properties. In the case of bio-fillers, there is the possibility of influencing the dispersion of the filler in the matrix, as well as the resulting properties of the elastomeric blends and composites, due to the change of the fillers pH. In this work, cellulose as a bio-filler for natural rubber was modified using acetic acid and zinc oxide. Cellulose treated at different pH with zinc acetate content was added as a filler to the composite with natural rubber. The pH values of the modified cellulose affected the vulcanization process as well as the physical-mechanical properties of the prepared elastomeric composites. The result of the study is the possibility of using the modification of cellulose bio-filler for the preparation of elastomeric composites with improved properties compared to elastomeric composites prepared without filler modification.

**Keywords:** natural rubber, cellulose, zinc acetate, surface modification, elastomeric composites

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### Introduction

The development of elastomeric composites and especially their composition depends mainly on the availability of raw materials as well as on the customer's ecological requirements. It is the demands of customers and the current pressure to reduce the carbon footprint of products made of elastomeric composites that are pushing alternative and bio fillers to the forefront. The matrix of elastomeric composites is most often natural rubber, due to its natural origin and excellent mechanical properties (high elasticity, good strength). Most bio-fillers, when they are mixed into an elastomeric matrix, reduce the mechanical properties of the composite, which is their biggest disadvantage as well as a block for massive application in industry [1]. By modifying the properties and structure of bio-fillers, it is possible to limit or eliminate their adverse impact on the matrix. One of the treatment methods in the case of bio-fillers is modification, which primarily uses chemical processes about preserve the most important property, namely biodegradation [2]. In the last few years, modified cellulose has become a popular filler in the preparation of elastomeric composites based on natural rubber.

### Materials and methods

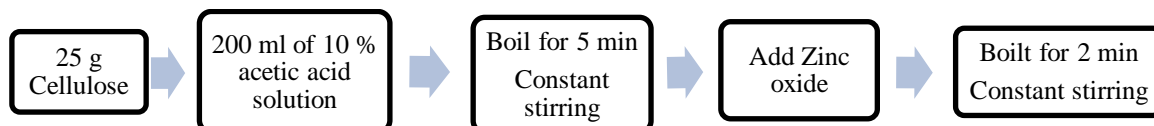
**Table 1** Materials used for preparation of elastomeric composites.

Materials	Producer
Natural rubber type SMR 10	Kuala Lumpur, Malaysia
Zinc oxide	SlovZink a.s., Košeca, Slovakia
Stearic acid	Setuza a.s., Ústí nad Labem, Czech Republic
TBBS	Duslo a.s., Šal'a, Slovakia

Oiled sulphur	Eastman Chemical company, Kingsport, TN, USA
Cellulose type GW70	Greencel Ltd. company Hencovce, Slovakia

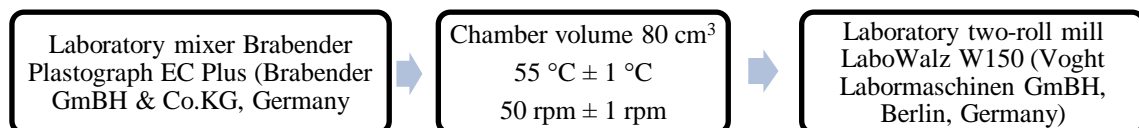
\*The filler for all prepared composites was in a concentration of 45 phr, as pure without treatment for the composite designated as CEL, or surface-modified versions for the CEL 1 and CEL 2 composites.

#### Surface modification of cellulose GW70



The surface-modified cellulose obtained in this way was used for the preparation of the elastomeric composite designated as CEL 1. For the preparation of the elastomeric composite designated as CEL 2, a washing process of the surface-modified filler was included into the process of modifying the filler before the drying operation to remove the unreacted acidic environment.

#### Preparation of elastomeric composites



**Table 2** Devices used for determination of composites properties.

Properties	The device used to determine the properties	Producer of device
Rheological properties and vulcanization characteristics	RPA 2000 (160 °C, 30 min)	Alfa Technologies Ltd., Akron, OH, USA
Hardness	Bareiss HPE II (Shore A)	Bareiss, Ont., Canada
Tensile properties	Shimadzu AG-X Plus (100 mm.min <sup>-1</sup> )	Shimadzu, Tokyo, Japan

#### Results and discussion

**Table 3** Rheological properties and curing characteristics.

Composite	M <sub>L</sub> (dNm)	M <sub>H</sub> (dNm)	t <sub>02</sub> (min)	t <sub>90</sub> (min)
CEL	3.0	29.87	6.15	12.17
CEL 1	1.7	22.6	6.54	21.79
CEL 2	2.13	26.93	6.49	14.24

The minimum torque corresponds to the stiffness of the composite at the beginning of the curing process [3]. The highest M<sub>L</sub> value and thus stiffness was achieved by the CEL composite with the filler content without surface modification. In the case of the elastomeric composite containing surface-modified cellulose without removing the unreacted acidic environment (CEL 1), a decrease in the M<sub>L</sub> value occurred. The acidic pH present in the elastomeric composite has an effect not only on the filler itself, which is the carrier of this pH, but also on the matrix. Natural rubber matrix is prone to degradation in the presence of acidic pH due to the occurrence of hydrolytic reactions (reduction of molecular weight and breakdown of matrix chains [4, 5]). Since M<sub>L</sub> expresses the stiffness of the unvulcanised composite, the degradation reactions already took place during the mixing of the composite, where the negative influence of acidic pH is amplified by the increased temperature during the mixing process. By removing the acidic unreacted environment from the surface-modified filler (CEL 2), the M<sub>L</sub> value increased. The difference in the M<sub>L</sub> values of the CEL 1 and CEL 2 composites can therefore be attributed to the negative effect of the unreacted acidic environment and the above-mentioned degradation processes caused by it. The CEL 2 composite still reached a lower M<sub>L</sub> value than the CEL composite, due to the improved cellulose dispersion in the NR matrix. The zinc acetate present in the surface-modified filler acts as a compatibilizer between the matrix and the filler, which

is proven to reduce the stiffness of the unvulcanized composite and thus the  $M_L$  value [6, 7]. The maximum torque ( $M_H$ ) of the prepared composites shows the same trend as the minimum torque. The highest  $M_H$  value was achieved by the CEL composite, with the content of surface-unmodified cellulose. Classic cellulose, i.e. without surface or chemical modification, only slightly cross-links with the matrix of the composite with natural rubber [8]. Thus, the cellulose present in the CEL composite is to a greater extent only mechanically located in the internetwork spaces, which increases the stiffness of the composite, because it limits the movement of the formed vulcanization crosslinks. The presence of an acidic unreacted environment contained in the cellulose after the modification process reduces the  $M_H$  value, as can be seen in the case of the CEL 1 composite. As above-mentioned, the acidic pH already affected the composite in the mixing process (hydrolytic reactions), but in addition to degradation reactions, pH also affects the rate of accelerator TBBS [9, 10]. By removing the unreacted acidic environment, the  $M_H$  value increases again (composite CEL 2), but despite the increase, it remains lower than the  $M_H$  value of the composite containing untreated cellulose. The removal of the TBBS accelerator limitation due to acidic pH can be seen in the curing characteristics of the NR composites. The scorch time of prepared composites ( $t_{s02}$ ), as the first of the curing characteristics, indicates the possibility of manipulation with the composite within a time frame at a given vulcanization temperature, without the risk of starting the vulcanization process itself [11]. The  $t_{s02}$  value is especially important when applying the composite to the production of products with complex shapes, where it is necessary to maintain the flow of the composite in the mold until the perfect filling of the entire mold is achieved [12]. The highest  $t_{s02}$  value is shown by the CEL 2 composite, however, the acidic pH present in the composite does not play a major role in this case, and the value is higher by only 0.39 min compared to the CEL composite and by 0.05 min in the case of the CEL 2 composite. From the point of view of  $t_{s02}$ , the composites are therefore on the same level, and the beginning of the vulcanization process was not significantly affected by the surface modification either. To create an optimal vulcanization network, and to prevent degradation of the created network, the time referred to as the optimum cure time with the designation as  $t_{c90}$  is used [13]. Composites with surface-modified cellulose had higher  $t_{c90}$  values because of the presence of acidic pH in CEL 1 and the influence of zinc acetate in CEL 2. Zinc acetate can form complexes with the vulcanization system, which may deviate the system from forming a crosslinking network, leading to an increase in the  $t_{c90}$  value. The first of the measured mechanical properties of the composites was the hardness, which indicates the ability of the composite to resist the action of external forces [14]. From the graphical processing of the hardness values, the surface modification of the filler did not significantly change the hardness value of the composite, which can be considered an advantage, as the composites achieved the same resistance to the indenter of hardness tester and thus to the action of external force.

**Table 4** Mechanical properties of prepared NR composites

Composite	Hardness (ShA)	Tensile strength (MPa)	Elongation at break (%)
CEL	77.42 ± 0.58	6.54 ± 0.42	347.58 ± 11.89
CEL 1	75.6 ± 0.31	6.78 ± 0.09	411.52 ± 6.82
CEL 2	76.92 ± 0.43	8.11 ± 0.16	483.96 ± 9.71

Tensile strength and elongation at break are significantly negatively affected in bio-composites or composites containing bio-fillers compared to commonly used fillers [15]. The surface modification of the cellulose filler resulted in an increase of the tensile properties values of the composites in the case of CEL 1 and CEL 2. The CEL 1 composite achieved only a slight increase (0.24 MPa) compared to the CEL composite, which was mainly influenced by the acidic pH present in the CEL 1 composite. As above-mentioned, acidic pH limits the vulcanization process (slows down the effect of the TBBS accelerator) as well as degrades the composite matrix during the mixing process. For this reason, the cross-linking in the composite was, so to speak, less frequent, which resulted in a slight increase in tensile strength, as the cross-linking was not affected to such an extent by the filler in the crosslinking network spaces, and the force is more evenly distributed over the elongation value. If the matrix of the CEL 1 composite was not affected by acidic pH and degradation during the mixing process, the composite would show a higher tensile strength value than in the case of the CEL 2 composite [16, 17]. The negative influence of the acidic unreacted environment is evident, with the highest breaking force achieved by the CEL 2 composite that did not contain it. The absence of acidic pH prevented matrix degradation, and the slight decrease in network density caused by zinc acetate ensured more even force distribution during the tensile test. Rupture during the test is typically due to exceeding matrix strength or defects introduced by adding fillers that act as stress concentrators. Therefore, if the vulcanization network is sparser, its limitation due to the influence of the filler as well as the defects caused by it during tensile stress is lower, which will cause an increase in elongation at break as well as tensile strength [18]. The

CEL 1 composite and its elongation at break were affected by the content of an acidic unreacted environment, causing both matrix degradation and a positive step, namely the limitation of cross-linking (in case the network density would not be limited, the degraded matrix would be more prone to rupture). Thus, the composite retained a greater part of its plastic deformation. After removing the unreacted acidic environment, in the case of the CEL 2 composite, the influence of matrix degradation disappeared, but the partially limiting effect of zinc acetate on reducing the network density was preserved.

## **Conclusion**

By surface modification of the cellulose bio-filler using zinc acetate, two variants of the modified filler were prepared for this publication, which were used for the preparation of composites. To compare the effect of the modification itself, a composite containing bio-filler without surface modification was also prepared. The surface modification with the content of an acidic unreacted environment negatively affected the matrix of the composite already in the mixing process due to hydrolytic reactions and subsequently the rheological properties and vulcanization characteristics of the composite. The negative impact of acidic pH was confirmed by the second variant of the surface modification with the removal of the acidic pH of the filler. However, the acidic pH content also showed a positive effect, especially in the case of tensile properties such as tensile strength and elongation at break, as it partially affected the density of the crosslinking network, which compensated the degradation of the composite matrix. This text highlights the significant improvement in the tensile properties of a composite material achieved by removing the unreacted acidic environment and incorporating surface-modified filler, particularly zinc acetate. The removal of the acidic pH not only improved the rheological properties and vulcanization characteristics but also had a notable effect on the tensile properties of the composite. The composite with surface-modified filler and without acidic pH achieved a 24% improvement in tensile strength and a 39% improvement in elongation at break compared to the composite with unmodified filler. Another advantage of surface modification is that it has a minimal effect on the hardness of the composite.

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