

# Influence of Filler on Structural and Surface Properties of Elastomeric Composites

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## Abstract

Characterization of elastomer composite morphology, mainly phase morphology, cure state variations, polymer-filler interactions, and filler phase distribution are critical in establishing the morphology-property relationships for composites consisting of elastomeric composites. This work deals with preparation of elastomeric composites filled with biopolymer. Natural rubber (NR) was filled with cellulose (CEL) in amounts 30 – 55 phr. Filler/plasticizer partition in elastomeric composites, compatibility and interfacial adhesions between matrix and filler can be established. Application of atomic force microscopy (AFM) to design better elastomer composites is present (3D surface topography). Dynamic mechanical properties of NR/CEL composites were measured in the temperature range from  $-95\text{ }^{\circ}\text{C}$  to  $100\text{ }^{\circ}\text{C}$ . The properties were compared with those from materials of the same composition but without filler (CEL). The laboratory tests show differences in two selected moduli Elastic and Loss. Glass transition temperature changes were determined at the peak maximum of Tan Delta ( $\text{Tan } \delta_{\text{max}}$ ).

## Keywords

Elastomer, Biopolymers, Polymers

## Introduction

The results of current research indicate that the use of fillers based on biopolymers is of practical and technological importance for industrial practice, because they significantly influence the properties of prepared polymer materials and composites, with a positively evaluated ecological and economic aspect [1]. Currently, the trend is to replace carbon black partially or completely, as the most commonly used filler in the rubber matrix, by using ecologically and economically acceptable modified additives based on natural polymers [2]. By using alternative additives to a polymer with a rubber matrix, it is possible to prepare polymer materials, or nanocomposites with desired properties [3, 4]. CEL is a natural macromolecular substance composed of  $\beta$ -D-glucopyranose units connected linearly in positions 1-4 and is among the most widespread polysaccharides and biopolymers produced by photosynthesis [5-7]. The repeating monomeric unit is cellobiose. CEL forms the framework of the cell walls of plants (cotton, flax, hemp, jute, sisal, etc.) and woody plants (wood CEL). It is characterized by good mechanical, sorption, and physico-chemical properties, thanks to which it is an important raw material for the textile, rubber, wood, pulp and paper, leather and food industries. The individual CEL macromolecules are partly regularly and partly loosely arranged with each other in the fiber with varying degrees of perfection (amorphous, mesomorphic, and crystalline). They create microfibrils, which are joined into fibrils and form the cell wall of plants and trees. In

ordered areas, microfibrils form a crystal structure. The space between the crystallites and the marginal areas of the microfibrils is formed by amorphous cellulose. The chemical structure of the cellulose macromolecule and the strong intermolecular hydrogen bonds conditioning the supramolecular structure of cellulose cause cellulose to be insoluble in water and common organic solvents [8, 9]. With the decline of petrochemical raw materials resources and the need for environmental protection, natural rubber could be mixed with biopolymers, which are cheap and biodegradable [10, 11]. Most biopolymers contain many hydroxyl groups and are polar, causing poor compatibility with natural rubber. This leads to deterioration of the mechanical properties (elasticity and rupture) of composites filled with biopolymer. Several studies focus on improving the mechanical properties of blends of natural rubber with biopolymers [12, 13]. Agricultural wastes, rice husks, cherry pits, palm tree bark, sisal and bagasse were used as fillers for natural rubber [14-16]. Natural rubber composites filled with cellulose whiskers are characterized by good mechanical properties [17, 18]. Cellulose is the most widespread natural polymer with interesting properties such as high mechanical strength, chemical stability, and biodegradability [19-21]. Biopolymers such as cellulose, starch, or xylans contain hydroxyl groups forming hydrogen bonds and therefore have a good affinity for water [22]. Due to their biodegradability, mechanical properties, low density, and easy availability, nanocelluloses from various renewable sources of raw materials can be considered as a suitable candidate for polymeric "green" filler [23-25]. By suitable surface treatment (physically or chemically) of cellulose, the interfacial adhesion between the filler and the matrix of natural rubber can be improved to prepare satisfactory filled NR composites. An effective method of chemical modification is the treatment of cellulose by silanization to reduce the hydrophilic nature of cellulose [26-28]. An interesting method of chemical treatment of the cellulose surface is esterification [29, 30]. From physical modification, plasma exposure can be used. Plasma treatment of the surface of materials is environmentally friendly and has other advantages. Many researches are carried out in this area. The effect of plasma discharge on glass, textiles, wood, and polymers improves their useful properties [31-33]. There are changes on the surface, the removal of organic impurities and a change in wettability. Low-temperature plasma sources such as DCSBD have shown their significant potential for ecological, safe, and energy-efficient surface processing of a wide range of materials [34, 35]. Properly adjusted filler can improve the mechanical and dynamic mechanical properties of the resulting composite in the elastomeric mixture. The interfacial adhesion between the filler and the elastomeric matrix affects the tensile strength, tangent delta ( $\tan \delta$ ) and storage modulus. A better interfacial adhesion between the filler and the matrix is reflected in a decrease in the height of the  $\tan \delta$  peak [12]. This is confirmed by studies [36, 37], where the surface modification of nanocellulose led to a decrease in the height of the  $\tan \delta$  peak in the resulting elastomeric composite compared to the composite filled with untreated cellulose. The present work described the preparation of elastomeric composites filled with biopolymer. Natural rubber (NR) was filled with cellulose (CEL) in amounts 30 – 55 phr. Filler/plasticizer partition in elastomeric composites,

compatibility and interfacial adhesions between matrix and filler can be evaluated. The morphology of composites was investigated using AFM. The mechanical characteristics of the composites were studied under dynamic conditions of DMA analysis.

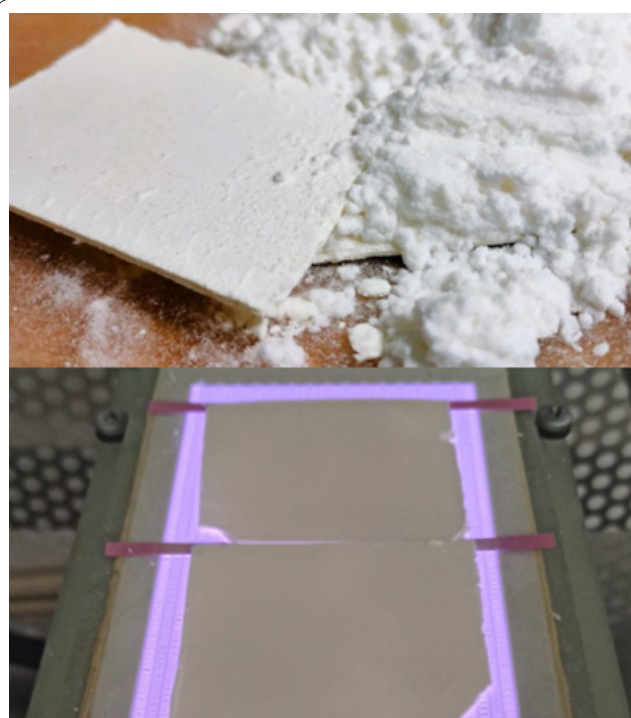
## Materials and Methods

### Materials

Natural rubber (NR – 1 ref.; type SMR 10; Lee Rubber; Kuala Lumpur; MY) was used as the matrix of the prepared elastomeric composites. Cellulose (samples 2 – 7) GW 70 (GREENCEL s. r. o.; Hencovce; SK) and a modified version (samples 2M – 7M) of GW 70/5 – silanized form (GREENCEL s. r. o.; Hencovce; SK) were used as filler. Zinc oxide (SlovZink a. s.; Košeca; SK) and stearic acid (Setuza a.s.; Ústí nad Labem; CZ) were used as sulfur vulcanization activators and Flavex 595 oil (Shell plc; London; GB) as a plasticizer. The vulcanization system of the prepared elastomeric consisted of N-tert-butyl-2-benzothiazole sulphonamide - TBBS (Duslo a. s.; Šal'a; SK) and oiled sulfur of the Crystex OT33 type (Eastman Chemical company; Kingsport; TN; US).

### Modification of filler

The used fillers GW70 and GW70/5 were modified before dosing into the composite using a plasma reactor KPR 20 (Research Institute for Man-Made Fibers, Svit, Slovak Republic). The power of the reactor electrode was set to a power of 350 W. The fillers in the form of a pressed plate (Figure 1) with a thickness of 2 mm were subjected to the plasma process for 4 minutes/sample area (Figure 1). The distance between the surface of the sample and the surface of the reactor



**Figure 1:** Cellulose (CEL) as filler: modified by compression and in its original state (top). DCSBD plasma treatment of CEL (bottom).

electrode was set to 0.25 mm. The modification was carried out by a plasma induced on a ceramic dielectric, namely DCSBD type (Diffuse Coplanar Surface Barrier Discharge), at a laboratory temperature of 20°C and air humidity of 31%. The safety of cellulose modification with plasma was monitored by a thermal camera.

### Preparation of elastomeric composites

Elastomer composites were prepared by one-step mixing in a Plastograph Bradender chamber (Brabender; Duisburg; DE) with a volume of 80 cm<sup>3</sup>. The mixing temperature was set to 110 ± 1 °C and the speed to 50 ± 1 rpm. After the mixing process, the composites were subjected to additional homogenization on a laboratory two-cylinder LaboWalz W150 (Voght Labormaschinen GmbH; Berlin; DE). After standing the mixture at room temperature for 24 hours, the prepared composites were subjected to determination of vulcanization characteristics on an oscillating-disk rheometer PRPA 2000 (Alfa Technologies Ltd.; Akron; OH; US). After determining the vulcanization characteristics, the elastomeric composites were vulcanized in a Fontijne LabEcon 600 vulcanizing press (Fontijne Presses; Vlaardingen; NL) into 2 mm thick plates.

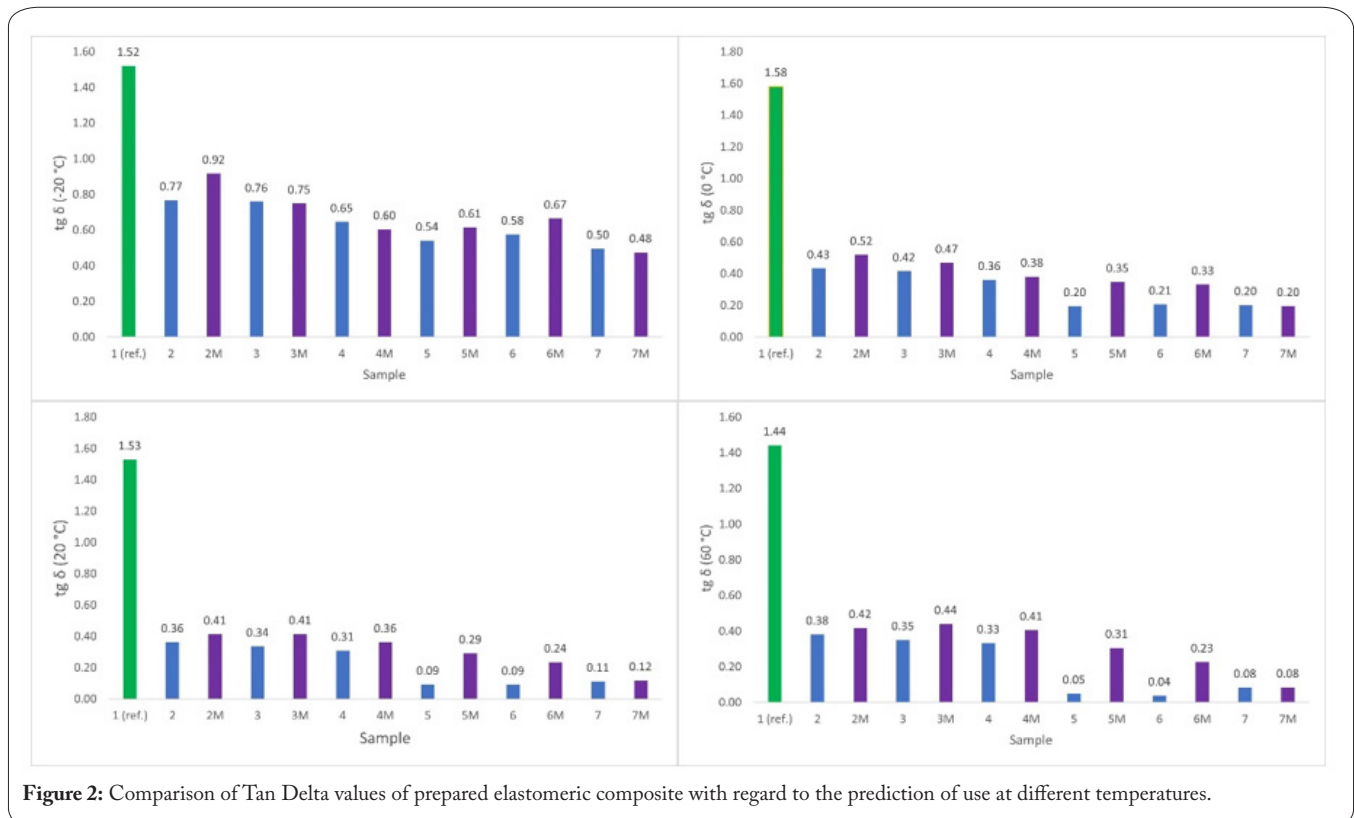
For dynamic-mechanical analysis DMA Q800 thermal analysis device Q800 from the manufacturer TA Instruments was used (TA Instruments; Boston; MA; US). Experimental setup: Tension film clamp; Temperature ranges from -100 to 100 °C; Heating rate of 3 °C.min<sup>-1</sup>; Frequency 60 Hz; operating software – TA Universal Analysis 2000. The elastic and loss modulus, Tan Delta and its values were measured and evaluated.

The measurement was performed in AC Tapping mode,

AC240TS – R3 tip. Images are topographic surface (height). Overlaid in colour is the phase channel, which creates a contrast based on the differences in the mechanical properties of individual areas. The observed difference in this area can and is height since it is the observed difference of probably a different phase/particle with a different “height” on the surface.

### Results and Discussion

To investigate the effects of CEL (modified by plasma/silanized and modified by plasma - M) on the dynamics of NR, DMA analysis was carried out. Tan Delta as a function of temperature for pure NR – reference and composites reinforced with DCSBD plasma modified cellulose (samples 2 – 7, with increasing phr of CEL is shown in table 1. Tan Delta for pure NR and composites reinforced with DCSBD plasma and silanized cellulose is shown in table 2. The Tan  $\delta_{max}$  is attributed to the glass transition temperature [38]. Tan Delta values in composites decreased with increasing filler content. Table 3 and figure 2 shows Tan Delta values at selected temperatures. This feature enables the prediction of properties for requirements such as: winter traction (tg  $\delta$  at -20 °C), traction on wet (surfaces) (tg  $\delta$  value at 0 °C), traction on dry surface (tg  $\delta$  value at 20 °C) and rolling resistance (tg  $\delta$  value at 60 °C). In general, the incorporation of filler is observed as a higher value of Tan Delta - a better mutual interaction of macromolecules at the internal level of the composite material. For selected applications, it was necessary to compare these values at selected temperatures (Figure 2). Tan Delta values for only plasma-modified cellulose and plasma-modified silanized cellulose showed little difference. By side-by-side comparison of the effect of increasing amount of CEL filler (figure 2 blue and purple columns), a decrease in Tan Delta value was noted at



**Table 1:** Tan Delta temperatures and values in elastomeric composites (filler CEL).

Sample	Tan $\delta_{max}$	
	Glass transition temperature (°C)	Value at peak max
1	-42.23	2.35
2	-35.82	1.22
3	-36.04	1.28
4	-37.96	1.20
5	-39.78	1.15
6	-37.94	1.09
7	-39.93	1.07

**Table 2:** Tan Delta temperatures and values in elastomeric composites (filler M – Modified CEL).

Sample	Tan $\delta_{max}$	
	Glass transition temperature (°C)	Value at peak max
1	-42.23	2.35
2M	-34.69	1.47
3M	-37.63	1.25
4M	-39.75	1.18
5M	-37.51	1.07
6M	-33.84	1.02
7M	-42.01	1.02

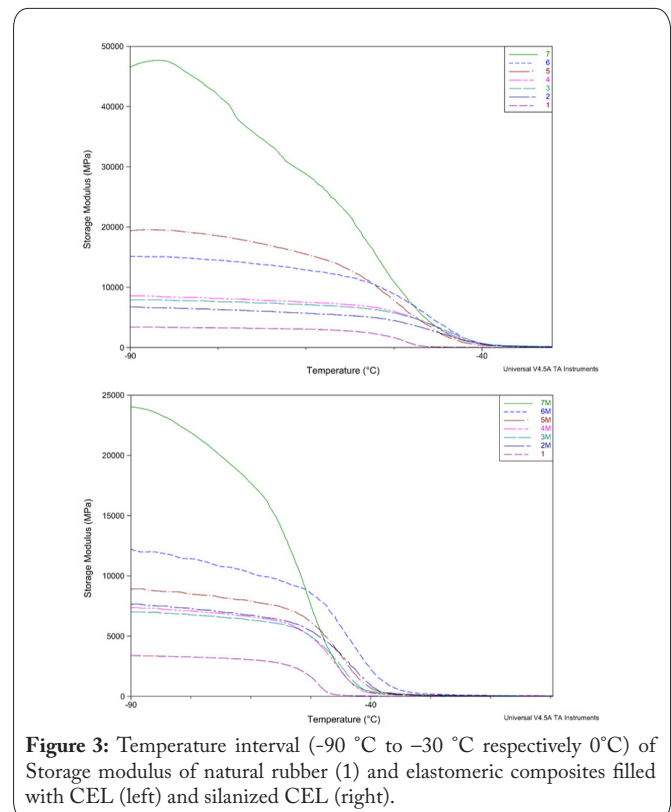
each of the selected temperatures/selected applications. The E' indicates the capacity of a material to store the input mechanical energy, and it decreased with temperature in three stages. At low temperatures, the material in the glassy state exhibited a high modulus **Figure 3**. In the NR sample, a glassy region is evident in the temperature range of -90°C to -55°C of the elastic modulus (E'). Natural rubber is hard glassy then. Very high values of the elastic modulus are achieved by the composites with the highest content of cellulose (samples 7 and 7M). In the region, which corresponds to the transition from the glassy state to the rubbery state, values of storage modulus decreased. The glass transition temperature of NR was determined at -55.53 °C. NR goes from a hard glassy to a rubbery state. Subtle deviations from the glass transition temperature of NR could be observed by adding filler, DCSBD plasma modified cellulose and silanized cellulose. The most significant change in the glass transition temperature was found in sample 5 (-63°C – cellulose modified only by DCSBD plasma), and in sample 7M (-41.6°C – silanized cellulose modified by plasma). With increasing temperature decrease of E' is observed (temperature interval -60 and -40°C). In the glassy region, all prepared composites are in frozen state. With temperature increase the composites became more mobile and the E' modulus decreased. In general, at higher temperatures

(temperature interval -40 to 100 °C) E' became a function of filler content, and the highest modulus was observed for the composite having the highest filler loading (**Figure 4**). CEL and silanized CEL can increase the stiffness of rubber composites. This improvement in storage modulus led to a decrease of the loss factor (**Figure 5**).

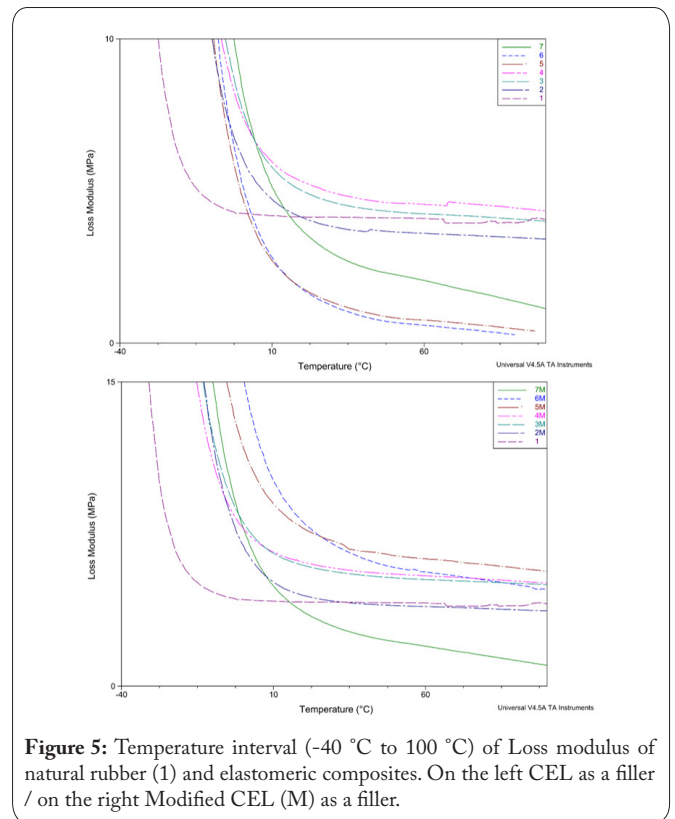
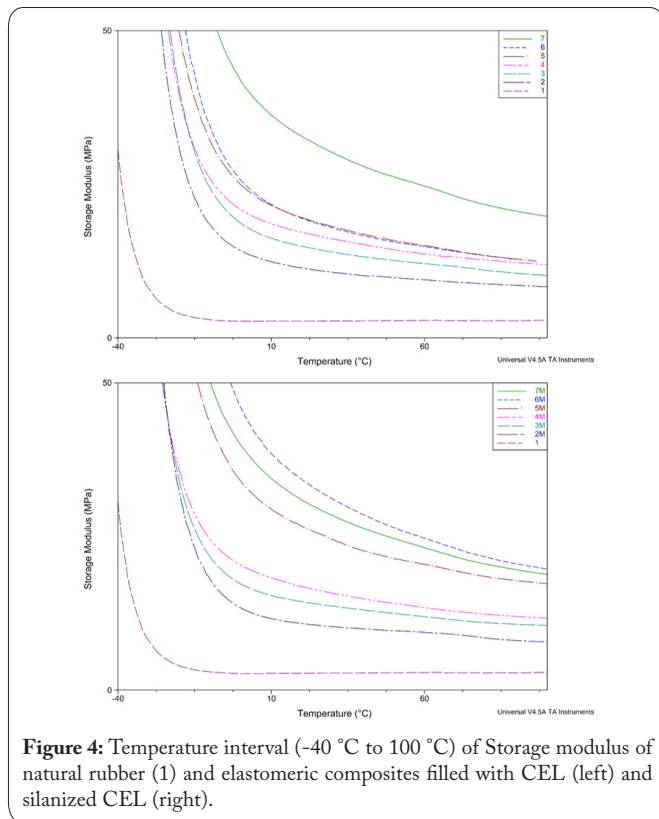
An important parameter to consider when analyzing the morphology of polymer composites is the size and distribution of fibrils. A suitable microscopic technique for evaluating the morphology of cellulose fibrils is SEM, TEM and AFM [39]. **Figure 6** shows AFM images of NR/CEL composites taken directly above the surface of the samples with the corresponding 3D projection of unfilled NR vulcanizate and selected samples of cellulose-filled elastomeric composites. The unfilled NR vulcanizate sample is characterized by good surface homogeneity, which implies that the vulcanization system and parameters were used in the correct way. The estimated arithmetic mean and surface roughness of the unfilled NR vulcanizate (1 ref.)

**Table 3:** Tan Delta values at selected temperatures.

Sample	Tan Delta at -20 °C	Tan Delta value at 0 °C	Tan Delta at 20 °C	Tan Delta at 60 °C
1	1.52	1.58	1.53	1.44
2	0.77	0.43	0.36	0.38
2M	0.92	0.52	0.41	0.42
3	0.76	0.42	0.34	0.35
3M	0.75	0.47	0.41	0.44
4	0.65	0.36	0.31	0.33
4M	0.60	0.38	0.36	0.41
5	0.54	0.20	0.09	0.05
5M	0.61	0.35	0.29	0.31
6	0.58	0.21	0.09	0.04
6M	0.67	0.33	0.24	0.23
7	0.50	0.20	0.11	0.08
7M	0.48	0.20	0.12	0.08



**Figure 3:** Temperature interval (-90 °C to -30 °C respectively 0°C) of Storage modulus of natural rubber (1) and elastomeric composites filled with CEL (left) and silanized CEL (right).



is  $R_a = 203.6$  nm and  $R_q = 254.2$  nm. For more accuracy parameters  $R_q$  (Table 4) and  $R_a$  (Table 5) were obtained from  $20 \times 20 \mu\text{m}$  images. In sample 5 (centre left) and 6 (centre right), the cellulose appears to be more finely dispersed in the matrix (this does not apply to sample 6M – image on the bottom). Analysis of the surfaces of NR/CEL composites with different contents of physically and chemically modified cellulose by means of AFM confirmed that the morphology of the surfaces of individual composites is significantly different from the morphology of unfilled NR vulcanizate. This is probably due to an increase in the knott density of the cellulose chains. NR composites with a cellulose content of 45 phr and 50 phr have  $R_a = 104.1$  and  $102.5$  nm,  $R_q = 143$  and  $134.6$  nm. From a comparison of the images in figure 6, it is clear that the cellulose has partially attached to the NR matrix. This causes changes in the surface, i.e., the surface roughness decreases and the morphology changes from nodular to granular.

### Conclusion

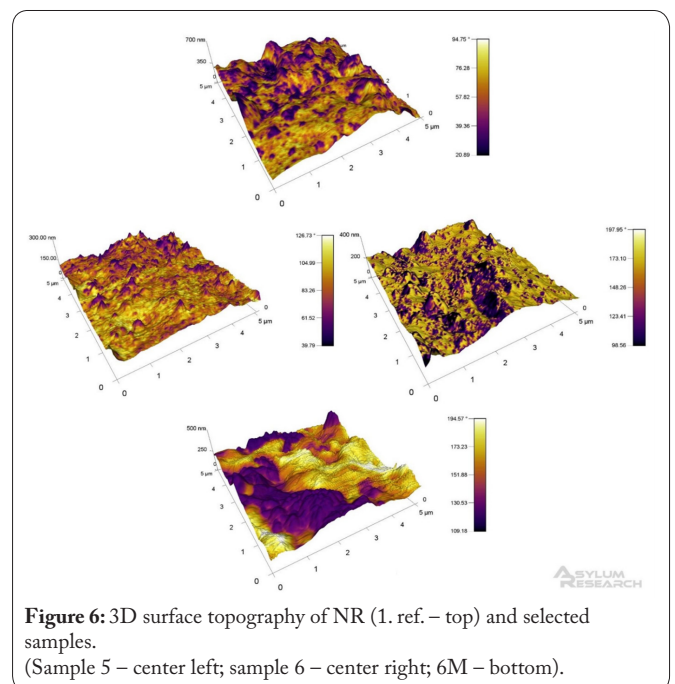
The study deal with the preparation of elastomeric composites filled with physically and chemically modified cellulose. The interfacial adhesion between the NR matrix and the cellulose filler was studied by means of AFM. Using DMA, the dynamic-mechanical properties of the prepared elastomeric composites with different cellulose content were evaluated. Plasma surface modification is considered a destructive surface treatment method that significantly changes the material's

**Table 4:**  $R_q$  (root mean square roughness) and  $R_a$  (average roughness) values of natural rubber and elastomeric composites (filler CEL).

Sample	1	2	3	4	5	6	7
$R_q$ (nm)	254.20	112.10	125.70	184.10	143.00	134.60	112.40
$R_a$ (nm)	203.60	83.80	83.90	135.10	104.10	102.50	84.40

**Table 5:**  $R_q$  and  $R_a$  values of natural rubber and elastomeric composites with modified CEL.

Sample	1	2M	3M	4M	5M	6M	7M
$R_q$ (nm)	254.20	121.80	115.00	111.70	163.70	129.20	138.70
$R_a$ (nm)	203.60	90.10	96.90	88.30	107.60	105.20	105.40



surface morphology. Modification of cellulose surface morphology could lead to increased interactions with modifying agents and solvents. Plasma is a new, highly efficient, environmentally friendly physical technique. It can be a suitable alternative for cellulose modification, which would lead to better utilization of cellulose in various fields. The differences in surface roughness observed in cellulose-filled NR composites may be related to filler/matrix interface phenomena that cause changes in polymer chain folding and directional anisotropy of polymer chain mobility. From the results, it can be concluded that the presence of cellulose as a filler in the elastomeric matrix significantly changes the surface roughness parameters.

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## Conflict of Interest

None.

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