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Effects of Filler Modification on the Properties of Elastomeric Composites

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The application of cellulose (CEL) as a filler in elastomeric composites (ECs) was studied, with cellulose examined in its untreated form (RAW), after DCSBD plasma modification, and ozone pre-treatment. Changes in surface fluorescence demonstrated that DCSBD plasma-modified cellulose achieved better dispersion in the elastomeric composite mixture, which also showed improved strength and elongation in static tensile tests. DMA analysis confirmed changes in visco-elastic properties, with DCSBD plasma-modified cellulose altering the glass transition temperatures of the Elastic and Loss modulus, as well as Tan Delta. SEM microscopy did not conclusively demonstrate the reinforcing effect of plasma-modified cellulose. Small property changes were observed with ozone pre-treated cellulose, similar to the unmodified cellulose composite mixture (NR).

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

1 Introduction

Cellulose is among the most widespread biopolymers found in nature, currently being produced due to their easy availability, industrial processability, low cost, and wide range of uses (chemical industries, medical, clothing) [1, 2, 3, 4] 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 purpose, it is necessary to modify the cellulose surface. There are many methods of fiber treatment based on mechanical, chemical [5], biological or physical action. However, it is important to consider whether the mentioned methods are effective, non-degradating and do not burden the environment. Chemical methods of cellulose treatment includes oxidation [8, 9], hydrolysis, esterification, etherification, silanization and are used to reduce crystallinity [7]. However, most chemical methods have the disadvantage that they are toxic and burden the environment [10].

One of the interesting method for the treatment of cellulose is atmospheric low-temperature non-thermal plasma (ATP) [11]. The application of ATP is a nowadays an emerging and insipiring scientific topic in the multidisciplinary research of materials treatment, for instance glass [12], wood [13], polymers [10, 14], textiles and fibres - cellulose [15, 16, 17, 18, 19]. One of the advantages, of using ATP is no-need for vacuum chamber during modifications. So it provides low-cost treatments, fast operations and presents environmentally friendly technique [20].

Atmospheric pressure plasma based on diffuse coplanar surface barrier discharge (DCSBD) was applied in this work. The DCSBD plasma can affect the wettability of different material's surfaces, including cellulose, via physicochemical reaction between the plasma environment and the material's surface. The DCSBD plasma generates non-thermal low-temperature plasma within the air conditions (ambient air as processing gas) which interactions can result in a variety of molecular, microscopic and surface modifications, (e.g. roughness, creation of functional groups, cleaning) [11]. Also, in accordance with the use of processing gas, the plasma treatment can lead to a material ablation, surface activation, functionalization and cross-linking [21]. In general, DCSBD plasma treatment results in partial decomposition and the formation of new functional groups on the polymer chain [22]. There is a change in the physicochemical properties of the polymer surface (wettability, adhesion, refractive index, chemical resistivity, slipperiness and biocompatibility [23]. As in work of Gerullis, et al. [11] authors modified the cellulose using DCSBD plasma to study the physicochemical changes and chemical structure of cellulose. Herein, the roughness increased with increasing treatment time. Some etching effect and oxygen moieties, resp. functional groups were formed. A study from Zemljič [24] dealt with the RF plasma treatment of cellulose, to improve of chitosan adsorption onto cellulosic fibric. Influence of plasma treatment based on DCSBD plasma on mechanical properties of cellulose-based fibres and their interfacial interaction in composite systems was evaluated in Valášek, et al [25].Herein, the plasma removed wax layer from natural vegetable fibres and caused unfavorable interaction – plasma decreased the cellulose content and as it comes to the lignin degradation in the surface layers.

From the comparative perspective of view can be used another physical surface treatment by ionization using corona discharge [26]. Advanced modifiers include ozone which can be created from oxygen or dry air [27]. Additionally, ozone can be used to treat the surface of polyester fibres [28], to depolymerisation of cellulose [29], to improve the solubility [30] of cellulose in alkaline solutions [31], removal of lignin from cellulose [32], and or, creating functional groups on cellulose [33].

Today, a lot of attention is paid to the use of cellulose in polymer composites [34]. In relation, composite systems consist of at least two phases [35]. The presented study was focused on the surface treatment of cellulose with ozone and DCSBD plasma in order to improve the interfacial adhesion between the filler (cellulose) and the hydrophobic polymer matrix (natural rubber) in the preparation of elastomer composite systems (ECs). Furthermore, to investigate the physical and mechanical properties of prepared composite systems. A few papers in the literature investigate the plasma treatment of cellulose and its effect of resulting properties of polymer composite system. In this case, the polymer (elastomer) composite system refers to the cured rubber filled with carbon black/cellulose, with addition of activators, curing agents (sulphur), accelerators, stabilizators, plasticizers, etc. Authors Kazemi, et al. [36] studied the effect of plasma treated cellulose fibres in order to partially replace carbon black in natural rubber hybrid composites. In here, the composite system filled with 50 % of modified cellulose and 50 % of carbon black exhibited in better elongation at break, tensile modulus at 100 %, storage modulus at 25 °C than those filled with 100 % of carbon black. Or, as in work of Huang, et al. [37] the effect of plasma activated pre-silanization of cellulose nanofibers on the vulcanization characteristics, Payne effect, dynamical-mechanical properties of natural rubber composite was studied. As previously, the incorporated modified cellulose improved physical and mechanical properties and processing safety of NR composite.

When examining the effects of these modification processes, it is important to consider not only the mechanical properties of the composite but also its environmental aspects, such as biodegradability and sustainability. Comparing cellulose modified by plasma and ozone can provide valuable insights into the optimal utilization of cellulose as a filler in composite materials for various applications. The results of such comparisons can have significant implications for the development of environmentally sustainable materials with high performance and a wide range of applications. The presented study presents findings from investigating the impact of DCSBD plasma and ozone as pretreatment of cellulose in the function of a filler in elastomeric composite. The influence of DCSBD plasma and ozone is examined in the context of: changes in surface fluorescence of prepared composite mixtures, observation of cellulose dispersion on the surfaces of composite mixtures using SEM, static tensile testing, and changes in selected modules of dynamic mechanical analysis, namely viscoelastic characteristics.

2 Material and methods

In this study, the plasma reactor KPR 20 has been used. It is a semi-automatic device designed for surface treatment of different materials and is equipped with two types of ceramic dielectrics (also called electrodes) that can generate a homogeneous DCSBD plasma layer. Ceramic dielectric used in this experiment was flat. On this ceramic surface some pads were used – to create an effective space (0.28 mm). This space is very important to electric discharges – when they are generated, they create a plasma. The DCSBD power unit was set at 350 W. The modification of CEL was performed in a distance from ceramic dielctric 0.28 mm for a 3 minutes/surface. This exposure time has been reached gradually and represents the sum of approximately three to six plasma adjustments. It was necessary to modify the pressed cellulose with plasma gradually. Such plasma modification gradually clogged the surface of the ceramic dielectric diet with small particles of cellulose. These subsequently prevented the development of the electrical microdischarges that provide plasma particles. The pretreatment of CEL was carried out in an ozone atmosphere using a simple ozone generator (total 45 minutes of exposition). Cellulose was in a pocket where the ozone from the generator was fed through the tube.

The fluorescence of the surfaces of prepared elastomeric compounds was determined by the Recognoil®2W device. It was thus possible to create fluorescent maps of elastomeric composite surfaces with unmodified cellulose, plasma modified cellulose and ozone treated cellulose. The results of fluorescence obtained from the fluorescent maps of the surfaces of the composite elastomeric mixtures could be compared to the actual visible state of cellulose dispersion. The results of fluorescence obtained from the fluorescent maps of the surfaces of the composite elastomeric mixtures could be compared to the actual visible state of cellulose dispersion. Cellulose has very high fluorescenice values, so it was possible to identify which surface of the prepared composite mixture. The surfaces of the surface of the surfaces were determined on the surface from above and below. 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. CEL max. [F.U.] = 15,937,500 [F.U.]. The dispersion of cellulose was observed for both the upper and lower surfaces of each prepared elastomeric composite.

When observing the impact of cellulose modification using ozone and DCSBD plasma through SEM imaging, images were taken at magnifications of 500x and 2,500x. This made it possible to identify potential positive effects of this modification – improvement in cellulose dispersion within the matrix and thus enhancement of mutual adhesion. The TESCAN VEGA 3 SEM microscope was used in secondary electron mode. Composite mixtures were previously coated with Au-Pa via SC7620 Mini Spuer Coater Quorum Technologies. SEM images of prepared composite mixtures were taken while observing the fracture surface of the prepared composite mixtures.

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. Tension film geometry was used to measure Elastic Modulus, Storage Modulus and TanDelta. From these curves tangens delta temperatures was set and calculated.

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.

As matrix for all prepared elastomeric composites, natural rubber type SMR 10 (Resinex, Czech Republic) was used. Cellulose type GW70 (Greencel Ltd. company Hencovce, Slovakia) served as filler. Stearic acid (Setuza a.s., Ústí nad Labem, Czech Republic), zinc oxide (Bayer, Kuala Lumpur, Malaysia) were employed as a activators and sulphur (Bayer, Kuala Lumpur, Malaysia) as a crosslinking agent. Commercial grade N-tert-butyl-2-benzothiazole sulphonamide (Duslo a.s., Šaľa, Slovakia) was used as an accelerator. Elastomeric composites were prepared by a one-step mixing process in a laboratory mixer Brabender Plastograph EC Plus (Brabender GmBH & Co.KG, Duisburg, Germany) with a mixing chamber volume of 80 cm^3. The mixing temperature was set to 55 °C ± 1 °C and the speed of the mixing to 50 rpm ± 1 rpm. The composites were allowed to stand at room temperature before further processing.

3 Results and discussion

Cellulose (RAW) achieves a high fluorescence value (15,973,500 F.U.) on the surface of the elastomeric composite. Exactly such values have often been observed in fluorescence maps of ECs with ozone-pretreated cellulose. The dispersion of cellulose as a filler in the prepared ECs was studied as the average fluorescence value of the surfaces of the above/top (first column) and below/bottom (second column) surfaces of all ECs: ozone pretreated cellulose, plasma-modified cellulose and cellulose not treated – RAW (Fig. 1 α). When examining the surface of the elastomeric composite from above, the dispersion of cellulose was highest based on the average fluorescence value of this surface for the elastomeric composite with ozone-modified cellulose = 4,292,084 ± 1,848,326 [F.U.]. The average fluorescence value of the top surface of the elastomeric composite was lower in the case of cellulose modification by DCSBD plasma = 2,371,596 ± 325,054 [F.U.]. A similar value of the average fluorescence value of the surface was recorded for the elastomeric composite whose cellulose was not modified = 2,250,068 ± 44,389 [F.U.]. When examining the surface of the elastomeric composite from bottom, the dispersion of cellulose was determined based on the average fluorescence value of this surface. The highest fluorescence value was recorded for the composite with unmodified cellulose = 4,725,040 ± 1,068,321 [F.U.]. This indicates that the UV radiation detector detected a high proportion of cellulose on such a surface. The average fluorescence value of the lower surface of the elastomeric composites decreases sequentially for ozone-modified cellulose 3,908,755 ± 792,929 [F.U.], with the lowest recorded average fluorescence value observed for the surface of the elastomeric composite with cellulose modified by DCSBD plasma = 2,371,596 ± 325,054 [F.U.]. This fact is also confirmed by visual observation. The reduction in the fluorescence value of the surface indicates that the surface contains a smaller amount of cellulose, which has high fluorescence. The high fluorescence of cellulose was reduced by better dispersing it in the matrix through DCSBD plasma modification.

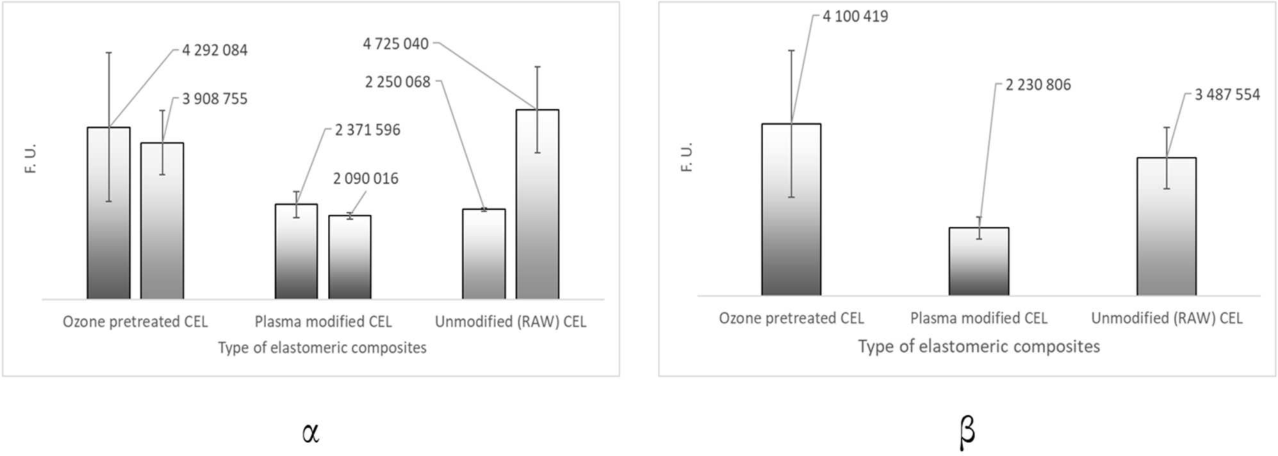
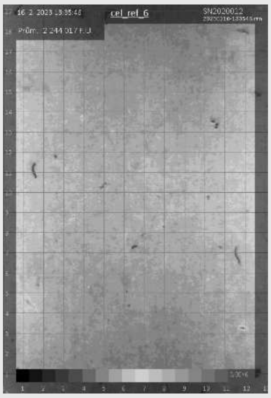
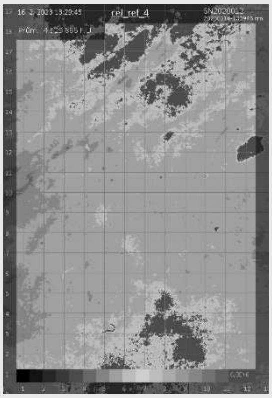


Fig. 1 *Average fluorescence values of individual ECs surfaces (a) and average fluorescence values of both ECs surfaces (β)*

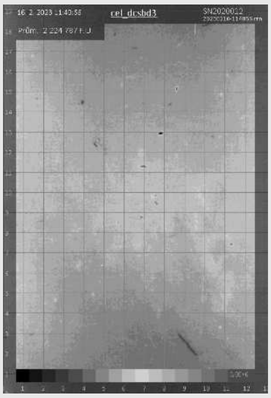
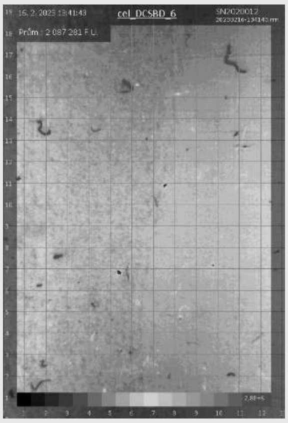
In comparing the average fluorescence values of the surfaces of different types of prepared elastomeric composites from both the top and bottom, differences were observed, Fig. 1**β**. The surface of the elastomeric composite with unmodified cellulose achieves an average fluorescence of 2,250,068 ± 44,389 [F.U.], while the bottom side exhibits an average fluorescence value of up to 4,725,040 ± 1,068,321 [F.U.]. This may indicate that such cellulose lacks sufficient dispersibility and has decreased (or was squeezed out during pressing) in the mixture, Tab. 1.

Tab. 1 *Average fluorescence of ECs surfaces with unmodified CEL according to the examined surface*

<table>
<tr><th colspan="2">Fluorescent value of TOP surface /Δ to average</th><th colspan="2">Fluorescent value of BOTTOM surface/Δ to average</th></tr>
<tr><td>2 244 017/Δ = -6 051
Most representative fluorescence map to average</td><td rowspan="6"> </td><td>5 009 491 /Δ = 284 451</td><td rowspan="6"> </td></tr>
<tr><td>2 285 013 /Δ = 34 945</td><td>5 119 677/Δ = -4 719 921</td></tr>
<tr><td>2 275 781 /Δ = 25 713</td><td>3 699 144/Δ = -1 025 896</td></tr>
<tr><td>2 201 942 /Δ = -48 126</td><td>6 450 752/Δ = 1 725 712</td></tr>
<tr><td>2 299 723 /Δ = 49 655</td><td>4 529 886/Δ = -195 154
Most representative fluorescence map to average</td></tr>
<tr><td>2 193 931 /Δ = -56 137</td><td>3 541 290/Δ = -1 183 750</td></tr>
<tr><td colspan="2">Average fluorescence = 2 250 068 ± 44 389 [F. U.]</td><td colspan="2">Average fluorescence = 4 725 040 ± 1 068 321 [F. U.]</td></tr>
<tr><td colspan="4">Average fluorescence (Top and Bottom) = 3 487 554 ± 556 355 [F. U.]</td></tr>
</table>

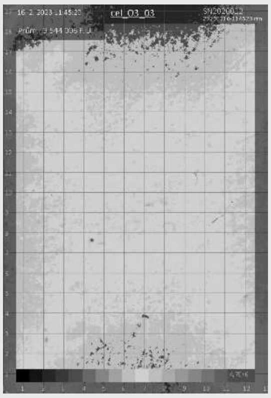
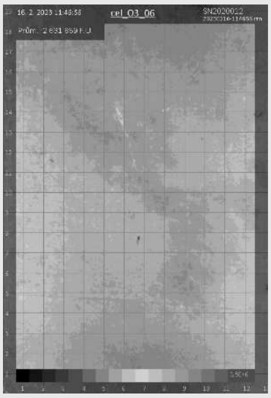
On the contrary, plasma-modified cellulose shows almost the same average fluorescence values on both surfaces of the prepared elastomeric composite = 2,371,596 ± 325,054 [F.U.] for the top and 2,090,016 ± 80,081 [F.U.] for the bottom. This means that the dispersion of DCSBD plasma-modified cellulose in the elastomeric composite prepared in this way is better, Tab. 2. 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 ECs is 2,230,806 [F. U.]. Therefore, the measured fluorescence values were the lowest, almost 52 % less than in the elastomeric composite 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 ECs.

Tab. 2 *Average fluorescence of ECs surfaces with plasma modified CEL according to the examined surface*

Fluorescent value of Top surface/Δ to average		Fluorescent value of Bottom surface/Δ to average	
2 134 585 /Δ = -237 011		2 087 281 /Δ = -2 735 Most representative fluorescence map to average	
2 176 498/Δ = -195 098		2 095 701 /Δ = 5 685	
2 224 787/Δ = -146 809 Most representative fluorescence map to average		1 973 295 /Δ = -116 721	
2 939 176/Δ = 567 580		2 124 381 /Δ = 34 365	
2 589 750/Δ = 218 154		2 045 851 /Δ = -44 165	
2 164 782/Δ = -206 814		2 213 588 /Δ = 123 572	
Average fluorescence = 2 371 596 ± 325 054 [F. U.]		Average fluorescence = 2 090 016 ± 80 081 [F. U.]	
Average fluorescence (Top and Bottom) = 2 230 806 ± 202 568 [F. U.]			

Cellulose pretreated with ozone can often be visually observed to aggregate. The highest average surface fluorescence value = 4,100,419 [F. U.], Tab. 3. Locally observed maximum fluorescence values on the fluorescence maps were evidence of cellulose aggregation.

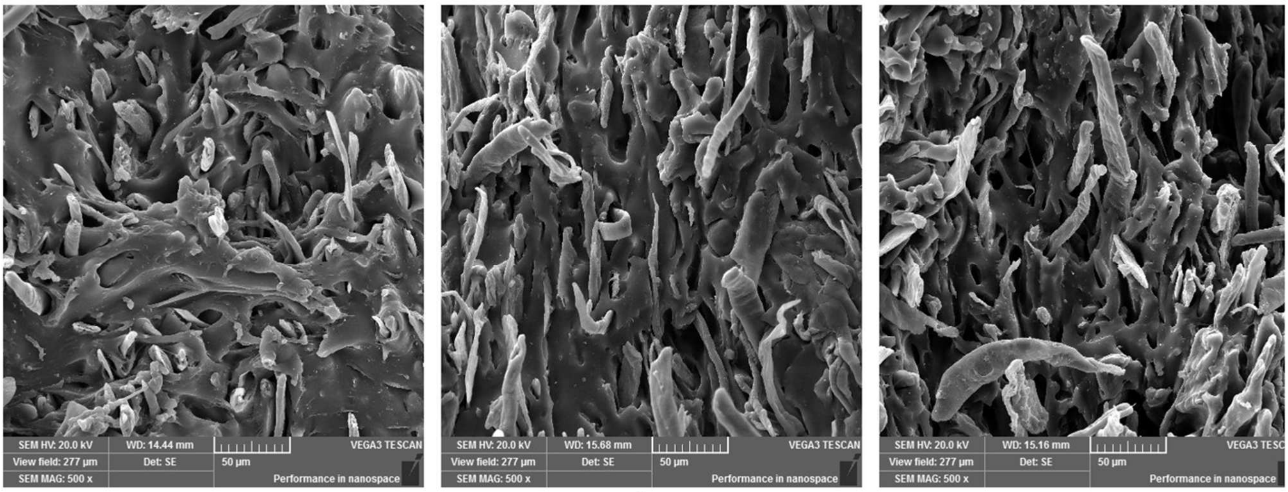
Tab. 3 *Average fluorescence of ECs with ozone pretreated CEL according to the examined surface*

Fluorescent value of Top surface/Δ to average		Fluorescent value of Bottom surface/Δ to average	
6 419 596/Δ = 2 127 512		2 631 869 /Δ = -1 276 886 Most representative fluorescence map to average	
3 058 265/Δ = -1 233 819		3 867 786 /Δ = 3 867 786	
6 884 402/Δ = 2 592 318		4 619 144 /Δ = 4 619 144	
544 006/Δ = -748 078 Most representative fluorescence map to average		4 523 671 /Δ = 4 523 671	
2 872 872/Δ = -1 419 212		3 901 305 /Δ = 3 901 305	
2 973 360/Δ = -1 318 724		10107507 * result marked as an outlier	
Average fluorescence = 4 292 084 ± 1 848 326 [F. U.]		Average fluorescence = 3 908 755 ± 792 929 [F. U.]	
Average fluorescence (Top and Bottom) = 4 100 419 ± 1 320 628 [F. U.]			

The average fluorescence value of the surfaces of ECs 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 ECs with ozone-pretreated cellulose, but higher than that of the surfaces of ECs with plasma-modified cellulose. From the point of view of statistics and the evaluation of the significance of the interval of the standard deviation of the measured fluorescence values of the surfaces of ECs, it can be concluded that the highest deviation calculated from the obtained fluorescence values of the surfaces confirms the inhomogeneous distribution and the observed aggregation of cellulose in ECs with ozone-pretreated cellulose. In contrast, the lowest standard deviation for plasma-modified cellulose in the ECs confirms its homogeneous distribution. Somewhere between the homogeneous distribution of plasma-modified cellulose and ozone-pretreated cellulose is the standard deviation interval of unmodified RAW cellulose. In the study [38], the examination of surfaces using UV radiation was also used.

Additionally, based on the standard deviation values for each surface, this modification exhibits the most homogeneous character. The prepared composite mixture with ozone-modified cellulose also shows average fluorescence values on both surfaces at a similar level: top = 4,292,084 ± 1,848,326 [F.U.] and bottom = 3,908,755 ± 792,929 [F.U.]. However, the standard deviation values indicate high differences in cellulose dispersion on/near the surface, with the average fluorescence values reaching high levels. This suggests that ozone-modified cellulose tends to be unevenly present near the surfaces in the elastomeric composite, as dispersed within/structured in the prepared elastomeric composite. This fact will require further research.

When comparing SEM images of elastomeric composites prepared with cellulose, with and without DCSBD plasma modification, such an image appears to be more detailed, with clearer differences in details and contrast compared to unmodified cellulose, Fig. 2γ and Fig. 2α. The SEM image of the elastomeric composite with plasma-modified cellulose appears as if the cellulose were dispersed more evenly. Additionally, these plasma-modified cellulose fibers give the impression of a more regular distribution and orientation in the composite mixture. Minimal cellulose dispersion can only be observed in the elastomeric composite with unmodified cellulose. The dispersion of ozone-modified cellulose is at the interface of both mentioned elastomeric composites. SEM images of elastomeric composites with cellulose modified (pretreated) by ozone appear less oriented and less regular than those with DCSBD plasma-modified cellulose, Fig. 2β. However, the image of the elastomeric composite with cellulose fibers modified by ozone appears more detailed and contrasting compared to the SEM image of the elastomeric composite with unmodified cellulose.



α β γ

Fig. 2 *SEM images of elastomeric composites with unmodified cellulose (a), ozone pretreated cellulose (β) and plasma modified cellulose (γ); The images were created by Ing. Andrej Dubec, PhD.*

The physical and chemical changes that could have occurred on cellulose fibers through the formation of functional groups, particularly with DCSBD plasma modification and partially with ozone modification, should lead to visible changes in the morphology of the cellulose fibers: changes in their thickness and surface texture. However, these effects were not observed in the prepared composite mixtures. Similarly, more detailed microstructures at the points of interconnection between cellulose fibers and the matrix were not directly observed. Such observations would provide direct and visible evidence that the adhesion of plasma-modified cellulose fibers, and partially ozone-modified cellulose fibers, is at a higher level in the prepared composite mixtures. This assertion could also be supported by observing smaller gaps and flaws in the improved adhesion between the matrix and plasma- and ozone-modified cellulose fibers. However, it was not possible to demonstrate these findings using SEM images, Fig. 3.

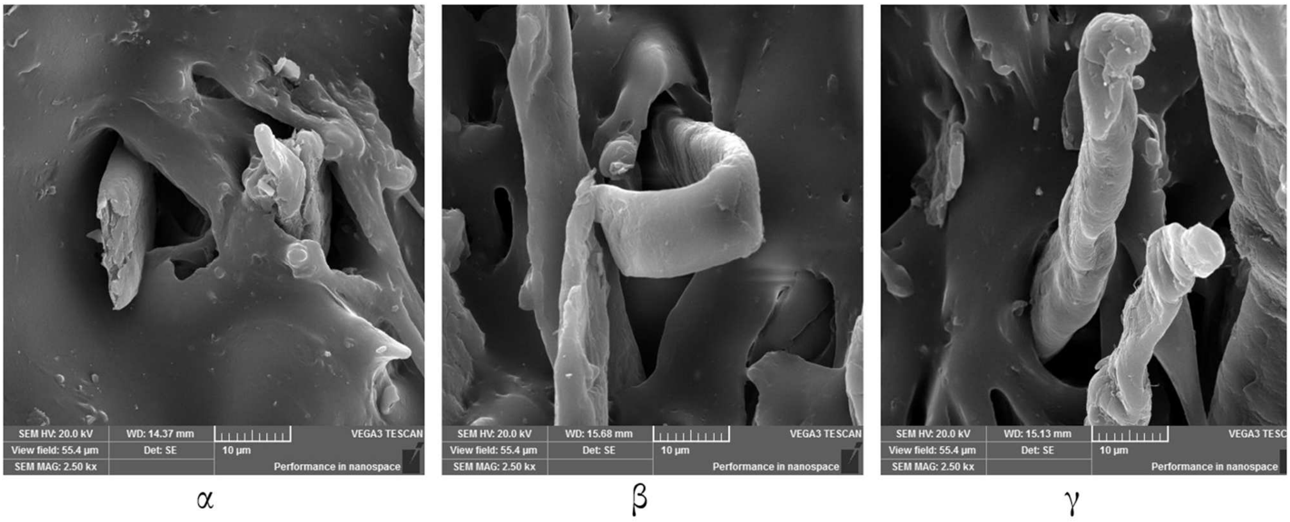


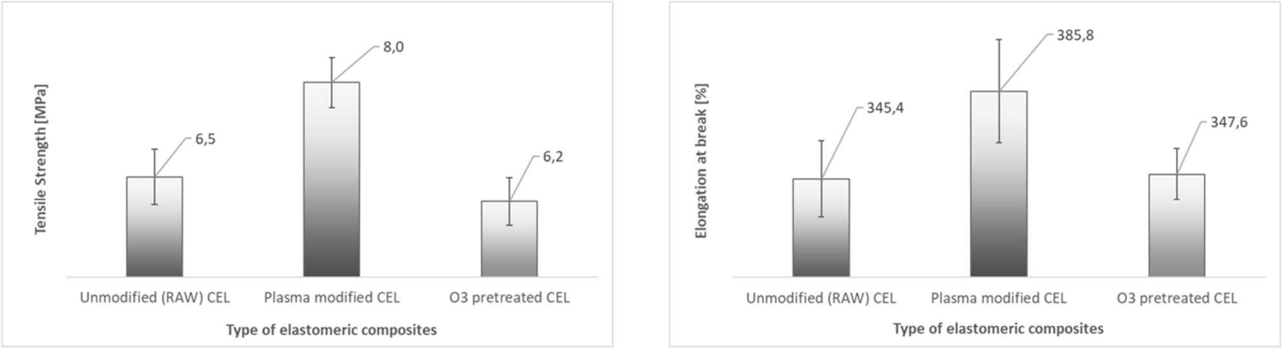
Fig. 3 *SEM images of elastomeric composites with unmodified cellulose (a), ozone pretreated cellulose (β) and plasma modified cellulose (γ). The images were created by Ing. Andrej Dubec, PhD.*

Due to the physical treatment of the cellulose filler, there was a decrease in the minimum torque M_{MIN} of the blends, as seen in Tab. 4. 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 blends, 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. Ozone can cause significant changes to cellulose [39, 40]. 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 blends delayed the vulcanization process.

Tab. 4 *Curing characteristics of prepared ECs*

Type of prepared EC/different type of CEL	Curing characteristics			
	M_{MIN} (dNm)	M_{MAX} (dNm)	T_{C90} (min)	T_{S02} (min)
Unmodified (RAW) CEL	3.0	29.9	12.2	6.2
Ozone pretreated CEL	2.3	29.0	12.3	6.2
Plasma modified CEL	2.6	30.1	14.4	7.6

The highest tensile strength (8 MPa) was measured for an ECs with plasma-modified cellulose, as seen in Fig. 4α. The ECs that contained cellulose in its original state (RAW) has a lower tensile strength (6.5 MPa). The ECs with ozone pretreated has the lowest tensile strength (6.2 MPa). The value of the tensile strength (TS) in the case of elastomeric composites depends on the interaction of the filler with the matrix as well as on the quality of the created crosslinking network during vulcanization. In the case of the same recipe of elastomeric composites only with modification of the used filler, it is possible to compare the cross-linking of individual composites using the MH value. The trend of the tensile strength values is like that of the MH values. The plasma modified CEL composites is characterized by the highest TS value. This is related to the plasma treatment of the filler before its incorporation into the composite. The plasma weakens the cellulose fibres, which are broken and shortened during the mixing of the composite, which reduces the negative effect of the length of the fibres and their influence on the density of the resulting network during vulcanization. In addition, the plasma tends to modify the surface of the fibres, which becomes rougher, which consequently causes higher mechanical adhesion in the matrix. The elastomeric composite containing unmodified cellulose achieved a lower TS value compared to plasma modified. Without treatment, the filler fibres were only subjected to the load during the mixing process and their length was not significantly reduced. Thus, during the tensile test, the fibres acted as stress concentrators and during the vulcanization process, they influenced the density of the formed crosslinking network, which was reflected in a lower value of TS. The effect of ozone on cellulose is mainly manifested during the delignification of fibres. The treatment and splitting of fibres by ozone is not as significant as in the case of plasma treatment of fibres. The elastomeric composite containing ozone pretreated CEL achieved comparable TS values to unmodified CEL [41, 42].



α β

Fig. 4 *Tensile strength and Elongation at break of prepared ECs*

The effect of cellulose on elongation at break of ECs has the same trend as in tensile strength, as can be seen in Fig. 4 β. The highest value of the elongation on break of the EC was measured in elastomeric composite 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 elongation at break (EaB) of elastomeric composites depends on several factors. The greatest influence has a type and content of filler as well as crosslinking density of the formed vulcanization bonds. In the case of the same filler content in elastomeric composites, its modification plays a role. Again, the trend of values is the same as for tensile strength. The highest value was achieved by the plasma modified CEL composite, which can be attributed to the modification itself and the above-mentioned breaking and shortening of the filler fibres. Shorter fibres compared to the unmodified version do not affect the flexibility of the matrix to such an extent. In addition to the fibres themselves, the flexibility of the matrix depends on the crosslinking bonds formed during vulcanization process, the density of which is influenced by the presence of the filler. Shorter fibres in the volume of the matrix create more space for the formation of crosslinking bonds, which is also reflected in the value of the rheological properties, namely MH. The elastomeric composite containing unmodified filler achieved the second highest EaB value and almost identical to the ozone pretreated composite.

In the case of samples of unmodified CEL and ozone pretreated CEL, a high occurrence of filler agglomerates was also proven, which reduce the flexibility of the matrix as well as the density and quality of crosslinks created during vulcanization [43, 44].

The addition of cellulose as a filler to ECs (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 as can be seen in Fig. 5. Depending on the maximum value of the Tan delta peak, there is a glassy transition of individual ECs at a temperature interval of approximately -41 to -39 °C in the following order:

- Elastomeric composite with plasma modified cellulose (-40.7 °C),
- Elastomeric composite with pretreated cellulose (-39.03 °C),
- Elastomeric composite with reference cellulose (RAW) (-39.46 °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 elastomeric composite has better damping properties, higher heat dissipation, but has a lower level of elasticity. The elastomeric composite 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. By comparing the Tan Delta curves of the prepared elastomeric composites, it has been proven that cellulose modification by plasma imparts lower viscosity to the composite compared to elastomeric composites with ozone-modified cellulose and unmodified cellulose. Evidence is found in the maximum peak value of the Tan Delta curve, which is lowest for the elastomeric composite with plasma-modified cellulose. This value is higher for the elastomeric composite containing ozone-modified cellulose. The reference value for observing the impact of modification can be derived from the elastomeric composite where cellulose was not modified.

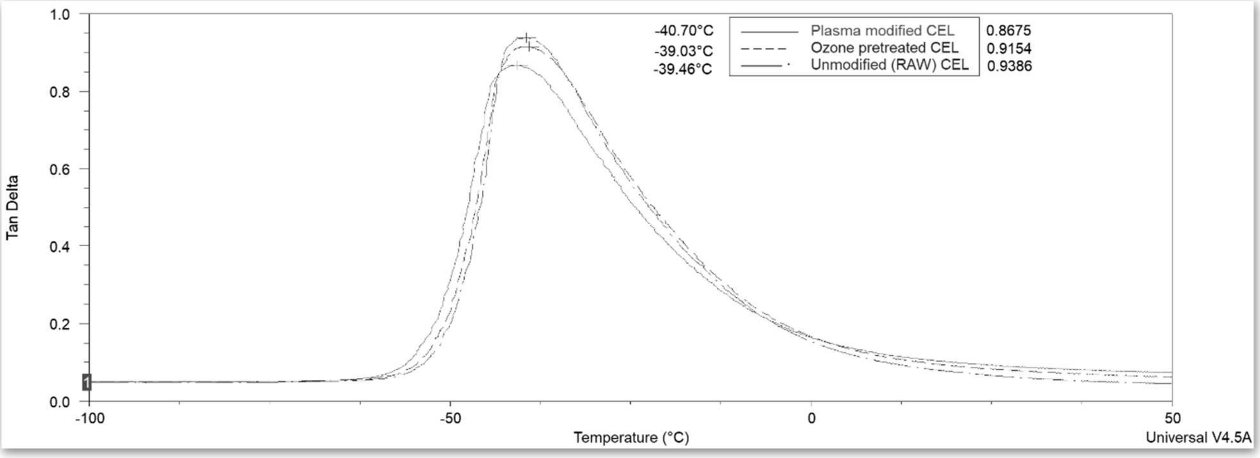


Fig. 5 *Tan Delta curves of prepared ECs*

The curves of the storage modules curves show a higher level of the elastomeric composite with plasma-modified cellulose. When comparing the course of the loss Modulus it is clear that the elastomeric composite 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 as seen in Fig. 6. The curves of elastic modulus demonstrate that the elastomeric composite with plasma-modified cellulose achieves higher load values, capable of withstanding cyclic mechanical loading compared to elastomeric composites with ozone-modified cellulose and unmodified cellulose as fillers. The ability of such a composite to return to its original form during cyclic deformations is therefore the highest. Similar results in shifts of Tan Delta temperatures are present in the study [45].

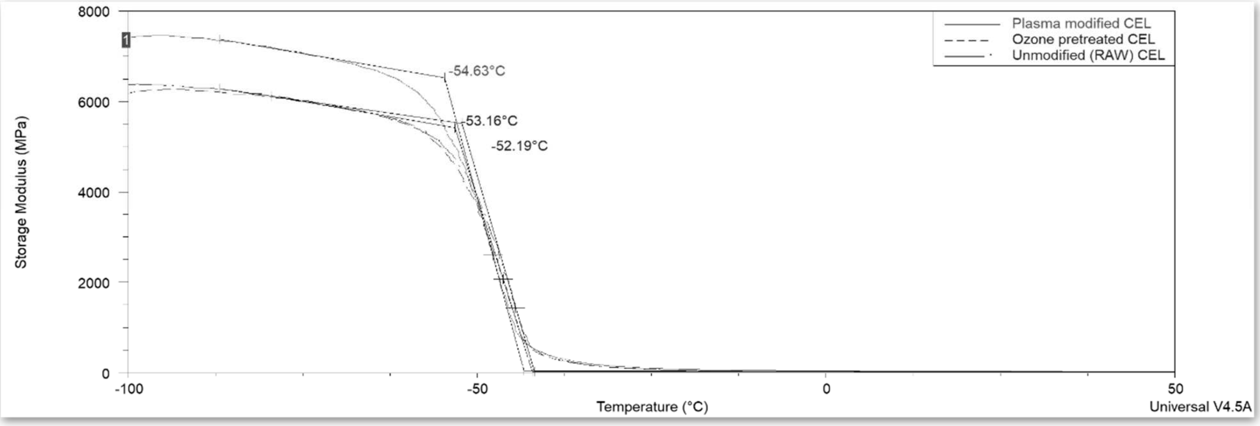


Fig. 6 *Storage Modulus curves of prepared ECs*

For the loss modulus, the glass transition temperatures of the examined ECs occur in the temperature range of approximately -48 to -46 °C as can be seen in Fig. 7. Evidence of the reinforcing effect of plasma-modified cellulose is reflected in the behavior of the loss modulus curves. This demonstrates that a portion of the energy during material deformation transforms into heat. This effect is an indication of how quickly the composite absorbs and releases energy during deformation changes. The loss modulus curves show that the elastomeric composite with plasma-modified cellulose achieves better values. The critical glass transition temperature for the elastomeric composite with plasma-modified cellulose is reached at the lowest recorded glass transition temperature of -47.95°C. Similar temperature region was observed in the study of [45].

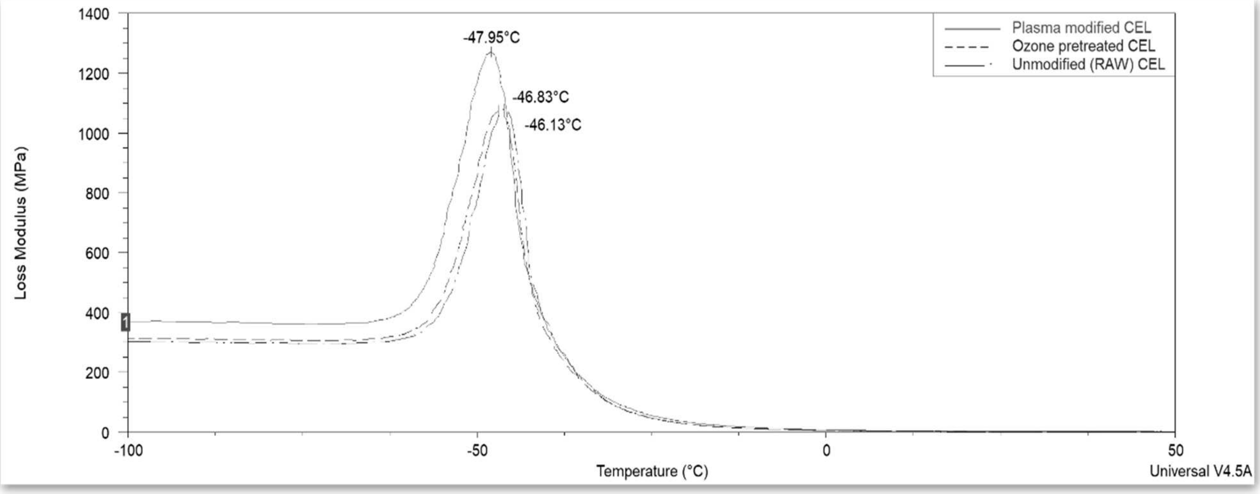


Fig. 7 *Loss modulus curves of prepared ECs*

4 Conclusion

In conclusion, elastomeric composites (ECs) were prepared using untreated (raw) cellulose (CEL), cellulose with ozone pretreatment, and DCSBD plasma-modified cellulose as fillers to investigate the impact of cellulose on the composite properties. Pretreatment and modification of cellulose with ozone and DCSBD plasma were found to influence filler dispersion, tensile strength, and elongation at break. Curing characteristics, glass transition temperatures, and Tan Delta values were also affected by these treatments. While both ozone pretreatment and DCSBD plasma modification exhibit similar ozone-related processes, the latter showed a more significant positive effect on cellulose modification. Additionally, DCSBD plasma treatment introduces heat and UV radiation, unlike ozone treatment alone. The physical treatment of cellulose filler led to a decrease in minimum torque, attributed to plasma-induced fiber damage and aging under ozone treatment. However, ozone treatment alone did not significantly affect the crosslinking network density. Plasma-modified cellulose samples demonstrated the highest maximum torque due to fiber breakage, enhancing crosslinking bond formation. Unlike ozone, plasma treatment has a lasting effect, particularly on fiber integrity and lignin preservation, which impacts the vulcanization process in rubber blends. Unmodified cellulose exhibits a high fluorescence level on the surface of the elastomeric composite. Such values are frequently observed in fluorescence maps of elastomeric composites with ozone-pretreated cellulose. The dispersion of plasma-modified cellulose is not visually detectable. The average fluorescence of these surfaces is considerably lower than that of composites with ozone-pretreated cellulose, being almost half as much. The distribution of untreated or unmodified cellulose is less visually like that of ozone-pretreated cellulose, showing less intense aggregation over a smaller surface area. The average fluorescence value for composites with RAW cellulose is higher than that of plasma-modified cellulose but lower than that of ozone-pretreated cellulose. Statistically the lowest standard deviation for plasma-modified cellulose indicates a more homogeneous distribution.

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