Diffuse plasma surface modification of natural rubber-based composite
(Rapid communication)

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Abstract: The article investigates the effect of diffusion plasma exposure time (30 s, 60 s) on the physicochemical surface properties of the natural rubber-based composite. X-ray photoelectron spectroscopy (XPS), scanning electron microscopy (SEM) with dispersive X-ray spectroscopy (EDS) were used to assess the properties. Wettability and surface free energy tests were also performed. The application of plasma leads to surface oxidation (EDS). The obtained properties did not change for 21 days, and the plasma exposure time had no significant effect on the physicochemical changes of the composite surface.

Keywords: diffused plasma, natural rubber, composites, surface modification.

Modyfikacja powierzchni kompozytu na bazie kauczuku naturalnego za pomocą plazmy dyfuzyjnej
(Komunikat szybkiego druku)

Streszczenie: W artykule zbadano wpływ czasu oddziaływania plazmy dyfuzyjnej (30 s, 60 s) na właściwości fizykochemiczne powierzchni kompozytu na bazie kauczuku naturalnego. Do jej oceny zastosowano spektroskopię fotoelektronów rentgenowskich (XPS), mikroskopię skaningową elektronową (SEM) z dyspersyjną spektroskopią rentgenowską (EDS). Przeprowadzono również badania zwilżalności oraz swobodnej energii powierzchniowej. Zastosowanie plazmy prowadzi do utleniania powierzchni (EDS). Uzyskane właściwości nie zmieniały się przez 21 dni, a czas ekspozycji plazmy nie miał istotnego wpływu na zmiany fizykochemiczne powierzchni kompozytu.

Słowa kluczowe: plazma dyfuzyjna, kauczuk naturalny, kompozyty, modyfikacja powierzchni.

Elastomeric composites have found applications in emerging markets and technologies due to their specific properties, including in fields such as electronics, technical manufacturing, chemistry, medicine, tires, and more. A crucial component in the assembly of elastomeric composites is rubber, whether natural or synthetic [1]. For some manufacturers, it is important to consider not only the processing properties of elastomeric composites but also their surface properties. Nowadays, atmospheric plasmas are frequently used as modification processes to activate the surface of materials, for example, by grafting different kinds of chemical groups onto the surface. [2–5]. For instance, Vaziranasab *et al*. [4] used the atmospheric plasma to achieve a superhydrophobic surface of HTV silicone rubber, while Rufaza-Silvestre, C. et al. [5] employed atmospheric plasma to improve adhesion.

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surface of HTV silicone rubber, while Rufaza-Silvestre *et al*. [5] used atmospheric plasma to improve adhesion.

Therefore, this work focuses on the influence of atmospheric pressure plasma on the surface chemistry, elemental distribution on the surface, wettability, and surface free energy of a natural rubber-based composite.

EXPERIMENTAL PART

Materials

Natural rubber-based composite was obtain by using natural rubber (NR SMR 10, Kuala Lumpur, Malaysia), carbon black N339, and silica (MAKROchem, Lublin, Poland), zinc oxide (SlovZinc, a.s., Košeca, Slovakia), sulfur (Istrochem a.s., Bratislava, Slovakia), Dusantox® 6PPD (Duslo, Šaľa, Slovakia), residual aromatic oils (Shell, Slovakia, s.r.o.), bezothiazyl-2-dicyklohexyl sulfonamide DCBS (Akrochem, Akron, Ohio, USA). Amount of component used is listed in Table 1.

T a b l e 1. Components of natural rubber- based composite

Component	Amount (phr*))
Natural rubber	100
Carbon black	52.5
Silica	8.0
Sulfur	10.0
6PPD	1.2
DCBS	3.0
ZnO	3.0

*) parts per hundred

Plasma surface modification and surface characterization

An atmospheric pressure diffuse plasma reactor (Research Institute for Man-Made Fibers, Svit, Slovak Republic) was used for the surface modification of an elastomeric composite. The reactor employed a grounded electrode embedded in 96% alumina and produced visually diffuse and homogeneous plasma. The rubber-based composite was exposed to diffuse plasma at a power of 375 W for durations of 30 and 60 seconds. The distance between the stationary plasma electrode and the elastomeric composite surface was maintained at 0.3 mm. The untreated elastomeric composite is referred to as ES0-0, the 30-second plasma-treated sample as ES3-0, and the 60-second plasma-treated sample as ES6-0.

Methods

Surface analysis was performed using X-ray photoelectron spectroscopy (XPS) with an ESCALAB 250Xi system (Thermo Scientific, R&D Centre for Low-Cost Plasma and Nanotechnology Surface Modifications CEPLANT, Czech Republic), equipped with a 500 mm Rowland circle monochromator and a micro-focused Al Kα X-ray source.

Following the chemical characterization, scanning electron microscopy with energy dispersive X-ray spectroscopy (SEM-EDS) was conducted using a Tescan VEGA 3 system (Brno, Czech Republic). Additionally, surface free energy (SFE) and wettability were measured using a 30DSE Krüss Advance goniometer (Prague, Czech Republic) based on the Owens-Wendt method. For this analysis, 10 droplets of both polar and non-polar liquids were applied to the surface.

RESULTS AND DISCUSSION

Surface chemical analysis

In Fig. 1, SEM-EDS layered images of chemical composition obtained from the as-received ES0-0, and plasma treated ES3-0, and ES6-0 surfaces are presented. It appears, that surface of not modified and modified plasma composites is mostly consisting of carbon, which correlates with XPS results below. As it can be seen in Table 2, the diffuse plasma treatment led to a decrease of carbon

a) b) c)

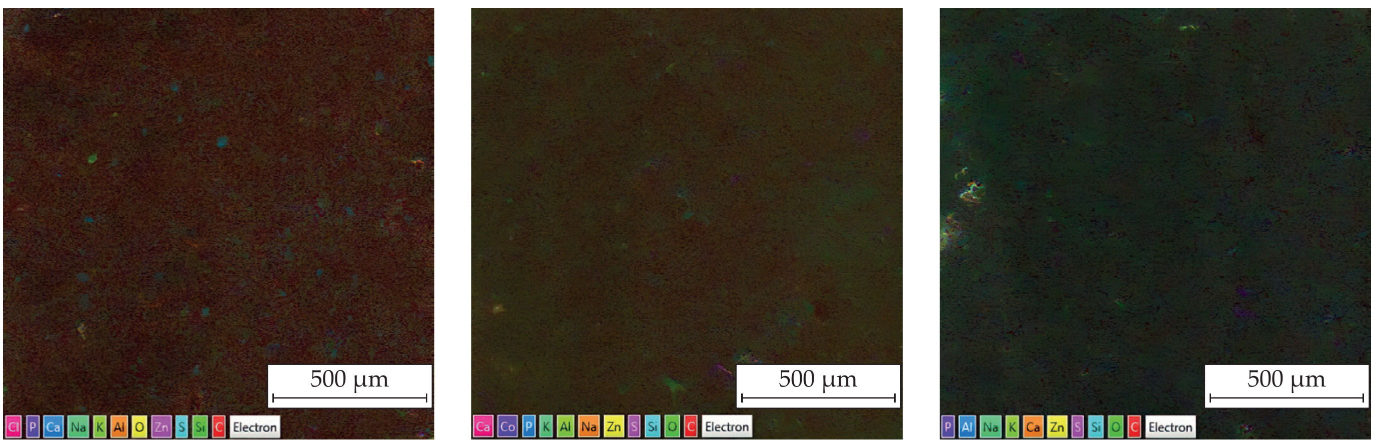

Fig. 1. SEM-EDS mapping: a) ES0-0, b) ES3-0, c) ES6-0

T a b l e 2. Elementary composition of natural rubber-based composites using SEM-EDS and XPS

Element	SEM-EDS, wt%			XPS, wt%		
	ES0-0	ES3-0	ES6-0	ES0-0	ES3-0	ES6-0
C	87.9	83.4	84.4	87.9	92.3	91.5
O	7.0	11.5	10.7	8.3	5.4	5.7
S	1.2	1.5	1.4	0.5	0	0.7
N	–	–	–	1.4	1.9	2.3

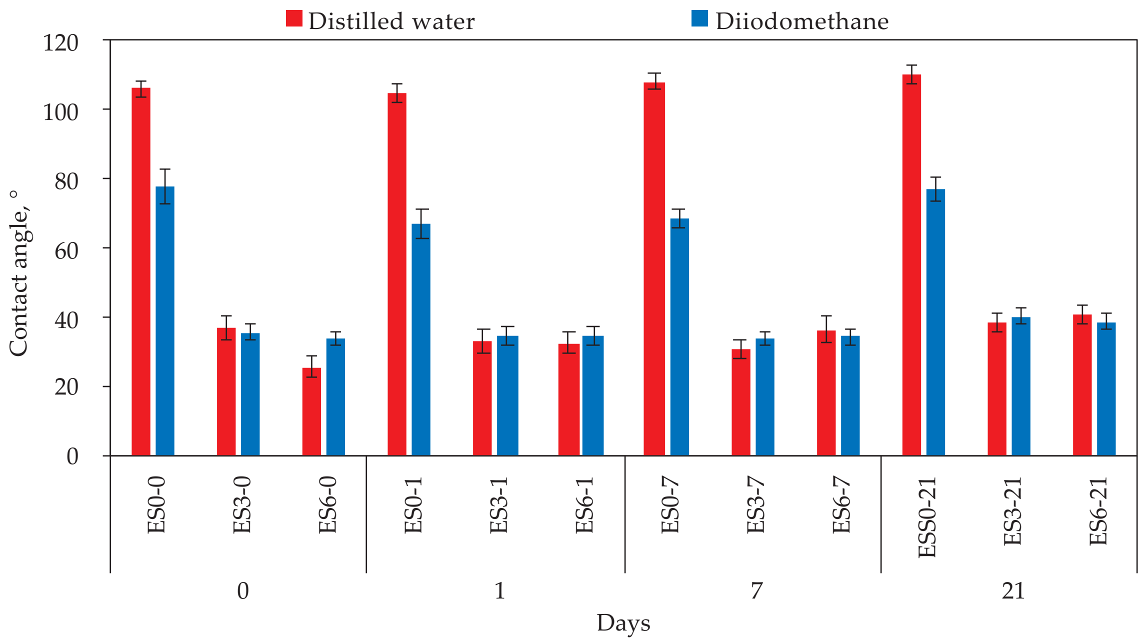

Fig. 2. Wettability of as-received natural rubber-based composite and plasma treated composite

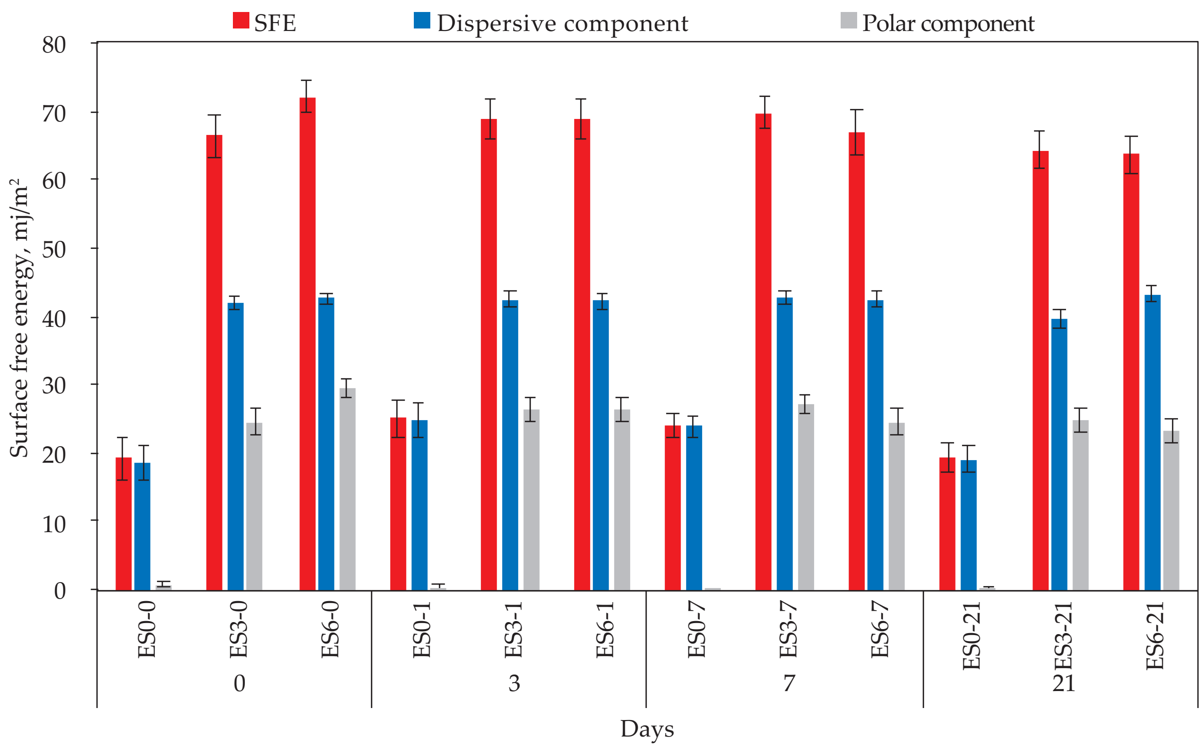

Fig. 3. Plasma activation expressed by SFE within 21 days

content with shorter treatment time along with the increase of oxygen. The introduction of oxygen results in the presence of surrounding atmosphere during plasma modification. According to Table 2, XPS surface analysis achieved completely opposite results. Despite this, XPS analysis revealed surface oxidation by the formation of C=O, O-C=O functional groups on the surfaces of ES3-0 and ES6-0, and sulfur oxidation was demonstrated by the identification of SO_4^- and SO_3^{2-} bonds, which correlates with SEM-EDS analysis.

The surface analysis was followed by characterization of wettability and surface free energy (SFE) both before and after plasma treatment. Measurements were conducted on day 0 (immediately after plasma treatment), as well as on the first day, seventh day, and twenty first day. As shown in Fig. 2 and Fig. 3, plasma treatment resulted in a significant increase in wettability and SFE, with greater exposure time within day zero. This phenomenon is attributed to the introduction of oxygen functional groups on the surface, which corelates with the polar component of SFE [6–8]. Notably, the durability of plasma treatment was remarkable, wettability and SFE values after 21 days were comparable with those measured on day zero.

CONCLUSIONS

Atmospheric pressure diffuse plasma was employed to modify the surface of natural rubber-based composite to investigate the effect of exposure time on surface chemistry. SEM-EDS analysis revealed surface oxidation for both 30- and 60-second treatment durations, showing a similar degree of oxidation in both cases. A comparable trend was observed in the wetting behavior and surface free energy (SFE). Consequently, this research indicates that varying the exposure time between shorter (30 s) and longer (60 s) durations does not significantly affect these surface properties. However, the diffuse plasma treatment exhibited exceptional activation durability.

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Authors contribution

S.Ď. – conceptualization, methodology, investigation, validation, writing-original draft, review and editing; M.P. – methodology, validation, supervision; D.O. – conceptualization, validation, supervision; R.J. – visualization; S.L. – investigation, references; S.B. – writing-review and editing, references; I.L. – conceptualization; T.K. – visualization.

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Conflict of interest

The authors declare no conflict of interest.

REFERENCES

[1] Alam N.M.: *Polymers* **2024**, *16(12)*, 1726. https://doi.org/10.3390/polym16121726

[2] Kenth S.J.: "Surface Modification of Plastics" in "Applied Plastics Engineering Handbook, Second Edition" (Meyer K.) Elsevier, Amsterdam **2017**, p. 443. https://doi.org/10.1016/B978-0-323-39040-8.00020-1

[3] Romero-Sánchez M.D., Martín-Martínez J.M.: *International Journal of Adhesion and Adhesives* **2006**, *26(5)*, 345. https://doi.org/10.1016/j.ijadhadh.2005.05.002

[4] Vazirinasab E., Jafari R., Momen G.: *Surface and Coatings Technology* **2019**, *375*, 100. https://doi.org/10.1016/j.surfcoat.2019.07.005

[5] Rufaza-Silvestre C., Carbonell-Blasco M.P., Pérez-Limiñana M.A. *et al.*: *International Journal of Adhesion and Adhesives* **2022**, *117(part B)*, 103010. https://doi.org/10.1016/j.ijadhadh.2021.103010

[6] Moreno-Couranjou M., Choquet P., Guillot J. *et al.*: *Plasma Processes and Polymers* **2010**, *7(12)*, 963. https://doi.org/10.1002/ppap.201000045

[7] Torregrosa-Coque R., Martín-Martínez J.M.: *Plasma Processes and Polymers* **2011**, *8(11)*, 1080. https://doi.org/10.1002/ppap.201100013

[8] Ďurišová S., Pajtášová M. Ondrušová D. *et al*: *Polimery* **2024**, *69(4)*, 245. https://doi.org/10.14314/polimery.2024.4.5

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