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The Effect of Plasma Treatment on Microstructure, Roughness and Curing of Rubber Blend

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In this paper, the effect of low-temperature atmospheric plasma on the surface of an elastomeric composite system, specifically uncured rubber, is considered. The effect of exposure time (2 s and 4 s), distance (0.5 mm) of atmospheric plasma was examined. Scanning electron microscopy was used to assess the structure and qualitatively chemical composition on the surface. It was revealed that atmospheric plasma based on a diffuse coplanar surface barrier discharge produces an oxidation of the rubber surface. Moreover, plasma treatment affects the surface topography and increases the roughness studied by atomic force microscopy already at 2 s exposure. However, the analogy of both exposure times does not significantly affect the selected specific properties. In terms of the processing properties of rubber and plasma treatment, the optimum cure time, scorch time, and torque values were evaluated using a rubber processing analyser. In this case, plasma treatment produced accelerated curing time compared to the reference rubber.

topics: atmospheric plasma, diffuse coplanar surface barrier discharge (DCSBD), rubber, scanning electron microscope (SEM)

1. Introduction

The term "plasma" often refers to the fourth state of matter, following solid, liquid, and gas. Over the past years, plasma became an effective tool for materials treatment. On the one hand, it provides fast and constructive material treatment, and on the other hand, it offers unique chemical features erected on the surface [1, 2].

Atmospheric pressure plasmas (APP) are formed in an open atmosphere at laboratory temperature, which enables easy generation of reactive plasma species, excited and ionized species, depending on the process gas applied, without requiring the use of vacuum facility [3].

APP plays an important role in many current industries and emerging fields, e.g., medicine, materials processing, agriculture or aerospace [3]. Diffuse coplanar surface barrier discharge (DCSBD) is commonly used in the textile fabrics processing, non-woven polypropylene (PP) fabrics [4] or other. Since the invention of the DCSBD plasma by a team of Mirko Černák, the DCSBD plasma was utilized in wood treatment [5], glass treatment [6], cellulose treatment [7] or polyoelfins [8]. Many research papers deal with the physical characterization of the DCSBD plasma using the methods of optical emission spectroscopy [9] and mass spectrometry [10]. In the specific case that interests us, the DCSBD consists of a system of parallel strip line electrodes embedded in 96 % alumina and cooled with dielectric oil. Due to the electrodes configurations, the DCSBD plasma creates macroscopically homogeneous plasma [10].

Several publications are focused on chemical modifications on the surface induced by DCSBD plasma, mainly via the formation of reactive oxygen and nitrogen species (RONS). For example, in the study of R. Talviste (2020) [5] the effect of DCSBD plasma on the surface characteristics on European beech (Fagus sylvatica) in the atmosphere of O_2, CO_2, N_2, and Ar was estimated [5]. The character of the formed functional groups on the modified surface and RONS depends on the type of gas used. In the study of T. Homola et al. (2013) [6], the effect of DCSBD on glass surfaces was assessed. Short treatment time led to the decrease in C–C covalent bonds and to surface oxidation. Besides polymers [2], glass and wood, the diffuse coplanar surface barrier discharge plasma can be used for the modification of soybeen seeds (food/agriculture), as in the publication of S. Ďurčányová et al. [11].

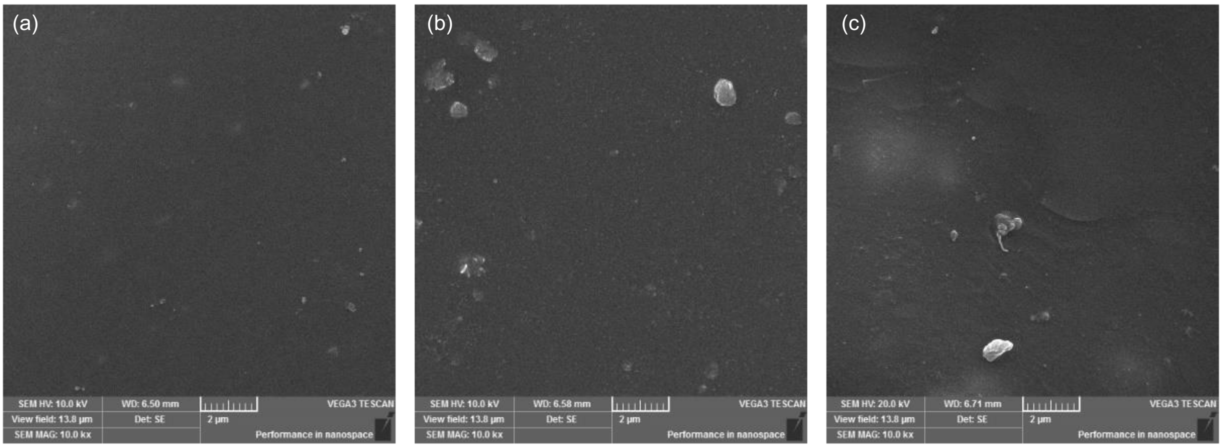

Fig. 1. SEM pictures: (a) untreated, (b) 2 s, (c) 4 s.

2. Material and methods

The NR/SBR blend, i.e., natural rubber/styrene butadiene rubber blend, was subjected to a plasma source. The main additives were: carbon black, silica, radium-E (RaE), curing agent, resins, cobalt sterate, benzothiazyl-2-dicyclohexyl sulfenamide (DCBS), etc.

KPR 200 — a laboratory line for in-line plasma processing (Research Institute for Man-Made Fibres, Svit, Slovakia) — was used. The plasma reactor KPR 200 was operating at 375 W. Scanning electron microscope Tescan VEGA 3 with energy dispersive X-ray (EDX) detector (Brno, Czech Republic) was used to characterize the surface morphology and chemical composition, and an atomic force microscope NT-206 (Microtest Machines Belarus) was used to distinguish surface roughness. The PRPA 2000 Alpha Technologies (Akron, Ohio, USA) was used to measure the curing and rheological properties at 160°C for 30 min.

3. Results

Figure 1 depicts scanning electron microscope (SEM) images of untreated rubber (panel a) and plasma treated rubbers at $10kx$ (panel b–c). A closer look at Fig. 1b shows a large number of globular shaped formations due to plasma treatment. The formations often refer to surface oxidation [12]. In Fig. 1c, some local corrugation can be seen.

The analysis of chemical composition was performed using SEM with EDX detector. As revealed in Fig. 2, the chemical analysis proved the presence of carbon, oxygen, silicon, sulphur, cobalt, zinc, etc. on the surface. After plasma treatment, the at.% of oxygen increased mainly at 4 s exposure. The chemical composition of the 2 s treatment was comparable to the untreated rubber. The supplemented analysis using X-ray photoelectron spectroscopy (XPS) (not provided here) showed C–O, O–C=O groups on the surface.

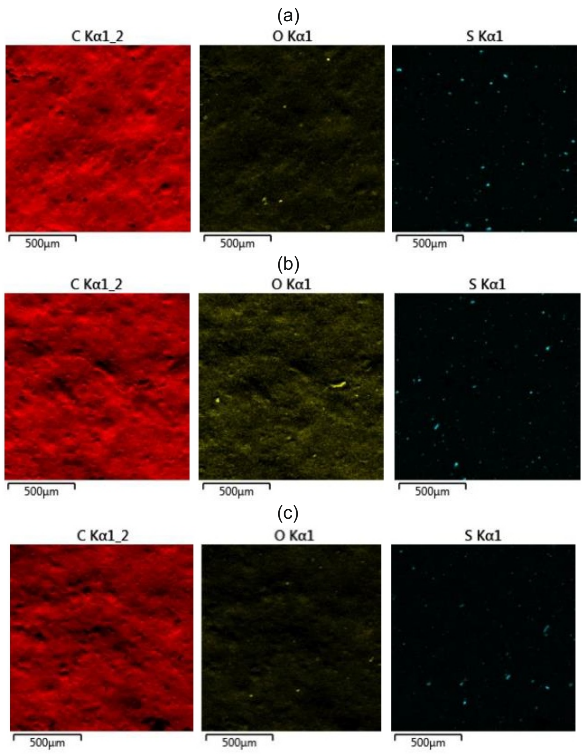

Fig. 2. SEM-EDX images of carbon, oxygen and sulphur: (a) untreated, (b) 2 s, (c) 4 s.

Figure 3 depicts 2D topography pictures of untreated (panel a) and plasma treated rubber (panel b–c). As can be seen, all surfaces are covered with scooped areas, comparable to the topography of untreated rubber. However, for the 4 s treatment (Fig. 3c), cracking is observed and the roughness

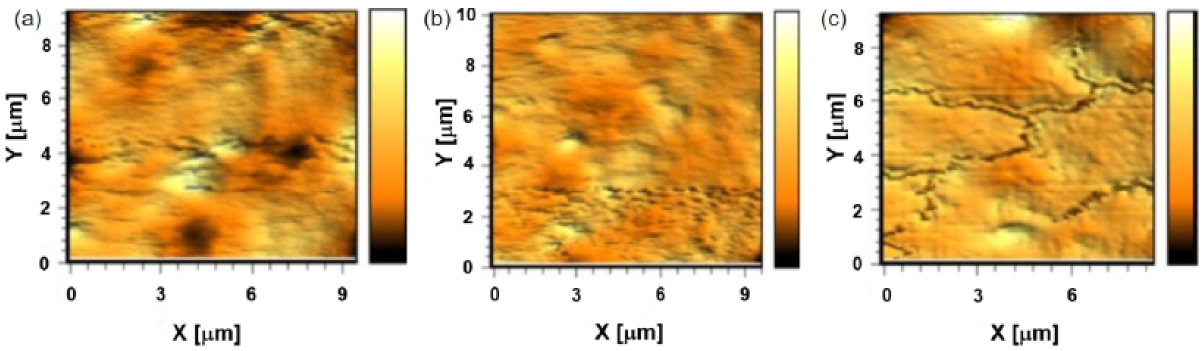

Fig. 3. Atomic force microscopy (AFM) pictures: (a) untreated, (b) 2 s, (c) 4 s.

TABLE I

Processing of rubbers.

Rubber	M_L [dNm]	M_H [dNm]	t_{s2} [min]	t_{90} [min]	CRI [min^{-1}]
Untreated	3.83	44.09	1.41	10.18	11.40
2 s	4.03	43.88	1.59	9.92	12.00
4 s	4.04	43.93	1.60	9.56	12.56

increased with longer exposure as follows: untreated rubber (18.25 nm); 2 s treatment (21.02 nm); 4 s treatment (22.72 nm).

The processing of rubbers was evaluated using cure test at 160°C for 30 min. As can be seen in Table I, the minimum torque (M_L), the maximum torque (M_H), the scorch time (t_{s2}), the optimum cure time (t_{90}) were investigated. The results demonstrated the efficiency of plasma discharge affects not only the surface characteristics but also their inner properties. Due to these observations we can suggest that plasma affects the speed of curing and the efficiency (energy) of further curing. The crosslinking of the surface sub-layer took place [13]. So that the optimum cure time decreased after plasma treatment for both the plasma-treated rubbers (2 s and 4 s), and the CRI index (colour rendering index) increased compared to the untreated rubber, while the rheology parameters of the plasma-treated rubbers maintained similar to those of the untreated rubber.

4. Conclusions

The effect of atmospheric plasma at two exposure times (2 s and 4 s) on the microstructure and micromorphology was explored. Plasma modified the structure of uncured rubber surface already at a low exposure time 2 s from a distance 0.5 mm. SEM and AFM revealed that plasma treatment slightly increased the roughness and formed globular formations on the surface, which was attributed to the surface oxidation by atmospheric plasma. The surface oxidation and the oxidation of sulphur were confirmed via XPS analysis. Plasma treatment and formatting of novel surface chemical composition caused an increase in surface roughness with longer exposure time. The research have demonstrated the effect of plasma on the development of partial crosslinking process seen by reducing the curing time (pre-curing).

Acknowledgments

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