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ATMOSPHERIC PRESSURE H_2O PLASMA TREATMENT OF POLYESTER CORD THREADS [1]

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Polyester cord threads, which are used as a reinforcing materials of rubber blend, have been treated in atmospheric-pressure H_2O plasma in order to enhance their adhesion to rubber. The atmospheric-pressure H_2O plasma was generated in an underwater diaphragm discharge. The plasma treatment resulted in approximately 100% improvement in the adhesion. Scanning electron microscopy investigation indicates that not only introduced surface polar groups but also increased surface area of the fibres due to a fibre surface roughening are responsible for the improved adhesive strength.

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1 Introduction

Due to their high strength and modulus, polyester (PES) fibres are particularly useful as a reinforcement for rubber blend, for example in conveyor belts and car tires. One troublesome aspect of the use of PES fibres as a rubber reinforcement is a low adhesion between the rubber matrix and the PES fibres because of the lack of binding sites on the fibre surface.

Sufficient adhesion between PES fibre and rubber is commercially obtained by using special adhesives, especially resorcinol-formaldehyde latex (RFL) treatment alone or with pretreatment by epoxides and blocked isocyanates is used. This type of adhesion improvement is, however, time-consuming, costly, and environmentally problematic.

It is known that hydroxyl radicals generated in low-pressure H_2O plasma may be used to incorporate hydroxyl functionality onto a polymer surface and thus to increase its surface energy and reactivity. The preferred polymers, which can be treated this manner, are polyaromatic polymers [1, 2] as, for example, polyester used in manufacturing

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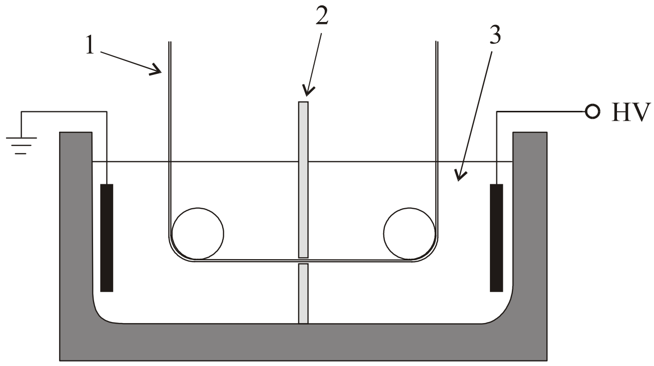

Fig. 1. Schematic of the experimental arrangement: 1 - treated cord, 2 - diaphragm, 3 - water solution.

of mentioned high performance tire cord. The plasma treatment techniques described in [1-3], however, suffer from the disadvantage of operating at low pressures thereby making the plasma equipment expensive and continuous operation difficult.

Underwater pulsed corona discharges generated in liquid water matrix at atmospheric pressure have been demonstrated to be effective in the production of hydrated electrons and hydroxyl radicals for the removal of low level of non biodegradable organic pollutants from underground and waste water [4-7]. Very few results, however, have been published on interactions of the active species generated in pulsed electrical discharges in water with polymer materials [8, 9].

The aim of this work is to explore the potential of the underwater diaphragm discharge for improving adhesive properties of PES tire cord. Comparing with other types of underwater electrical discharges, the main advantage of the diaphragm electrical discharges [7, 9-11] is that the discharge plasma is not in a direct contact with the metallic electrodes. This helps to eliminate potential problems with electrode oxidation and erosion due to a direct contact of the electrodes with highly reactive H_2O plasma.

2 Experimental

The H_2O-plasma treatment was performed using the diaphragm discharge arrangement illustrated by Fig.1. The treated PES cord thread (1) moved in the 1.2x10^{-3} m-diameter hole with a speed of 0.15 m/s. The diaphragm (2) made from a methyl methacrylate desk of 3-mm thickness was inserted between two planar duraluminium electrodes in tap water or water solution of KOH or NaCl (1). One of the electrodes was connected with a 50 kV pulse power supply operated at a frequency of 100 Hz.

Conductivity of distilled water based solutions of NaCl and KOH was changed from 1 000 μS.m^{-1} to 10 000 μS.m^{-1}. Conductivity of tap water was 45 000 μS.m^{-1}.

Two-ply tire PES cords (i.e. so-called greige cords) without a standard RFL adhesive

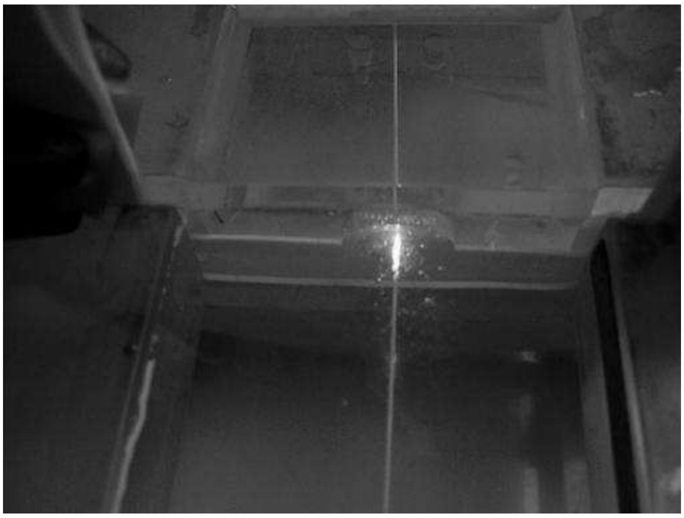

Fig. 2. Discharge generated in NaCl solution of 5 600 μS.m^{-1} conductivity at 40 kV. Exposition time was 1/500 s.

treatment used in this study were cords TREVIRA T 792, 1670 dtex 1x2, supplied by SH Senica a.s. The rubber blend in the form of slides containing natural rubber, styrene-butadiene rubber, and polybutadiene rubber was supplied by Matador a.s.

3 Results and discussion

In our experimental set-up the discharge starts at 20 kV apparently in the water vapour bubbles created due to heating and evaporation of water by ion current flowing through the hole. The discharge occurred inside and in the vicinity of the hole in the diaphragm and took the form of thin plasma channels propagating along the thread surface to the distance of several millimetres from the diaphragm, depending on conductivity of water solution and amplitude of the applied voltage. The discharge channel generated in NaCl solution of 5 600 μS.m^{-1} conductivity at 40 kV is displayed in Fig.2. In the discharge generated in similar experimental conditions the electron number density of 2.10^{18} cm^{-3} and electron temperature of 1.104 K were measured using optical emission spectroscopy method [9]. Fig. 3 exemplifies typical applied voltage and electrode current waveforms.

The adhesion between polyester cords and rubber blend after dynamic strain was characterised by dynamic adhesion measurements (Henley test method) according to STN 62 1464, where the adherence of the rubber to the cords is measured before and after alternating mechanical stressing (using a Henley test machine, 24 hours at 80°C at an angle of 45°C with a frequency of 7.5 Hz).

The best adhesion levels measured for the plasma-treated samples in each water based solution (NaCl, KOH, tap water) are shown in Table1. Presented numbers are

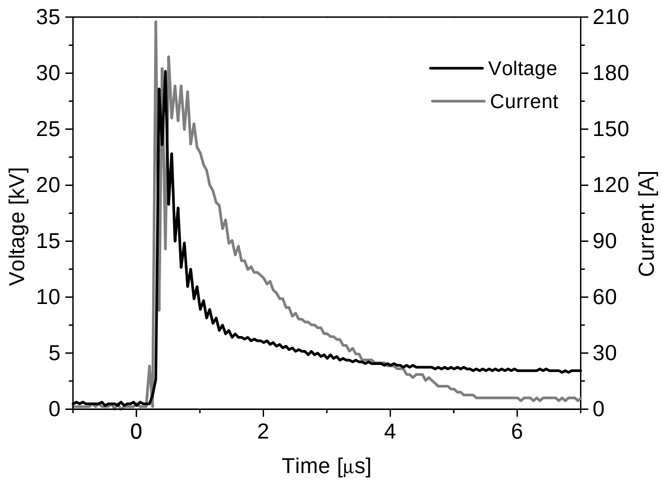

Fig. 3. Electrode voltage and current waveforms measured in NaCl/ H_2O solution of 5 600 μS.m^{-1} conductivity.

Tab. 1. The best adhesion levels obtained by H2O-plasma treatment in various water-based solutions. Adhesion of untreated cord is 76.3 ± 27.4 N. Adhesion of commercial RFL treated cord is 174.1 ± 29.9 N.

Solution	Conductivity [μS.m^{-1}]	Adhesive strength [N]	Standard deviation [N]
NaCl/H_2O	5 600	159.8	13.7
KOH/H_2O	1 400	142.3	26.9
tap water	45 000	97.5	25.7

the averages of six measured values with standard deviations. The results in Table 1 indicate that the plasma treatment using the described method resulted in roughly 100% increase in the adhesive strength of the PES cord/rubber interface. In the given set of experimental conditions the maximal more than 100% increase in the adhesive strength was obtained using the NaCl/H_2O solution of 5 600 μS.m^{-1} conductivity. These results, however, are extremely tentative and there is still ample room for an optimalization of the plasma treatment characteristics and a better understanding of the underlying physical and chemical processes. The observed plasma treatment effects can be partly understood from Fig. 4 which compares scanning electron microscopy images of the untreated and plasma treated cord surfaces. It can be seen that while the untreated fibres surface is quite smooth, the plasma-treated surface is roughened. Consequently, we suppose that a mechanical anchorage from the increased surface roughness contributes significantly to the observed increase in cord/rubber adhesion.

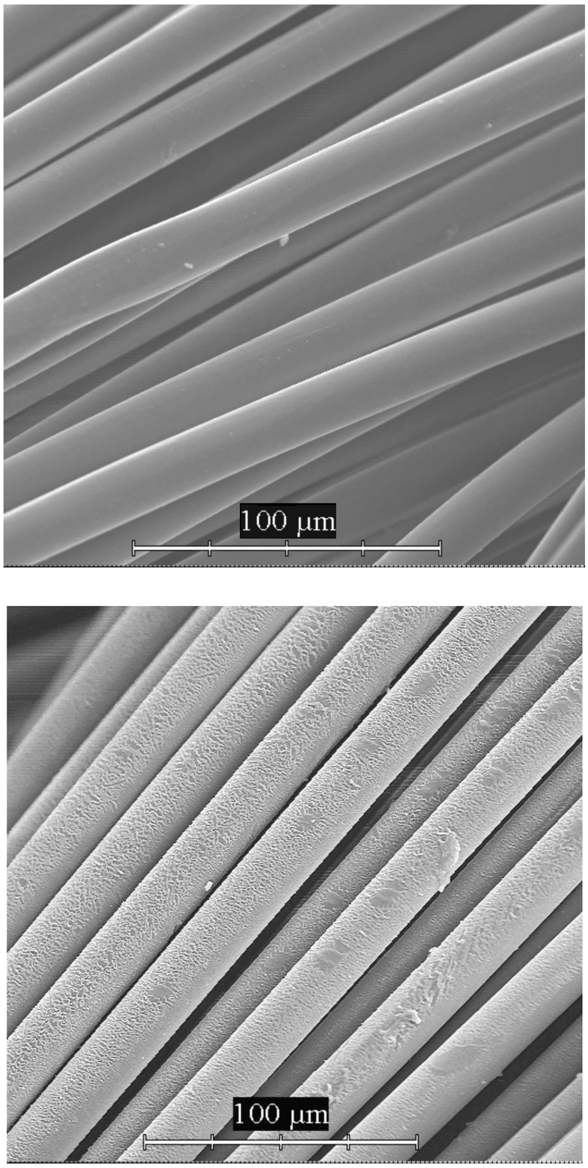

Fig. 4. a) (upper panel) b) (lower panel) Comparison of scanning electron microscopy photographs of the untreated (a) and (b) plasma treated cord threads surfaces.

Based on the known production of hydroxyl radical and other reactive species in underwater pulsed electrical discharges it is reasonable to expect that beside the physical changes seen in Fig. 4 the plasma treatment induced also changes in the fibre surface chemical composition. To experimentally verify this speculation we attempted to analyse the plasma-induced surface chemical changes using FTIR technique. The FTIR study, however, failed to reveal any reproducible plasma-induced chemical changes because the untreated PES cord has strong absorption bands in regions, where -OH groups could be identified. Thus, the surface changes induced by the atmospheric-pressure plasma treatment have not yet to be identified and should be the topic for further experimental investigations using ESCA technique.

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