Atmospheric Plasma surface treatment of Styrene-Butadiene Rubber

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Introduction

Thermoplastic rubbers are widely used in a large number of applications (e.g. footwear, adhesives manufacturing, molded or extruded goods). Due to the non-polar nature of these rubbers, poor adhesion is achieved with polar polyurethane (PU) adhesive thus, a surface treatment is required to chemically modify the rubber surface and produce suitable joints.
Surface treatments have been demonstrated to be suitable for the improvement of adhesion and wettability properties of non-polar synthetic rubbers. Over the last two decades progresses in adhesion of rubber were achieved by changing of the ingredients in rubber composition or by modifying surfaces by the use of a chemical agent (halogenation, cyclization, etc.) or using high energy irradiation such as bombarding the surface by electron beam or gamma irradiation.
Actually, wet-chemical treatments are not well acceptable because of environmental and safety considerations and question on uniformity and reproducibility. Plasma surface treatment process was been proposed as an environmentally friendly and have gained large acceptance because it can be easily integrated into existing production lines and because their effectiveness in the treatment of several materials with different shapes and sizes.
The effectiveness of plasma treatment on enhancement of adhesion depends on the gas used to generate the plasma and also on the formulation of the rubber. Vulcanized rubbers like, styrene-butadiene rubber (SBR), are especially difficult to bond due to low molecular weight ingredients in their formulation that may migrate to the rubber surface limiting its interaction with the adhesive.
This study attempts to find an alternative treatment to improve the adhesion of SBR surface and PU adhesive. Plasma treatments were performed in an air plasma system from Acxys and were selected three types of SBR rubbers with different percentages of styrene-butadiene which were provided by Procalçado. The effect of experimental variables such as distance, speed and scan number on the adhesion of PU adhesive was evaluated and compared with halogenated SBR rubbers.

Keywords: SBR Rubbers; Surface treatment; Atmospheric Plasma; Adhesion; Aging

Experimental

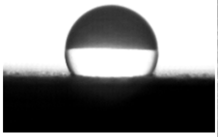
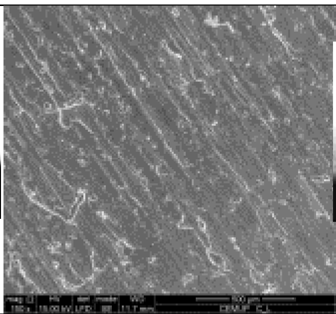
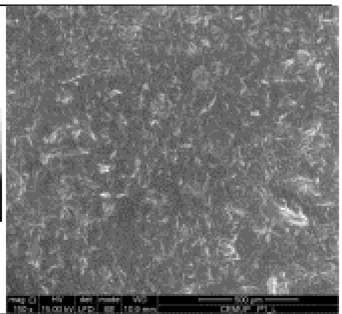
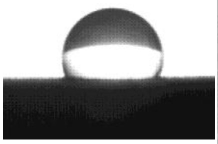
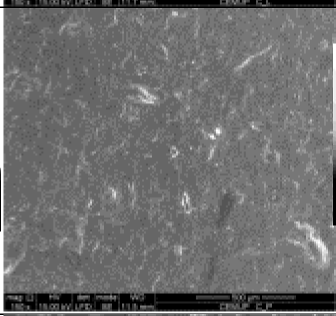
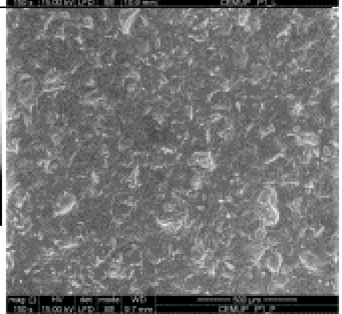
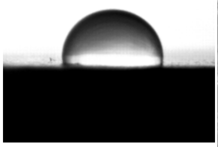
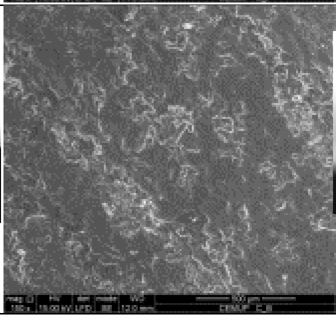
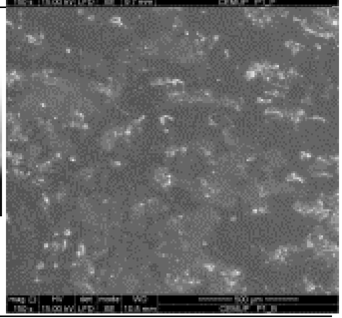
The wettability of the as-received and surface treated SBR rubber was evaluated by contact angle measurements using a home-made goniometer. Drops of deionized water (18 MΩ.cm) were placed on the surface rubber using a microsyringe (Hamilton Instruments). Contact angle values were measured immediately after plasma treatment. Contact angles were obtained after digital image treating using image J.
SBR rubber/PU adhesive/leather joints were made use two test pieces with the same dimensions. The leather surface was roughened and then, was treated with a primer solution

and 30 minutes later, PU adhesive was applied with brush on the rubber treated and leather. After 60 minutes, the PU adhesive was reactivated at 80 °C for 5 seconds and the adhesive-coated rubber and adhesive-coated leather were immediately placed into contact at a pressure of 5 bar for 10 seconds. Adhesive joints were conditioned for 72 hours at room temperature. The adhesive strength of the treated surfaces is evaluated by T-peel tests.
The T-peel strength measurements were performed using a Jupiter instrument, at a peeling rate of 0.1 $m.min^{-1}$ performed according to ISO 17708:2003. Each reported adhesive strength value is the median of three bonded samples.
The morphological modifications produced on the treated SBR rubbers were analyzed using a JEOL JSM-840 Scanning Electron Microscope (SEM) using a 20 kV electron beam.

Results and discussion

The plasma treatment produce a decrease in contact angle values compared to as-received SBR rubber as shown in data displayed in table I indicating improved wettability of the surfaces after plasma treatment.

Table I. Contact angle and SEM images of the rubber samples used in this work, before and after plasma treatment.

	As-received rubber		After plasma treatment	
	Contact angle	SEM micrographs	Contact angle	SEM micrographs
SBR 1	 $(110 \pm 4)^o$		 $(39 \pm 7)^o$	
SBR 2	 $(104 \pm 2)^o$		 $(41 \pm 2)^o$	
SBR 3	 $(101 \pm 2)^o$		 $(47 \pm 6)^o$	

The improved wettability can be ascribed to chemical and morphological surface modifications on the SBR rubber produced by the plasma treatment.

The SEM micrographs (x150) of the as-received SBR rubber show a homogeneous flat surface with some patches likely due to paraffin wax. When SBR rubber was treated with plasma, the surface morphology is rougher.

After optimization of the experimental parameters the aging of the plasma treated surfaces was studied for 30 days in order to monitor the effectiveness of the plasma treatment.

Figure 1 shows the effect aging effect of plasma treatment, for three different rubbers, on the T-peel strength results.

The SBR rubber surface was effectively modified by air plasma treatment and the adhesion properties were greatly improved. After to 2 days of treatment, the T-peel strength values were higher than the specification to footwear adhesion and the trend of the T-peel strength values shows that one month after plasma treatment, there is no signal of treatment degradation.

This study shows that plasma treatment is a viable alternative to improve adhesion strength of SBR rubber and can easily substitute the halogenation process.

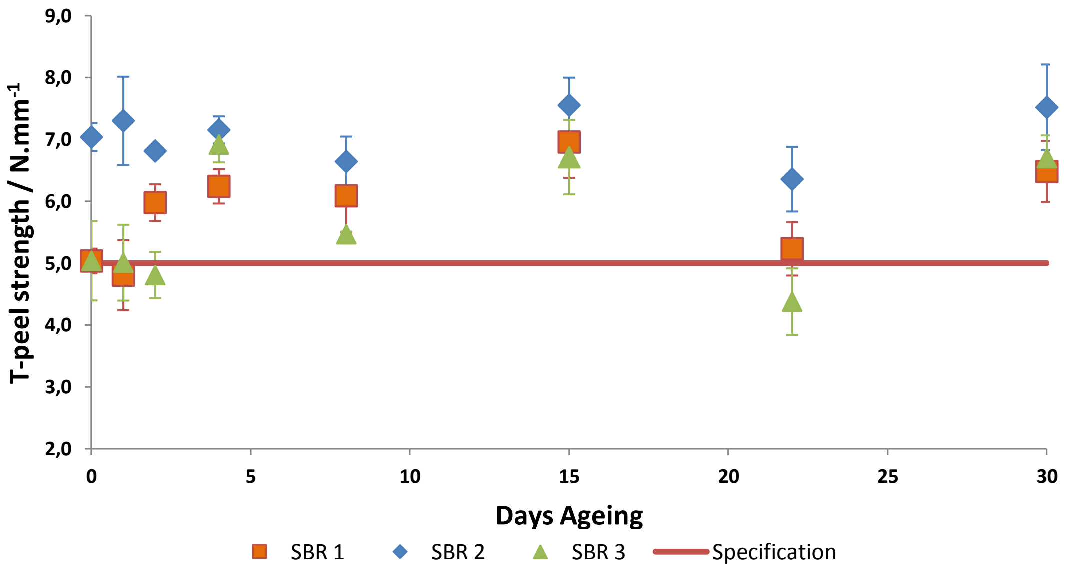


Figure 1. Effect of time, after plasma treatment of different rubbers, on the T-peel strength results.

References:

J. Tyczkowski, I. Krawczyk-Kłys, S. Kuberski, P. Makowski, European Polymer Journal 46 (2010) 767–773

J. Tyczkowskia, I. Krawczyka, B. Wożniakb, Surface and Coatings Technology 174 –175 (2003) 849–853

J.M. Martín-Martínez, M.D. Romero-Sánchez, Eur. Phys. J. Appl. Phys. 34 (2006) 125–138

María D. Romero-Sánchez, José Miguel Martín-Martínez, International Journal of Adhesion & Adhesives 26 (2006) 345–354

Maryline Moreno-Couranjou, Patrick Choquet, Jerôme Guillot, Henri-Noël Migeon, Plasma Process. Polym. 6 (2009) 397–S400

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