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Surface treatment with UV-ozone to improve adhesion of vulcanized rubber formulated with an excess of processing oil



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ABSTRACT

An excess of processing oil was intentionally added in the formulation of vulcanized styrene-butadiene rubber for analyzing the effect on the treatment with UV radiation combined with ozone (UV-ozone) in improving the adhesion to waterborne polyurethane adhesive in footwear. Due to the excess of processing oil in the rubber, poor adhesion was expected. Both the length of the treatment and the distance between the UV radiation source to the rubber surface were studied, and the effects of the treatment on the surface chemistry, wettability and surface energy, and topography of the rubber were analyzed. The treatment of the rubber with UV-ozone removed hydrocarbon moieties and zinc stearate from the surface, and surface oxidation (C–O, C=O and COO⁻ groups formation) occurred. As a consequence, improved wettability and increased surface energy (mainly due to the polar component of the surface energy) were obtained. The increase in the length of treatment and for a distance of 3–5 cm from the rubber to the UV radiation source favored the effectiveness of the UV-ozone treatment. Besides, whereas the UV-ozone treatment for 3 min produced the ablation of surface contaminants mainly, longer lengths of treatment (i.e., 6–9 min) caused roughness and cracks on the rubber surface. The UV-ozone treatment also caused heating of the surface. Finally, the treatment with UV-ozone increased the adhesion of the rubber to waterborne polyurethane adhesive, the highest adhesion was obtained in the joints made with UV-ozone treated rubber for 3 and 6 min at a UV radiation source–rubber surface distance of 5 cm.

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1. Introduction

Styrene-butadiene rubbers (SBRs) are commonly used as sole materials in footwear industry but their low surface energy [1] prevent good bonding to polyurethane adhesives, and surface treatments are mandatory to achieve good adhesion. In the existing literature, several surface treatments for rubbers have been proposed including abrasion and chemical treatments such as halogenation [2] or cyclization [3]. Solvent-based chlorination is the most widely used surface treatment for vulcanized rubber because an improvement in the mechanical adhesion (due to surface heterogeneities and cracks) and chemical adhesion (due to carbon-chlorine and carbon-oxygen functionalities) is produced. However, chlorination of rubber requires long times of reaction, organic solvents are needed, and chlorine is produced, being environmentally unacceptable and causing potential health problems. As a consequence, cleaner and faster radiation-based

treatments have been proposed for rubber. Low-pressure plasma treatment improves the adhesion of rubbers due to the formation of polar moieties on the surface and ablation of low molecular weight compounds, but this treatment is difficult to carry out on line as vacuum is required [4]. On the other hand, UV radiation treatment combined with ozone has been shown effective in improving the adhesion of rubber to waterborne polyurethane adhesive [5].

Bolland [6] and Keller [7] proved the oxidant attack of the UV radiation in elastomers, and Blake and Bruce [8] studied the oxygen absorption speed on natural rubber after UV radiation exposure. When ozone is added during UV treatment, peroxy radicals are formed rendering carbonyl and carboxyl functionalities that increased the wettability of the treated polymer [9,10]. The concentration of peroxy groups depended on the ozone concentration and the exposure time of the surface to ozone, among other factors [11]. The UV-ozone treatment affected only the outermost surface of the elastomers [12] and has been shown effective in improving the adhesion of several polymers [13,14].

The effect of exposure to different ozone concentrations in conjunction with UV radiation on the surface modification and

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adhesion of block styrene-butadiene-styrene (SBS) rubber was studied [5]. Improved wettability, creation of oxygen-containing moieties at the surface, and ablation of the SBS rubber surface were obtained, more markedly by increasing the length of treatment. Whereas the treatment of SBS rubber with ozone only produced low peel strength values, adhesion was highly improved after UV or UV-ozone treatment. The modifications produced by UV and UV-ozone treatment were not restricted to the outermost SBS rubber surface but a thicker surface layer is modified, resulting in chain scission and the creation of low molecular weight oxidized material on the surface [5]. The additional ozone incorporated during UV radiation treatment enhanced the effects of UV-only treatment and improved the adhesion of SBS rubber. On the other hand, Romero Sánchez *et al.* [15] compared the effects produced by corona discharge and UV-ozone surface treatments in SBS rubber. They found that both treatments modified the rubber surface by creating C–O, C=O, and COO[−] moieties and improved wettability. The treatment with corona discharge did not create surface roughness but the treatment with UV radiation produced cracks on the rubber surface that favored the mechanical adhesion to solvent-borne polyurethane adhesive. Later study [16] showed that the UV-ozone treatment also produced the migration of the zinc stearate to the treated rubber surface decreasing adhesion.

Torregrosa Coque *et al.* [17] studied the incidence of different additives in the formulation of rubber on the effectiveness of the UV-ozone treatment, concluding that the migration of oils and lubricants competed negatively with the surface oxidation decreasing adhesion to solvent-borne polyurethane adhesive. The influence of adding 10 wt% calcium carbonate as filler in rubber surface treated with UV-ozone radiation has been studied [18], and although the improvement in wettability was similar in the rubber with and without filler, the presence of calcium carbonate inhibited the modifications produced for short length of treatment, decreasing the adhesion, while the surface oxidation of the filled rubber was favored for longer treatment times.

One drawback of the UV-ozone treatment of several polymers is the heating of the surface caused by the IR irradiation associated to the UV radiation treatment that caused deterioration of the adhesion [19]. To avoid it, two methods had been proposed: to perform a discontinuous UV radiation treatment and to add a thin film of water on the material just after treatment.

Considering the negative effect of low molecular weight additives in the effectiveness of the UV-ozone treatment of rubber, the aim of this study was to explore the potential of UV-ozone treatment in vulcanized rubber containing an excess of processing oil in its formulation. UV-ozone treatment of this rubber will be optimized for producing good adhesion to waterborne polyurethane adhesive, an aspect that will have great potential in avoiding the use of organic solvents and chemical in the bonding of upper to sole in footwear manufacturing.

2. Experimental

2.1. Materials

The vulcanized styrene-butadiene rubber used in this study (named as RC) was manufactured and provided by Invulsa (Quel, La Rioja, Spain) and its typical formulation is given in Table 1. RC rubber contains silica as filler and zinc stearate, which can be formed during the vulcanization by reaction of zinc oxide and stearic acid, and it contains an excess of paraffinic oil that was intentionally added for analyzing the effect of this low molecular weight additive in the performance of the UV-ozone treatment.

For adhesive joints formation, waterborne polyurethane dispersion Dispercoll-U54 (Bayer Materials Science AG, Leverkusen,

Table 1
Typical formulation of RC rubber.

Component	Percentage (phr) ^a
SBR rubber 1502	70
Natural rubber	30
Precipitated silica	30
Sulfur	1.5
Benzothiazole disulfide	1.5
Tetramethyl tiuram disulfide	0.5
Poly(ethylene glycol) (M _w =6000)	1.1
Zinc oxide	1.5
Stearic acid	1.5
Phenolic antioxidant	0.5
Microcrystalline paraffin wax	1.0
Paraffinic oil	7.0

^a phr=parts per one hundred parts of rubber.

Table 2
Some characteristics of the waterborne polyurethane dispersion.

Solids content (1h at 105 °C) [20]	50 wt%
Brookfield viscosity (23 °C, Spindle S62, 100 rpm)	133 mPa.s
pH	7.2 ± 0.1
Surface tension (23 °C, Nouy Ring)	54 mN/m
Density (20 °C) [20]	1.1 g/cm ³
Average particle size [20]	200 nm

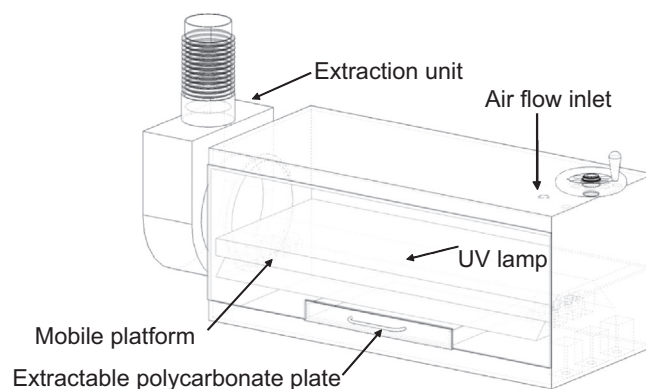


Fig. 1. Scheme of the UV-ozone treatment unit.

Germany) was used. This is an aqueous dispersion of anionic polyurethane of high molecular weight. Its main characteristics are given in Table 2.

2.2. UV radiation-ozone (UV-ozone) treatment

UV-ozone treatment was carried out in equipment made in polycarbonate provided with low-pressure vapor grid mercury lamp (American Ultraviolet, Upland, CA, USA) (Fig. 1). Continuous UV radiation of the rubber was carried out. For avoiding heating of the rubber surface a continuous air renovation was used.

The UV lamp provides a radiation intensity of 10 mW/cm² measured at a distance of 5 cm from the lamp and produces UV radiation at the wavelengths of 254 nm (almost 90% of the total) and 185 nm (which is responsible of ozone formation by oxidizing air introduced continuously in the equipment). The equipment has an extraction unit to avoid high concentration of ozone and excessive heating of the lamp during treatment. The rubber sample is placed in an extractable polycarbonate plate which distance to the lamp can be varied. UV-ozone treatment was carried out by varying the distance between the UV lamp and the

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