

Addition of ozone in the UV radiation treatment of a synthetic styrene-butadiene-styrene (SBS) rubber

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Abstract

The effect of exposure to different ozone concentrations, in conjunction with UV radiation, on the surface modification and adhesion properties of a block synthetic styrene-butadiene-styrene (S6) rubber was studied. The treatment time varied between 10 s and 30 min. Three different surface treatments were investigated: ozone only (O₃), UV radiation in the presence of air, and UV radiation in the presence of externally generated, supplemental ozone (UV/O₃). The surface modified S6 rubber was characterized using contact angle measurements (ethylene glycol, 25 °C), Fourier transform infrared spectroscopy using an attenuated total reflection attachment (ATR-IR), X-ray photoelectron spectroscopy (XPS), and scanning electron microscopy (SEM). T-peel tests of surface modified S6 rubber/polyurethane (PU) adhesive/leather joints were carried out to quantify the changes in the adhesion properties.

The O₃, UV and UV/O₃ treatment of S6 rubber improved wettability, created oxygen-containing moieties at the surface, and resulted in ablation of the surface (removal of a thin rubber layer from the treated S6 rubber surface). Different surface modifications were produced using each treatment and these modifications were enhanced with increasing treatment time. Whereas the UV and UV/O₃ treatments created C=O and COO⁻ moieties on the S6 rubber surface, the O₃ treatment produced a lower degree of oxidation (predominantly O–H moieties). For short treatment time, O–H and C–O moieties were dominant, and the increase in the length of treatment lead to more oxidized moieties (C=O, COO⁻). Lower degree of oxidation was obtained with O₃ treatment as compared to that obtained with UV and UV/O₃ treatments.

Adhesion was highly improved after UV and UV/O₃ treatments of S6 rubber, more markedly with increasing treatment time. A moderate increase in peel strength of the joints produced with O₃-treated S6 rubber was produced and an adhesion/cohesive failure in a thin rubber layer was observed irrespective of treatment time. On increasing the treatment time with UV and UV/O₃, the adhesive joints showed different loci of failure: adhesion + cohesive failure in a thin rubber layer for the S6 rubber treated for 2 min with UV or UV/O₃, and cohesive failure in the S6 rubber treated for 30 min with UV or UV/O₃ treatments.

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1. Introduction

Thermoplastic rubbers styrene-butadiene-styrene (SBS) are block copolymers of soft, elastic butadiene and hard, tough styrene, which do not require vulcani-

zation to provide dimensional stability. These thermoplastic rubbers are widely used in the manufacture of footwear, adhesives manufacturing, molded or extruded goods and as modifiers for asphalt and other resins. Because of the non-polar nature of SBS rubbers, poor adhesion is found when used with polyurethane adhesives in footwear industry, and surface modification of the SBS is required to produce suitable joints [1,2].

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Several surface treatments for thermoplastic rubbers have been proposed in the literature including various chemical (halogenation, cyclization—treatment with sulphuric acid) and physical (corona discharge, low pressure plasma) treatments [3–5]. In this study, UV radiation (184.9 and 253.7 nm) in the presence of air or supplemental ozone is proposed as a surface treatment to improve the adhesion of a difficult-to-bond thermoplastic styrene-butadiene-styrene rubber.

The surface modifications produced by UV treatment of several polymers have been studied previously [6]. Bolland [7] and Keller [8] established the mechanisms of the oxidative attack of UV radiation on low molecular weight hydrocarbons similar to rubber; the generation of free radicals on the polymer surface was recognized as the key parameter of the oxidative degradation.

UV radiation (wavelength = 185 nm) removes contaminants from many surfaces by reacting with atmospheric oxygen to form atomic oxygen and ozone, both strong oxidizers. Ozone absorbs the 254 nm UV radiation and dissociates into molecular oxygen and atomic oxygen. The type and degree of rubber surface modifications depend on the ozone concentration [9]. Some authors have demonstrated that ozone can generate peroxy radicals, unstable species that decompose to form hydro-peroxide, carbonyl and carboxyl functionalities, these groups being responsible for the increased wettability of treated polymer and rubber surfaces [10–12]. The number of peroxy groups that are created depends on the ozone concentration and the exposure time of the rubber to ozone, among other factors [13,14].

Treatment with ozone in the absence of UV light has been used previously to increase the adhesion of polypropylene, polyethylene, polyurethane and polyethylene terephthalate [13,15–16]. Double bonds in the polymeric chains are susceptible to oxidation and ozone attack through an ionic mechanism [17].

Several papers in the literature have shown that the combined treatment of UV radiation with ozone (additional to the ozone generated by the UV radiation) produces more effective and faster oxidation of polypropylene, polyethylene terephthalate and polyethylene surfaces than either ozone only or UV treatment. Different reaction mechanisms are implied for each treatment [18–25].

Previous studies [26,27] showed that the extent of the rubber surface modifications produced by UV treatment depended on the treatment time and the concentration of the ozone produced in situ by the UV radiation. In this study, additional ozone was supplied by means of an ozone generator during UV treatment of a styrene-butadiene-styrene (S6) rubber surface, and the surface modifications produced with ozone only (O₃), UV radiation, or UV/O₃ as a function of treatment time have been investigated.

2. Experimental

2.1. Materials

An oil extended (45 phr non-staining paraffinic oil) thermoplastic block styrene-butadiene-styrene (S6) rubber containing 32 wt% styrene was used in this study. Some properties of the S6 rubber are given in Table 1.

To determine the adhesion properties, surface treated-S6 rubber/polyurethane adhesive/leather joints were prepared. Table 2 shows some of the properties of the chromium-tanned bovine leather used to produce the adhesive joints. The polyurethane adhesive solution was prepared by dissolving 18 wt% polyurethane pellets (Desmocoll 540, Bayer, Leverkusen, Germany) and 2 wt% fumed silica (Aerosil 200, Degussa, Hanau, Germany) in an acetone/toluene (80:20, w:w) mixture. To facilitate the dispersion of the fumed silica in the polyurethane and avoid further settling, the adhesive solution was prepared in two consecutive steps: (i) The fumed silica was mixed with a small amount of the solvent mixture at 2500 rpm for 15 min in a laboratory mixer to facilitate the dispersion; (ii) The polyurethane pellets were added to the solvent-fumed silica mixture, simultaneously adding all of the solvent; the mixture was stirred in the laboratory mixer at 2000 rpm for 2 h, 30 min until an homogeneous solution was obtained. The viscosity of the solution was 4.4 Pa.s at 25 s⁻¹ as measured by a rotational rheometer (Rheolab MC 100 Physica).

Table 1
Some properties of the styrene-butadiene-styrene (S6) rubber

Property	Value
Ash content	0.3 wt%
Density	0.94 g/cm ³
Modulus 300%	1.9 MPa
Tensile strength	12 MPa
Elongation-at-break	1100%
Abrasion resistance	100 mm ³
Shore a hardness	43
Thickness	5 mm

Table 2
Some properties of the chromium-tanned bovine leather used to prepare the adhesive joints

Property	Value
Tensile strength	13 MPa
Elongation-at-break	60%
Ash content, 950 °C	< 5 wt%
Thickness	2 mm

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