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Applied Surface Science 252 (2006) 5714–5722
applied surface science
www.elsevier.com/locate/apsusc

Modification of rubber surface by UV surface grafting

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Received 5 October 2004; received in revised form 5 July 2005; accepted 21 July 2005
Available online 12 September 2005

Abstract

Rubber surface is subjected to ultraviolet radiation (UV) in the presence of allylamine and radiation sensitizer benzophenone (BP). Fourier transform infrared spectral studies reveal the presence of allylamine on the surface. The presence of irregular needle shapes on the surface as observed in scanning electron micrographs also confirms the polymerized allylamine on the surface. Allylamine coatings have been further confirmed from atomic force microscopy (AFM) analysis. Thermogravimetric analysis (TGA) reveals that allylamine coating on the rubber surface lowers the thermal degradation rate. The contact angle between the water and rubber surface decreases for the modified rubber surface confirming the surface modification due to UV surface grafting.

PACS: 61.80.Ba; 33.20.Ea; 68.37.Hk; 68.37.Ps; 81.70.Pg

Keywords: UV grafting; Allylamine; Atomic force microscopy; Contact angle

1. Introduction

Polymer materials have been widely used in various industrial applications because of its superior mechanical, optical or electrical properties. However, their use is sometimes limited due to the surface characterization. It is, therefore, interesting to modify the surface in a controlled manner to enhance wettability, printability, adhesion and compatibility with other materials or with biological components. The most important feature of the surface modification is that the surface properties of the treated material can be modified without changing their intrinsic bulk properties [1].

Surface modification of hydrophobic polymer surface into a hydrophilic or vice versa can be achieved by wet (acid, alkali), dry (plasma) and radiation treatments (ultraviolet radiation and laser)

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doi:10.1016/j.apsusc.2005.07.069

without affecting the bulk properties [2]. In general, photografting is performed by irradiating the light on the polymer to modify the surface properties of a polymer in the presence of a solvent containing monomer. The energy sources commonly used are high-energy electrons, X-rays, UV and visible light. Many different routes can be employed to introduce graft chains onto the surface of polymeric substrates depending on the system of interest [3–5]. The effects of plasma treatment on the surface of polymeric materials were discussed in detail comparing the energies of plasma with those of the chemical bonds in polymers [6]. Gancarz et al. [7] modified polysulfone membranes with acrylic acid using plasma-initiated graft polymerization. Oehr et al. [8] grafted allyl alcohol and glycidyl methacrylate monomer onto a polymer surface, and discussed the influence of gases used to activate the polymer surface for grafting.

Ultraviolet energy (UV) has been extensively applied for surface graft polymerization of polymers with the aid of a photoinitiator or photosensitizer, such as benzophenone (BP). Earlier reports concerned with UV irradiation at the vapor phase of monomer and sensitizer under a reduced pressure [9] or in the presence of inert gas [10]. The surface of polyethylene (PE) and polystyrene (PS) was modified by grafting with acrylamide [11]. Guo et al. [12] performed photografting of polyacrylamide onto the polyethylene terephthalate (PET) film surface in the aqueous solution. They compared the factors on grafting yield in the presence of various photosensitizer including benzoin, dimethyl ether, 2-hydroxyethyl benzoin, and ethyl ether benzophenone. They have also discussed the effects of monomer concentration and reaction temperature on the grafting yield. Lee and Ryu [13] and Yu and Ryu [14] used acrylamide and glycidyl methacrylate as a monomer to modify the surface characteristics of vulcanized styrene-butadiene rubber (SBR) using UV.

In this paper, the surface of natural rubber (NR)/SBR blend is subjected to UV surface grafting in the presence of allylamine and has been characterized with Fourier transform infrared spectra (FTIR), scanning electron microscopy (SEM), atomic force microscopy (AFM), thermogravimetric analysis (TGA) and contact angle measurements to understand the surface modification by allylamine grafting.

2. Experimental

2.1. Materials

Allylamine used for the surface modification of rubber was procured from Kanto Chemical Co. Inc., Japan. Acetone solvent was obtained from Duksan Chemical Co. Ltd., Korea. Unvulcanized NR/SBR rubber sheet with tire compound composition were provided by Dong-A tire Co., Korea.

2.2. Allylamine modification of rubber

Allylamine solution of various concentrations (0.5, 1.25 and 2.0 mol) was prepared by dissolving the allylamine in 1000 mL of acetone. 0.125 mol of benzophenone was added to the allylamine solution. Cured rubber sheets were soaked into the allylamine solution for about 3 h followed by 3 h drying in ambient temperature. The dried allylamine modified rubber sheets were then exposed to UV radiation using 400 W medium-pressure mercury lamp at 25 °C in the closed chamber with the quartz window. UV radiation time was varied as 15, 30 and 45 min.

2.3. Sample designation

Rubber samples are designated as $RA_{b/c}$, where R represents the rubber, A represents the allylamine solution and suffixes *b* and *c* represents allylamine concentration and radiation time. Sample designations are represented in Table 1.

2.4. Characterization

Unmodified and allylamine modified rubber samples were subjected to IR characterization in the range

Table 1
Sample designation

S. No.	Sample designation	Allylamine concentration (mol/1000 cc of acetone)	UV exposure time (min)
1	$RA_{0/0}$	0	0
2	$RA_{1.25/0}$	1.25	0
3	$RA_{1.25/15}$	1.25	15
4	$RA_{1.25/30}$	1.25	30
5	$RA_{1.25/45}$	1.25	45
6	$RA_{0.5/30}$	0.5	30
7	$RA_{2.0/30}$	2.0	30