

Material Characterisation

UV surface modification of waste tire powder:
Characterization and its influence on the properties
of polypropylene/waste powder compositesA.M. Shanmugharaj^a, Jin Kuk Kim^b, Sung Hun Ryu^{a,*}^aCollege of Environment and Applied Chemistry, Kyung Hee University, Yongin, Kyunggi-Do, South Korea^bDepartment of Polymer Science and Engineering, Gyeongsang National University, Jinju, South Korea

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Abstract

Waste tire powder was subjected to ultraviolet radiation (UV) in the presence of allylamine and radiation sensitizer benzophenone. Fourier Transform Infrared spectral studies revealed the presence of allylamine amine on the surface of the rubber powder. The higher value of nitrogen to carbon X-ray counts obtained from energy dispersive X-ray analysis also demonstrates the presence of amine on the powder surface. Surface energy measurements were done by a dynamic wicking method. Improvement in tensile strength and elongation at break were observed for the PP/modified rubber powder and is attributed to the chemical interaction between the surface of the modified rubber powder and maleic anhydride grafted PP.

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Keywords: Waste tire powder; UV surface modification; Polypropylene**1. Introduction**

Scrap tires, being a form of post-consumer waste, have been subjected to incineration or landfill. However, these methods result in severe environmental problems such as air pollution. Reuse or recycling of these scrap tires becomes an important social subject and recycling of waste rubber powder by means of blending with polymeric material has become an important topic in recent years. The technical and commercial feasibility of using waste rubber powder as a filler have been demonstrated in many applications, such as roofing and shoe soles. It is a cost-effective way to produce a material that can be processed like plastic and also retains some of the elasticity of rubber. Many efforts have been made in recent years to increase the quality of plastic/waste rubber powder composites.

Recently, surface-modification techniques have been adopted for recycling of scrap rubber powder [1]. McInnis et al. [2] modified the ground rubber powder by a gas–solid reaction with chlorine containing gas. The role of surface modified rubber powders in the toughening of the epoxy polymers has been studied by Bagheri et al. [3]. The influence of various irradiation techniques on the effective reuse of the waste rubber has been extensively studied by various researchers [4,5]. Ultraviolet energy (UV) has been extensively applied to modify the surface properties using monomers and photosensitizer. Lee and Ryu [6] and Yu and Ryu [7] used acrylamide and glycidyl methacrylate as a monomer to modify the surface characteristics of vulcanized styrene butadiene rubber (SBR) using UV. They found that photografting reaction with a monomer is an efficient way to modify the surface characteristics of vulcanized SBR, which is one of the major components of tires.

In this paper, the waste tire powder was subjected to UV surface grafting in the presence of allylamine. The grafted surface has been characterized by Fourier Transform Infrared spectra (FT-IR), scanning electron microscopy

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(SEM), thermogravimetric analysis (TGA) and contact angle measurements to understand the surface modification due to allylamine grafting. The modified rubber powder was then incorporated in the polypropylene matrix and its role on the properties of the blend has been investigated.

2. Experimental

2.1. Materials

Waste rubber powder was obtained from the Dong-A Co. Allylamine and acetone was purchased from Kanto Chemical Co., Inc., Japan and Duksan Chemical Co. Ltd, Korea, respectively. Polypropylene, maleic anhydride grafted polypropylene (MA-PP) (Polybond™ 3200) and benzophenone were obtained from Samsung Chemicals, Korea, Uniroyal Chemical Company, USA and Lancaster Synthesis, England, respectively.

2.2. UV photografting of rubber powder

Allylamine solution (1.25 mol) was prepared by dissolving the allylamine in 1000 mL of acetone and 0.125 mol of benzophenone was added to the allylamine solution. Rubber powder was immersed in the allylamine solution for 3 h followed by 3 h drying at ambient temperature. The allylamine treated rubber powder was then subjected to UV radiation using a 400-W medium-pressure mercury lamp for 30 min.

2.3. Preparation of polypropylene/waste rubber composites

A blend of PP and MA-PP was melted for 2 min at 200 °C, followed by the addition of the calculated amount of waste rubber powder in a Brabender Plasticorder at a speed of 50 rpm, and the mixing was continued for 5 min. It is then dumped and pressed at 200 °C for 2 min using a Carver press to prepare 0.15 mm thick sheet.

2.4. Sample designation

Rubber powders are designated as PA_{b/c}, where P represents the rubber powder, A represents the allylamine solution and suffixes b and c represent allylamine concentration and UV radiation time, respectively. Sample designations of rubber powders are represented in Table 1.

Table 1
Sample designation of rubber powders

Sample designation	Rubber powder content (g)	Allylamine content (mol)	UV radiation time (min)
PA _{0/0}	100	0	0
PA _{1.25/30}	100	1.25	30

0.125 mol of benzophenone is used as sensitizer for all cases.

Table 2

Compositions of the polypropylene/waste rubber composites

Sample designation	PP	MA-PP	Unmodified rubber powder (PA _{0/0})	Modified rubber powder (PA _{1.25/30})
P	100	–	–	–
PPA _{0/0/10}	100	5	10	–
PPA _{0/0/20}	100	10	20	–
PPA _{0/0/30}	100	15	30	–
PPA _{1.25/30/10}	100	5	–	10
PPA _{1.25/30/20}	100	10	–	20
PPA _{1.25/30/30}	100	15	–	30

The composition of polypropylene/waste rubber composites are shown in Table 2.

3. Characterization

3.1. Fourier transform infrared (FT-IR) spectroscopy

About 0.01 g of unmodified or allylamine modified rubber powder was mixed with 1 g of potassium bromide (KBr) and pelletized using a hydraulic press at a pressure of 10 kPa. Samples were subjected to IR characterization in the range of 4000–400 cm^{−1} using a Perkin–Elmer 2000 spectrophotometer. The spectra were obtained at a resolution of 4.0 cm^{−1} in the transmission mode. FT-IR spectra of polypropylene-waste rubber composites were taken in the range of 4000–650 cm^{−1} in the attenuated total reflectance mode (FTIR-ATR) using a zinc selenide crystal.

3.2. Scanning electron microscopy/energy dispersive X-ray (SEM/EDX) analysis

Scanning electron microscopy studies of unmodified and modified rubber powders were done using a Stereoscan 440 (Leica, Cambridge). Samples were coated with gold. The relative amounts of carbon and nitrogen X-ray counts were measured using the energy dispersive X-ray analyzer facility of the microscope. SEM photographs of the unmodified and modified rubber powders have been taken under a magnification of 100× and the tensile fractured samples have been taken under a magnification of 1000×.

3.3. Surface energy measurements by wicking method

The surface energies of unmodified and modified rubber powders were calculated by the measurement of contact angle using a dynamic wicking method. The rubber powders (2 g) were tapped 200 times and packed in a graduated capillary tube (5 mm inner diameter, 50 mm long). The tube was placed vertically and in contact with liquid (water or ethylene glycol) in a beaker. Then liquid penetrates into the empty spaces of the powder column by capillary action. The

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