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Radiation crosslinking of styrene–butadiene rubber containing waste tire rubber and polyfunctional monomers

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HIGHLIGHTS

- The effect of γ radiation on SBR blended with waste tire rubber was studied.
- Two polyfunctional monomers were used to increase the crosslinking.
- Mechanical properties of the blends were increased with absorbed dose.
- TMPTA containing blend showed higher tensile strength and thermal stability.
- Comparison with sulfur crosslinking was also done.

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ABSTRACT

The objective of this study was to investigate the influence of polyfunctional monomers (PFMs) and absorbed dose on the final characteristics of styrene–butadiene rubber (SBR) mixed with waste tire rubber (WTR). A series of SBR/WTR blends were prepared by varying the ratios of WTR in the presence of PFMs, namely trimethylolpropane trimethacrylate (TMPTMA) and trimethylolpropane triacrylate (TMPTA) and crosslinked using gamma rays. The physicochemical characteristics of the prepared blends were investigated. It was observed that tensile strength, hardness and gel content of the blends increased with absorbed dose while the blends containing TMPTA showed higher tensile strength, gel content and thermal stability as compared to the blends containing TMPTMA. Higher thermal stability was observed in the blends which were crosslinked by radiation as compared to the blends crosslinked by sulfur. These blends exhibited higher rate of swelling in organic solvents, whereas negligible swelling was observed in acidic and basic environment.

1. Introduction

With the increase in industrialization and globalization, the global production rate of rubber tire has increased tremendously. However, only a little of this rubber is used when these materials become worn out and of no longer use (Adhikari et al., 2000). The growing stockpiles of waste tire are conspicuous in every country which ultimately threaten the environment (Sreeja and Kutty, 2003). Although several mitigation steps such as combustion, land filling, pyrolysis and reuse as an additive have been adopted for the treatment of waste tire, yet all these processes have limitations leading to serious ecological concerns (Awang et al., 2007). Due to the crosslinked nature of waste tire rubber, it is difficult to degrade and/or reprocess. As an alternate approach, researchers have used chemical and physical processes to break the three dimensional networks or rubber which can lead to its easy processability with other materials (Scuracchi et al., 2007). In view of the enormous economic and environmental burden of such waste-piles, an eco-friendly approach is needed to recycle and/or reuse this rubber waste product (Adhikari et al., 2000; Kim and Park, 1999).

Previously, it has been reported that the waste tire rubber can be successfully converted into powder and used as an additive with other polymers (Yasin et al., 2012; De and De, 2011; Lee et al., 2009; Meszaros et al., 2008; Kim et al., 2007; Naskar et al., 2001). Various methods have been employed to crosslink the polymeric materials including electron beam and gamma radiations. Compared to other crosslinking methods, radiation crosslinking is a simple and an eco-friendly process which has already been commercialized (Chmielewski and Haji-Saeid, 2004; Yasin et al., 2005; Anis Sakinah et al., 2011). In radiation crosslinking, PFMs are

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incorporated into the elastomers to lower the absorbed dose and improve the properties without degradation (Vijayabaskar and Bhowmick, 2005; Chaudhari et al., 2005; Basfar et al., 2002; Yasin et al., 2002). The present work is focused on the recycling of waste tire rubber using gamma rays and SBR. Previously, WTR was blended with ethylene–propylene–diene rubber (EPDM) and crosslinked using electron beam. The resulting blends demonstrated good physicochemical properties (Yasin et al., 2012). Herein, styrene–butadiene rubber has been selected as base polymer and series of blends containing varying content of WTR and PFMs were prepared. These blends were gamma irradiated to crosslink the polymer/PFMs components. The physicochemical characteristics including mechanical properties, thermal stability, swelling index, gel fraction and hardness of the crosslinked blends were also investigated. The blends crosslinked in the presence of TMPTA exhibited higher physicochemical properties compared with the blends crosslinked using TMPTMA.

2. Experimental and methods

SBR-1502 (23.5% styrene; Mooney Viscosity, ML_1 52) was supplied by Korea Kumho Petrochemical Co., Ltd. WTR having particle size of 80 mesh (an accepted value of ≤ 180 μm) produced from used tire was obtained from Malaysia. TMPTMA, TMPTA, stearic acid (SA) and zinc oxide (ZnO) were purchased from Sigma-Aldrich Chemie (Steinheim, Germany). Carbon black (SRF type), sulfur, antioxidant (p-phenylenediamine), paraffin oil and polyethylene wax were of commercial grade. All the reagents were used without further purification.

2.1. Preparation of blends

SBR/WTR blends were prepared using two-step procedure. In the first step, SBR was masticated in a roll mill at 60 °C. During mastication, WTR 10–20 phr (parts per hundred parts of polymer), carbon black (10 phr), polyethylene wax (5 phr), paraffin oil (7 phr), ZnO (5 phr) and SA (2 phr) were added. The term "masticated rubber" is used to represent roll mill mixed rubber. In the second step, the masticated rubber was blended in Thermo Haake Polylab Rheomix Internal Mixer at 120 °C using banbury rotors. The blending was carried out at 60 rpm for 15 min. One blend contained TMPTMA at 4.4 phr and other contained TMPTA at 3.8 phr. To prepare sulfur-crosslinked blends, sulfur (2 phr), dibenzthiazyldisulphide (1 phr), and 2-bisbenzothiazole-2,2′-monosulfide (1 phr) were added during melt blending of masticated rubber. The sulfur crosslinked blends did not contain PFMs. The blends were heat pressed into 2 mm thick sheets using Gibitre hot press at 150 °C and 150 kg/cm^2 pressure for 3 min. Sulfur containing blends were vulcanized in hot press at 150 °C and 150 kg/cm^2 for 30 min. SS_1 and SS_2 identification codes are used to represent sulfur crosslinked formulations containing 10 phr and 20 phr WTR, respectively.

2.2. Gamma irradiation

Irradiation of the prepared blends was carried out using ^{60}Co gamma irradiator (Model JS-7900, IR-148) in air at dose rate of 0.9 kGy/h at the Pakistan Radiation Services, Lahore. The absorbed dose was varied from 25 kGy to 100 kGy at an increment of 25 kGy.

2.3. Gel content analysis

The gel content of the irradiated blends was measured using Soxhlet extractor following the ASTM 2765 method. The small pieces of samples were wrapped in a steel mesh and extracted in boiling xylene for 8 h. Afterwards, the samples were dried in a vacuum oven until the constant weight. The gel content (%) was calculated according to the following formula:

$$\text{Gel content}(\%) = W_1/W_0 \times 100 \quad (1)$$

where W_0 and W_1 represent the weights of sample before and after extraction respectively.

2.4. Tensile properties

The tensile properties of blends were measured following ASTM D412-1998a standard using a uniaxial tensile testing machine (Model: BSS-500 kg, SANS, Transcell Technology, Shenzhen, China). The tests were performed at a crosshead speed of 200 mm/min at ambient temperature (~25 °C). Five specimens of each sample were tested and the average results are reported.

2.5. Thermogravimetric analysis

The thermal stability of the blends was investigated using thermogravimetric analyzer (Mettler-Toledo TGA/SDTA851^e, Schwarzenbach, Switzerland). The analysis was performed under nitrogen (40 mL/min) at heating rate of 20 °C/min from 50 °C to 550 °C.

2.6. Hardness testing

The hardness of samples was evaluated following ASTM D2240 standard using an Asker DD2 durometer. The unit of hardness is expressed in Shore A and average of five reading is reported.

2.7. Solvent uptake studies

The solvent uptake of the blends was evaluated by immersing small pieces of specimens into various solvents at ambient temperature (~25 °C). Chloroform, kerosene oil, xylene, NaOH (12%) and H_2SO_4 (10%) were used for the solvent uptake studies. After 24 h, samples were taken out from the solvent and the wet surfaces were cleaned with lint free paper. The swelling was calculated using the following equation:

$$\text{Swelling}(\%) = W_2/W_1 \quad (2)$$

Here, W_1 and W_2 represent the initial and final (swollen) weights of the sample respectively.

3. Results and discussion

3.1. Gel content analysis

The extent of crosslinking of the blends after exposure to gamma rays and as a function of the type of PFMs was evaluated by gel content analysis. Sulfur crosslinked blend (SS_1) exhibited gel content value of 83.6%. The gel content of the radiation crosslinked blends are illustrated in Table 1. As can be noted from the table, the gel content of the blends increased with absorbed dose upto 75 kGy and leveled off at higher dose. This increase in gel content of the blends with absorbed dose can be attributed to the

Table 1
Gel content of gamma irradiated SBR/WTR blends.

Sample	25 kGy	50 kGy	75 kGy	100 kGy
$TMPTA_{10}$	68.3	68.8	79.6	69.7
$TMPTMA_{10}$	57.6	60.6	73.0	69.7