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Effect of electron beam irradiation on the properties of natural rubber (NR)/styrene–butadiene rubber (SBR) blend

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ABSTRACT

In this study, physico-mechanical properties of NR/SBR blends cured by electron beam irradiation and sulfur were compared. The NR/SBR blends were prepared using a two-roll mill. Electron beam irradiations of 100–400 kGy were applied to cure the blends and changes in physico-mechanical properties were studied as a function of irradiation. Also, oil resistance and the effect of thermal ageing on mechanical properties of the blends were investigated. The results show that the irradiated blends have better mechanical properties than those cured by sulfur system. The irradiation cured samples also exhibited better heat stability than the sulfur cured samples. The blend cured by the highest dose shows the lowest swelling and high oil resistance compared with the other samples cured by irradiation.

1. Introduction

Elastomeric blends are frequently used in the rubber industry to obtain desirable physical properties, process ability and lower cost. Blends can offer a set of properties that are not possible with neither component of the blends (Findik et al., 2004; Ramesan et al., 2005). The NR/SBR blends are important in rubber industry and exhibit improved oxidative stability compared to pure component. The mechanical properties of the NR/SBR blends could be improved (Fan et al., 2001; Manshaie et al., 2009; Medhat et al., 2009). The properties and performance of a rubber product depend on the chemical nature of rubber and vulcanization conditions. Therefore, optimization of rubber properties by different vulcanization methods is required so that the rubber product performs satisfactorily during service life (Basfar et al., 2002; Fan et al., 2001). Normally, rubbers are vulcanized by systems based on sulfur or peroxide. The common feature of these systems is that they all require activation energy in the form of heat. This heat (150–180 °C) may affect the final properties of the product by a variety of uncontrolled side reactions (Magda, 2007). Therefore, irradiation has been widely used as an alternative to conventional chemical methods of rubber crosslinking (Wang et al., 2009). Irradiation process reduces the curing time and energy consumption. On the other hand, in irradiation curing, the curing process is carried out at ambient temperature in a shorter time interval under closely controlled conditions such as irradiation, irradiation rate, penetration depth (in case of electron beam curing), etc. and these are the main advantages over the thermal cured rubber system. The type of crosslink formed by the irradiation-curing method (–C–C–) gives rise to better mechanical properties at higher service temperature. This might be reflected in better high-temperature performances as higher hot-tear strength (Basfar et al., 2002; Nishitsuji et al., 2007; Magda, 2007). It is well known that interaction of electron beam irradiation with a polymer results in the formation of free radicals formed by dissociation of the excited state or by ion molecular reaction. The vulcanization reaction or chain scission occurs during the irradiation of polymer. Electron beam irradiation process does not employ chemical agents such as peroxides. Using small amounts of coagents such as ethylene glycol dimethacrylate (EGDMA), trimethylol propane trimethacrylate (TMPTA) or trimethyl-propane trimethacrylate (TPTA) can help to reduce the dose required for vulcanization. Two important factors in irradiation are irradiation and temperature. The reaction mechanism of electron-beam curing system is shown as follows (Hafezi and Nouri khorasani, 2007):

$$\text{polymer(PH)} \xrightarrow{\text{high Eng radiation}} \text{PH}^* \quad \text{(excited state)}$$

$$\text{PH}^*\text{(excited state)} \rightarrow \text{PH}^+ + 1e^-$$
$$\text{PH}^* \rightarrow \text{P}^\circ + \text{H}^\circ$$
$$\text{PH}^+ + \text{PH} \rightarrow \text{P}^\circ + \text{PH}_2^+$$
$$\text{P}^\circ + \text{PH}_2^+ + 1e^- \rightarrow \text{P}^\circ + \text{P}^\circ + \text{H}_2$$
$$\text{P}^\circ + \text{P}^\circ \rightarrow \text{P–P} \quad \text{(crosslinked polymer)}$$
$$\text{P}_1\text{H}^* + \text{P}_2\text{H} \rightarrow \text{P}_1\text{H} + \text{P}_2\text{H}^* \quad \text{(energy transfer)}$$
$$\text{H}^\circ + \text{PH} \rightarrow \text{P}^\circ + \text{H}_2$$

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Many studies have been carried out to investigate the effects of sulfur content on mechanical, thermal and electrical properties of SBR and NR blends (Manshaie et al., 2009; Wimolmala et al., 2009) but reports on the effect of electron beam irradiation on these blends are scarce. Hence, the aim of this research is to compare physico-mechanical and chemical resistance properties of NR/SBR blend vulcanizates with electron beam and sulfur-curing processes.

2. Experimental

2.1. Materials

The basic materials in this research and their sources are styrene–butadiene rubber (SBR-1502) provided by Poliran Co., Iran, with density 1.04 (g/cm^3) and Mooney viscosity 40–50 (ML1+4, 100 °C). Ribbed smoked sheets in the name of RSS1 from Malaysia were used as natural rubber with density 0.95 (g/cm^3) and Mooney viscosity 84 (ML1+4, 100 °C). The solvent ethanol was of commercial grade with density 0.789 g/cm^3 and supplied by local chemical suppliers. Brake oil DOT4 was provided by Fouman Shimi Co., Iran, with kinematic viscosity 2.1 cSt @ 100 °C and paraffinic rubber processing oil Behran 840 was obtained from Behran Oil Co., Iran, with kinematic viscosity 5.1 St @ 100 °C.

2.2. Compounding and sample preparation

Fixed master batch formulation of the compound was used for both electron beam and sulfur curing systems as shown in Table 1. Sulfur curing system ingredients and their suppliers are given in Table 2.

Compounding, sheeting and vulcanization of rubber blends were carried out in accordance with ASTM D3182. All rubber blends were prepared on a two-roll laboratory mill (diameter 200 mm and working distance of 750 mm). The roll temperature was kept at 70 °C during mixing. Mixing time was 12 min and mixing speed was 60 rpm. After compounding, the sheeted rubber compounds were conditioned at a temperature of 23 °C for 24 h. For sulfur curing, cure characteristics of mixes, scorch time (t_{S2}), cure time (t_{C90}), minimum torque (ML) and maximum torque (MH) were determind using a Hiwa Rheometer model 100 according to ASTM D2084. Sulfur curing was carried out in an electrically heated press at 160 °C under pressure (1 MPa) to obtain optimum cure time to prepare sheets (2 mm thick). Dumbbell test specimens were cut from the sheets. For electron beam curing, fixed formulation of master batch compounds was compression-molded between aluminum foil at 160 °C under pressure (1 MPa) in an electrically heated press to prepare sheets of 2 mm thickness. Dumbbell shape test specimens were cut from the sheets. The samples were marked 100–400 referring to irradiation in kGy.

Table 1
Fixed master batch formulation.

Material	Amounts (phr)[a]	Manufacturer
SBR	70	Poliran, Iran
NR	30	Malaysia
Carbon black N330	50	Pars Co., Iran
Zinc oxide	5	Gostar Jam c ., Iran
Stearic acid	1	Minko Co., Malaysian
Paraffin wax	1	Roz Polymer Co., Iran
TMQ[b]	1	Bayer Co., Germany
IPPD[c]	1	Bayer Co., Germany

[a] Part per hundred of rubber.
[b] 2,2,4-trimethyl-1,2-dihydroquinoline.
[c] N-isopropyl-N′-phenyl-P-phenylendiamine.

Table 2
Sulfur curing system.

Material	phr	Manufacturer
Sulfur	2	Razi Petrochemical Co, Iran
TMTD[a]	1	Bayer Co., Germany
CBS[b]	1	Bayer Co., Germany

[a] Tetramethylthiuram disulfide.
[b] N-cyclohexy-2-benzothiazole sulfonamide.

2.3. Irradiation

Electron-beam irradiations were carried out in the Yazd Irradiation Proccessing Center using an electron beam accelerator RHODOTRON TT200. This accelerator operates at 10 MeV and the irradiation process was carried out under atmospheric conditions. The samples were put on a conveyor belt. To avoid an excess increase in the sample temperature a dose of 25 kGy irradiation was given in every pass and the total irradiation given to each sample was controlled by the total number of passes (e.g. a sample needs eight irradiation passes to get a total of 200 kGy irradiation). Dosimetry was carried out using cellulose tri-acetate (CTA; ISO/ASTM 51650: 2005(E)). The total deviation in this irradiation dose was about $\pm$5%.

2.4. Gel fraction

Gel fraction, expressed as the fraction of insoluble weight, was obtained by extracting the soluble part in toluene for 24 h at room temperature, and drying the insoluble part in a vacuum oven at 50 °C. The gel fractions were calculated using simple mathematical relations:

$$\text{gel fraction} = W_1/W_0 \quad (1)$$

where W_0 is the initial weight of the polymer and W_1 the weight of the insoluble portion of the polymer. The reported results are the averages of three samples.

2.5. Mechanical properties

Tensile strength and elongation at break were measured using dumbbel type specimens according to ASTM D412. Tensile tests were carried out on a Hiwa 200 tensometer at 500 mm/min cross-head speed at room temperature. Hardness tests were carried out using shore A Durometer according to ASTM D2240. The percentage of abrasion resistance was measured according to DIN5356. The test conditions and procedure of compression set testing followed ASTM D395 Method B (under a constant deflection in air). Resilience test was carried out using ASTM D1054, performed by Hiwa 300. The effect of thermal ageing on the mechanical properties of the NR/SBR blend was studied by keeping the dumbbel samples in an air oven at 100 °C for 48 h. The NR/SBR samples were then conditioned at ambient temperature for 24 h before testing according to ASTM D573. The changes in tensile strength, elongation at break and hardness before and after the thermal ageing conditions were then evaluated. Three samples were tested for each set of experiments.