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Electron beam irradiation of polycarbonate reinforced acrylonitrile butadiene rubber

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ABSTRACT

The effects of electron beam irradiation and polycarbonate (PC) concentration on the properties of acrylonitrile butadiene rubber (NBR) were investigated. The electron beam irradiation doses were from 25 to 150 kGy, whereas the PC contents were from 10 to 30 phr. It was found that the mechanical properties of NBR such as tensile strength (TS), hardness and tear strength (*Ts*) were remarkably improved by the incorporation of PC, while elongation at break (E_b) and thermal properties were decreased. However, the improvement in TS of NBR/PC blends was strongly dependant on PC content, in which maximum improvements need higher doses. On the other hand, the maximum value of *Ts* for all the blend ratios was at 25 kGy, whereas the hardness increases with increasing irradiation dose. Moreover, it was observed that the fuel resistance of NBR/PC was higher than NBR and decreases by increasing the content of PC.

1. Introduction

Over many decades, reinforcement of rubbery materials was the interest of many researchers to fulfill industry's need for high performance materials. Carbon black was found to be the most important reinforcing agent in rubber materials industry. But due to its polluting nature, and its dependence on petroleum made researchers to develop other reinforcing agents.

One of the methods to improve the performance of polymers is by simple blending. Although blending is an easy method for the preparation of thermoplastic elastomers (TPEs), most of the TPE blends are immiscible. Very often the resulting materials exhibit poor mechanical properties due to the poor adhesion between the phases [1,2]. In immiscible blends, the situation at the blend interface is critical as a high-interfacial tension and a poor adhesion between the phases are observed. Compatibilization was found to improve the properties of immiscible polymer blends by providing stable morphology, and good interfacial adhesion [3–6]. Different techniques have been developed to alleviate this problem. One of these techniques used to improve the morphology stabilization of polymer blend is the crosslinking by electron beam irradiation [7]. Coran and Patel [8] selected a series of TPEs based on different rubbers and thermoplastics. It was shown that the ultimate mechanical properties of these dynamically cured blends were increased similar to the rubber and plastic with respect to the critical surface tension for wetting and the crystallinity of the plastic phase.

Polycarbonate (PC) as an engineering thermoplastics has found many applications in several industrial fields due to high toughness, good ductility, high glass transition temperature, excellent optical clarity and dimensional stability. It was found that blends of polycarbonate and acrylonitrile–butadiene–styrene showed improved flow and impact strength, while polycarbonate–polyester blends using either poly(butylene terephthalate or polyethylene terephthalate) showed improved chemical resistance. Other blends of PC are with polyurethane, polyetherimides, acrylate–styrene–acrylonitrile, acrylonitrile–ethylene–styrene, and styrene maleic anhydride [9] were investigated. A wide range of elastomers, e.g., ethylene propylene diene rubber (EPDM), nitrile rubber (NBR), chlorinated polyethylene (CPE), hydrogenated nitrile rubber (HNBR), and ethylene acrylic rubber (ACM) were also blended with PC [10]. Overall these blends, CPE/PC and HNBR/PC blends showed best strength, whereas EPDM/PC and HNBR/PC showed the best thermal stability.

In the present work, nitrile butadiene rubber and polycarbonate blends as incompatible blends are studied. To insure homogenous mixing and also to overcome the degradation reaction of NBR that may arise during mixing at high temperature, polycarbonate in methylene chloride as a paste is mixed with NBR on a roll mill. PC content was between 10 and 30 phr. The prepared blends were exposed to electron beam irradiation under atmospheric conditions to doses up to 150 kGy. The mechanical, physical and thermal properties of the prepared blends were investigated before and after irradiation.

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2. Experimental

2.1. Materials

Acrylonitrile butadiene rubber (acrylonitrile content 40%), commercial name KRYNAC 40:50 Bayer of density 0.98 g/cm^3 was used throughout this work. Polycarbonate Macrolon amorphous polymer type 31001 fabe (Bayer, Middle East of Egypt) having a density of 1.2 g/cm^3 was used. The prepared PC:NBR blends have the following composition 10:100, 15:100, 20:100, and 30:100 by weight and their densities are 0.9966, 1.004, 1.01, and 1.023 g/cm^3, respectively.

2.2. Preparation of NBR/PC blends

Polycarbonate has high softening temperature (148 °C) and also its flow temperature reaches 300 °C, hence conventional melt blending may cause degradation to NBR at such high temperature. Therefore, PC was pasted in methylene chloride (35%) and mixed with NBR at different concentrations namely 10, 15, 20, and 30 phr on a rubber mill. After that, the blends were transferred to an oven at 50 °C and left to a constant weight to insure complete solvent evaporation. Blends were finally sheeted, again into slabs of about 1 mm thickness; the sheets were covered from both sides with polyester sheet before being pressed in a clean polished mold of an electric press. The molds were brought to 160 °C and held at this temperature for at least 5 min at a pressure of 5 MPa.

2.3. Irradiation procedure

Irradiation of samples was carried on the electron beam accelerator (isolated core transformer type) supplied by High Voltage Engineering, USA. Irradiation was done at beam current of 5 mA, energy of 1.5 MeV, in which every pass results in a dose of 25 kGy to avoid surfaces heating. The irradiation process was carried out under atmospheric conditions.

2.4. Mechanical measurements

2.4.1. Tensile properties

Five individual dumbbell-shaped specimens were cut out from the sheets using a steel die of standard width (6.2 mm). The tensile strength (TS) and elongation at break point (E_b) were determined at a crosshead speed of 250 mm/min on a rubber tensile testing machine (Hung Ta Instrument Co., Ltd.) HT-9112 Taiwan.

2.4.2. Hardness

The hardness of specimens was determined using durometer type A (Model 306L) instrument from Pacific Trasducer Corp., Los Angeles, USA. The method was carried out according to (ASTM D 2240, 2000) specification, and the units of hardness are expressed in Shore A.

2.4.3. Tear strength (Ts)

Tear strength was determined according to ASTM D 624-00 Hung Ta (HT-9112, Taiwan) rubber testing machine.Tear strength is defined as the maximum force required to cause a rupture of a type C (right angle) test piece, divided by the thickness of the test piece.

$$Ts = F/d \tag{1}$$

where F is the maximum force, in kgf and d is the median thickness of each test piece, in mm.

2.5. Crosslinking density measurements

It has been shown that the true stress (σ) in simple extension can be considered as a sum of two contributions [11,12]:

$$\sigma = \sigma_0(\lambda) + G_e(\lambda^2 - \lambda^{-1}) \tag{2}$$

where σ is the true stress (nominal stress multiplied by λ), λ is the extension ratio, σ_0 depends on the chemical nature of the rubber but the crosslink density, parameter G_e depends on the degree of crosslinking [12]. According to Zang et al. [13], Mc (molecular weight between crosslinks) can be estimated from the value of G_e as follows:

$$\mathrm{Mc} = A_\phi \rho RT/G_e \tag{3}$$

The prefactor A_ϕ was assumed to be equal to 1; T is absolute temperature, ρ is the density of the specimens, R (8,314,472 cm^{-3} Pa K^{-1} mol^{-1}) is the gas constant.

2.6. Physico-chemical measurements

2.6.1. Effect of fuel

Irradiated samples to different doses in triplicates were weighed to the nearest mg (M_1). They were then transferred to flask 2/3 filled with fuel D (50 vol.% of commercial gasoline + 50 vol.% of toluene). Heating has been carried out at 100 °C for 22 h. After that, the flask is allowed to cool to room temperature. The samples were then blotted lightly with filter paper to remove the remaining liquid fuel. They were then reweighed again (M_2).

The percentage change in weight was then calculated using the following equation:

$$\text{Change in weight, } \% = \frac{M_2 - M_1}{M_1} \times 100 \tag{4}$$

2.6.2. Soluble fraction

Measurement was carried out according to ASTM D 84-2765. The samples of irradiated rubbers, about 0.2 g were accurately weighed and transferred to a special round-bottomed flask 2/3 filled with dimethyl formamide (DMF) and heated for 24 h. After extraction, the samples were lifted and standardized for 2 h in a fuming hood before drying. The samples were dried to constant weights in a dry oven at 50 °C.

Application of Charlesby–Pinner equation: This equation [14] is generally applied with the aim of obtaining correlation between irradiation and crosslinking density by estimation of the solubility of irradiated polymeric blends. The equation is as follows:

$$S + S^{0.5} = p_0/q_0 + 1/q_0 uR, \tag{5}$$

where S is the soluble fraction, p_0/q_0 is the probability of degradation to crosslinking, R is the radiation dose in Mrad, and u is the degree of polymerization before irradiation.

2.7. Thermogravimetric analysis measurements

The thermogravimetric analysis (TGA) was carried out using a TG-50 instrument from Shimadzu (Japan). The heating was carried out at temperature range from room temperature to 600 °C at a heating rate of 10 °C/min under nitrogen gas atmosphere.

3. Results and discussion

3.1. Mechanical properties

3.1.1. Tensile strength

Fig. 1 shows the effect of irradiation dose on the tensile strength (TS) of NBR and PC/NBR blends of different ratios of PC. It can be