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Remarkably enhanced thermal stability of an irradiation-crosslinked ethylene–octene copolymer by incorporation of a novel organic/inorganic hybrid nano-sensitizer

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HIGHLIGHTS

- A novel organic/inorganic hybrid nano-sensitizer is proposed.
- The sensitizer was facilely prepared by the coupling activation modification.
- Radiation induced crosslinking of POE was enhanced by the nano-sensitizer.
- The thermal deformation resistance of irradiated nanocomposites was enhanced.
- The tensile strength of irradiated nanocomposites was improved

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ABSTRACT

We report a novel method to improve the anti-thermal-deformation performance of an ethylene–octene copolymer (POE) using vinyl functionalized silica nanoparticles (M-SiO_2) as a sensitizer to enhance radiation-induced crosslinking. The M-SiO_2 nanoparticles were prepared by coupling commercially available silica nanoparticles with KH570 (γ-methacryloxypropyl-trimethoxysilane, γ-MPS) and were blended with POE by melt blending. Then, the mixture was irradiated with γ-rays under a nitrogen atmosphere to form the crosslinked POE/M-SiO_2 nanocomposite. The novel nanocomposites were characterized, and the results showed that the gel fraction was proportional to the content of M-SiO_2 in the loading range studied in this work. When the content of M-SiO_2 was 10 wt%, the gel fraction of POE was increased by approximately 50%, and the softening temperature ($T_{0.5D}$) increased from 104.4 °C to 224.6 °C after a 120 kGy dose of radiation. The tensile strength of the POE/M-SiO_2-10 nanocomposite was better than that of the neat POE copolymer irradiated with an absorption dose up to 100 kGy. In contrast, the elongation of the POE/M-SiO_2-10 nanocomposite was lower than that of the neat POE irradiated under the same conditions, due to the increased degree of crosslinking by radiation. These results clearly demonstrated that the use of M-SiO_2 as an irradiation sensitizer effectively enhanced the radiation-induced crosslinking of POE.

1. Introduction

Thermoplastic elastomers (TPE) that combine the flexible, low-modulus properties of elastomers with the processing advantages of thermoplastics continue to become more popular in a variety of applications (Wang et al., 2011). In recent years, ethylene–octene copolymer (POE), which is classified as a TPE, was produced using the constrained geometry catalyst technology (CGCT) by Dow Chemical Company (Bensason et al., 1997). POE has excellent mechanical and cryogenic properties and is not only widely used in toughening thermoplastics, wire and cables (Wang et al., 2011) but also in packaging materials and biomedical materials (Benson et al., 1999). However, the low heat distortion temperature and the large permanent deformation of POE certainly precludes POE products from steam or dry-heat post-processing. Crosslinking is an important way to improve the thermal stability of POE (Schulze et al., 2008; Wang et al., 2011). There are three main crosslinking methods, including peroxide crosslinking, silane crosslinking, and radiation crosslinking (Wang et al., 2011), of which radiation crosslinking stands out as a rapid, clean, and effective method to enhance the shape stability of POE at elevated temperatures (Hui et al., 2009).

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Some studies have focused on the effect of irradiation on POE (Benson et al., 1999; Li et al., 2002). Li et al. reported that the gel fraction of POE is approximately 5% when irradiated with a 40 kGy radiation dose (Li et al., 2002). To improve crosslinking, various multifunctional monomers with vinyl groups, such as triallyl isocyanurate (TAIC) (Nagasawa et al., 2011), trimethallyl isocyanurate (TMAIC) (Zhu et al., 2013), di(trimethylol propane) tetra-acrylate (DTMPTA) (Schulze et al., 2008) and trimethylol propane trimethacrylate (TMPTMA) (Chowdhury and Banerji, 2005; Zhu et al., 2013) have been used as crosslinking promoters. However, these sensitizers are small organic molecules and could separate out from the polymer matrix during extended storage before irradiation. This timeline can be typical in applications of POE, such as in food packaging. As a result, the radiation crosslinking yield can decrease, and the spatial distribution of polymer the network can be heterogeneous.

Polymer based nanocomposites have attracted considerable interest because of their extraordinary properties, such as unique electronic, optical, thermal, and mechanical properties. It is worth mentioning that, on one hand, the addition of a nanofiller can improve the stiffness of composites. On the other hand, it is very difficult for nanofiller to move in a polymeric matrix at room temperature due to the rigid structure of the nanofiller and the interfacial interactions between the polymer and nanofiller molecules. Therefore, the problem of migration for organic sensitizers can be solved using nanofiller. A few studies have reported that radiation induced effects on polymer reinforced with unmodified nanomaterials (Dubey et al., 2009; Hui et al., 2009). Additionally, as reported, the addition of fillers composed of atoms of higher atomic number ($Z > 10$) increases the electron density of these hypothetical materials in electron-beam lithography, and therefore the frequency of elastic and inelastic collisions suffered by an incident electron increases accordingly (Jeyakumar and Henderson, 2003). Silicon or titanium atoms are high atomic number species that are typically used in this application. Thus, silica nanoparticles have been shown to promote radiation crosslinking (Hui et al., 2009). Based on a combination of these findings, an organic/inorganic hybrid nanosensitizer (modified silica) was prepared using coupling activation modification.

In this work, the organic coupling agent with a vinyl group was tethered to the surface of nanosilica. The obtained organic/inorganic hybrid could be used as a sensitizer that would overcome the drawbacks of organic sensitizers. The effect of the modified nanosilica on radiation induced crosslinking behavior and thermal deformation resistance of POE was investigated. We also demonstrate the use of functional silica as a hybrid sensitizer for enhancing radiation induced crosslinking.

2. Experimental

2.1. Materials

Ethylene–octene copolymer (POE) pellets were purchased from Mitsui Chemical Co., Ltd. (Tokyo, Japan). The melt flow index of POE is 3.6 g/10 min, the weight-average molecular weight is approximately 1.5×10^5 g/mol, and the density is 0.870 g/cm^3. Silica nanoparticles (15 nm) were kindly provided by Nanjing Emperor Nanomaterial Co., Ltd. (Nanjing, China). Cyclohexane (C_6H_{12}, 99%), n-propylamine (C_3H_9N, 99%) and γ-methacryloxypropyl-trimethoxysilane (γ-MPS, 99%) were received from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). All the chemicals were used without further purification.

2.2. Preparation of hybrid nano-sensitizer

In this work, the organic/inorganic hybrid nano-sensitizer (M-SiO_2) was prepared using a previously reported procedure (Wilson et al., 2005). The detailed procedure was as follows: 30.0 g nanosilica, 3.2 ml γ-MPS and 0.84 ml n-propylamine were added into a 1000 ml round bottom flask containing 600 ml cyclohexane with continuous stirring at room temperature for 35 min, and then kept at 65 °C for an additional 30 min at atmospheric pressure. The solvent and volatile byproducts were removed using a rotary evaporator at 65 °C. Finally, the powder was vacuum-dried at 80 °C for 24 h.

2.3. Preparation and irradiation of nanocomposites

POE and modified nanosilica were dried at 105 °C for 12 h under vacuum condition and then were mixed at 140 °C in a Brabender Plasti-Corder PL2100 mixing machine at a mixing speed of 45 rpm for 12 min. The contents of nanosilica were 5, 10, 15, and 20 wt%. The prepared samples were labeled as POE/M-SiO_2-m, here m represents the concentration of nanosilica (in wt%), and M-SiO_2 represents modified SiO_2. The mixtures were hot pressed at 140 °C under a constant pressure of 18 MPa for 2 min. Nanocomposites sheets thus obtained were subjected to gamma radiation in a nitrogen environment using ^{60}Co source with a source activity of 9.2×10^4Ci. The absorbed dose ranged from 40 to 120 kGy, with a 10 kGy/h dose rate.

2.4. Characterization

The silanized nanosilica was identified using a Fourier Transform Infrared Spectroscopy (FTIR) spectrometer (Thermo Nicolet 8700, USA) with a 400–4000 cm^{-1} wave range, 32 scans and 4 cm^{-1} resolution. A blank KBr pellet was used for the collection of the background spectrum.

Thermogravimetric analysis (TG 209 F1, NETZSCH instruments Co., Ltd., Germany) of modified nanosilica was performed from 30 to 700 °C at a heating rate of 10 k/min under a nitrogen atmosphere.

The gel content of composites was determined by a solvent extraction method according to ASTM D2765-01 (Kamphunthong and Sirisinha, 2010). The percent gel content was calculated using the following formula:

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

where W_g is the final weight of the samples and W_0 is the initial weight of the samples. The results are the average of three measurements for each sample.

The value of p_0/q_0, D_g, and G can be calculated by the Charlesby–Pinner equation (Huang et al., 1993)

$$s + s^{1/2} = p_0/q_0 + 1/(q_0\mu_1 D) \quad (2)$$

$$G = 0.48 \times 10^6/(M_w D_g) \quad (3)$$

where s is the sol fraction, p_0 is the fracture density per unit dose in 10 kGy, q_0 is the crosslinking density, μ_1 is the number-average degree of polymerization, D is the absorbed dose, D_g is the dose of gelation, G is the radiation chemistry yield and M_w is the weight-average molecular weight of the polymer.

The deformation–temperature curves were measured on GTS-III-type thermal deformation measuring instrument (Shanghai Donghua Kaili Technology of New Material Co., Ltd., China) using a probe with a 2.5 mm diameter under compression stress of 200 Pa at a heating rate of 3 °C/min. The softening temperature was recorded when the deformation reached 0.5 mm, and is denoted herein as $T_{0.5D}$.

The tensile test was performed using an Instron Model 5969 tensile tester (Instron Corporation, USA). The test was conducted at a crosshead speed of 200 mm/min, and all reported values are the averages of five test specimens.