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Synergistic effect of combination of Irganox 1010 and zinc stearate on thermal stabilization of electron beam irradiated HDPE/EVA both in hot water and oven

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Abstract

Thermo-oxidative stability of HDPE/EVA blends can be considerably increased by combination of a high-molecular weight phenolic antioxidant and zinc stearate. In this work, the post-irradiation thermal stability of HDPE/EVA blends has been studied. High-density polyethylene and its blends with ethylene-vinylacetate copolymer in both pure form and mixed with Irganox 1010 and zinc stearate were exposed to electron beam radiation at doses between 80 and 150 kGy, at room temperature, in air. In order to evaluate the thermal stability of the samples, post-irradiation heat treatments were done in both hot water bath at 95 °C and in an oven at 140 °C. The mechanical properties and changes in the chemical structure were determined during thermal aging in hot water and oven. The gel content was enhanced by increasing EVA concentration in all applied doses. The stabilized blends have lower gel content than the unstabilized samples. From the results of heat aging treatments it was observed that the thermal stability of the unstabilized blend samples was lower than HDPE. Thermal stability of the samples has been improved by incorporation of Irganox 1010 and zinc stearate. Formation of hydroxyl group was insignificant for stabilized samples during heat aging in both conditions. Also, the changes in the value of oxidation induction time (OIT) for the stabilized samples were negligible after prolonged immersion in hot water.

Keywords: Polyethylene; PE/EVA blend; EB irradiation; Antioxidant; Zinc stearate

1. Introduction

Antioxidants are of great importance in the manufacture of plastics. A series of published papers have dealt with the nature of antioxidant and its influence on the stability of polymers (Gal et al., 1983; Novakovic et al., 1985; Gal et al., 1985). In many applications such as pipes, not only the thermal stability of polymeric materials, but also the resistance of mixed antioxidants as well as other additives to extraction into water are crucial (Matsui et al., 2002). The consumption and physical loss of stabilizers depend on the nature of the additives, the nature and geometry of the polymer samples, the environment and the solubility of the stabilizers in the polymer. The consumption of the stabilizers occurs during chemical reaction in the presence of light, heat, and radiation, while the physical loss of the stabilizers occurs by diffusion toward the polymer surface by evaporation, washing-out, or diffusion into the material in contact with the polymer. The consumption and loss of the stabilizers accelerate the aging of the polymer more than thermal-oxidation or photo-oxidation (Haidar and Karlsson, 2001). Allen et al. have reported some preliminary studies on the migration of phenolic antioxidants from the irradiated polyethylene into foodstuff. It has been shown that the antioxidants concentration in the extract decrease with radiation dose (Allen and Leathard, 1988; Allen et al., 1990).

Generally, antioxidants in polymer blends exposed to ionizing radiation to modify the properties of the polymer

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have to satisfy some additional requirements. For example, they should be stable in the radiation field or should not interfere with the crosslinking process.

The objective of this work is to identify the effect of ionizing radiation and post-irradiation thermal treatments in hot water and oven on consumption and loss of Irganox 1010 and zinc stearate from HDPE/EVA blends to develop HDPE/EVA compounds that upon electron beam irradiation yield materials with better mechanical properties and service temperature.

2. Experimental

HDPE (melt flow index of 0.4 g/10 min) was supplied from Bandar Emam petrochemical Co., Iran. EVA with 18% vinyl acetate content and melt flow index of 1.85 g/10 min was prepared from Hyundai petrochemical Co., Korea.

Irganox 1010 and zinc stearate (melting point 130 °C, insoluble in hot water) were prepared from Ciba Gigy and Merck Co., respectively.

The sample compositions are presented in Table 1. The compounding was carried out using a small laboratory size single-screw extruder (Axon ab Co.). The L/D ratio of the screw was 20 within a 160–190 °C temperature profile.

The homogenous extrudate was ground in a Retschmuhle cutting mill. Sheets with the thickness of 2 mm were prepared in a hydraulic Collin Press at 160 °C for 2 min. The films for IR test were prepared with the thickness of 0.15 mm.

Irradiation was carried out in air condition using a Rhodotron-type electron beam accelerator at acceleration voltage of 5 MeV. The dose rate was 50 kGy/pass.

Gel content was determined by the method of soxhelt extraction with xylene for 12 h at 140 °C. The remaining samples were dried in a vacuum oven at 70 °C for 24 h.

Tensile properties were determined according to ASTM D638 on a tensile machine model Zwick 1425. The crosshead speed was 50 mm/min. Relative value of tensile strength has been expressed as $(Ts)_1/(Ts)_0$, where $(Ts)_0$ is initial amount of tensile strength and $(Ts)_1$ is the amount of tensile strength after thermal aging.

FTIR analysis was performed with a Bruker IFS—45 Fourier transform infrared spectrometer. The variations of hydroxyl index (A3365/A1895) were measured to monitor relevant chemical changes during the thermal aging in hot water and in accelerated conditions. The absorbance of 3365 and 1895 cm^{-1} attributed to hydroxyl and reference groups, respectively.

Oxidation induction time (OIT) measurements were carried out using a Differential Scanning Calorimetry (DSC) Mettler TC 10 A Thermal Analyzer under oxygen gas at 200 °C.

To study the thermal aging properties, a number of irradiated samples were placed in a hot water bath at 95 °C for 1500 h and the others in an oven at 140 °C up to 36 and 800 h for unstabilized and stabilized samples respectively. In order to study the migration of the additives and thermal stability of the samples, the irradiated thin films at 150 kGy, which had been aged for 1500 h in hot water, were placed in the oven at 140 °C with air inflation.

Table 1
The base formulation of the samples (% w/w)

Code	PE	EVA	Irganox 1010	Zinc st.
A2–A5	80–20	20–50	1	1
B0–B7	100–30	0–70	–	–
C3	70	30	1	–

3. Results and disscussion

3.1. Gel content

Fig. 1 shows that the gel fraction of the unstabilized samples increases rapidly up to dose of 200 kGy and then increase gradually with further increase in dose. Increase in gel content in blends was enhanced by increasing of EVA concentration in all applied doses. Increasing of amorphous phase in blend samples is the main reason for higher crosslinking in the blend samples (Hassanpour et al., 2003). It can be seen in Fig. 2 that the stabilized blends C3 and A3 have lower gel content than the unstabilized one (B3). This is due to the fact that antioxidants such as Irganox 1010 are substances, which react very fast with any type of free radicals induced by the irradiation process. This inhibits crosslinking as a consequence of the radical deactivation (Jaworska et al., 1991; Tripodi et al., 1991). As a result, the antioxidant delays the growth of the molecular structure through crosslinking and limited the amount of gel fraction of C3 and A3. Moreover, this figure shows that the amount of gel content is the lowest for A3. This indicates that combination of Irganox 1010 and zinc stearate reduces radiation-induced crosslinking of the blend.

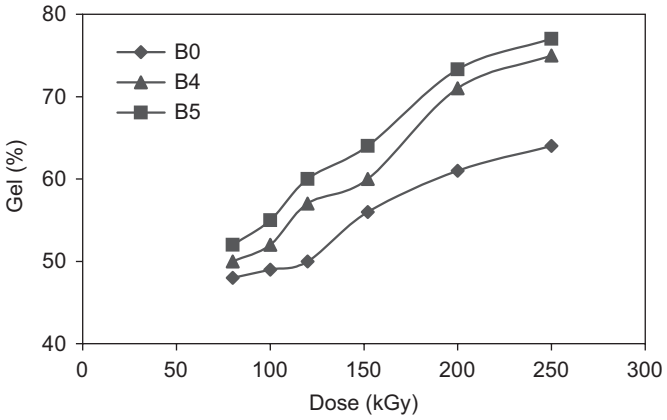

Fig. 1. Gel formation vs. dose for HDPE/EVA with different blend.