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Nuclear Instruments and Methods in Physics Research B 265 (2007) 265–270

NIM B Beam Interactions with Materials & Atoms

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Characterization of gamma-stabilized PP with blends of hindered amine/phenolic stabilizers

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Abstract

In this work, the effect of γ radiation at doses of 25 and 50 kGy on polypropylene (PP) stabilized with a binary system of antioxidants of the phenol-hindered amine type (BHT–Chimassorb 994) at different compositions (0.1/0.2, 0.1/0.5, 0.1/0.8) was studied. The results showed that the carbonyl index (I_c) of the stabilized samples drastically decreases when compared to that of the pure PP sample. Nonetheless, the I_c values of the different stabilized samples were very similar after irradiation. On the other hand, the average molecular weights (M_w and M_n) and melt flow index (MFI) values decrease in all the samples after irradiation. This effect is less pronounced in PP with 0.1/0.8 of the binary blend of antioxidants. The melting and crystallization peak temperatures and the crystallinity degree remained almost unchanged and the tensile properties such as Young's modulus and tensile strength did not vary either, except for the elongation at break, which decreases in less proportion in those blends of PP with the antioxidants, independently of the absorbed dose.

PACS: 81.82.P; 82.35.L

Keywords: γ Radiation; Stabilization; PP; Hindered amine; Hindered phenol; Stabilizers

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1. Introduction

Ionizing radiation, specifically γ radiation, is one of the methods most commonly used for sterilization purposes, because it decomposes the DNA molecules in living organisms. It can be applied simultaneously to sterilize a great deal of products with low energy consumption. γ Irradiation allows the sterilized materials remain as such for long periods of time.

A large number of medical supplies that need to be sterilized are made with polymers. In this work, surgical clothing made of a high-melt flow index PP is of special importance. γ Radiation applied to this polymeric material produces free radicals, which can react and originate chain scissions or long chain branching and cross-linking, thereby modifying its structure, molecular weight, tensile properties, etc. As a consequence, the addition of stabilizers to protect its integrity seems mandatory.

On the other hand, the presence of oxygen affects the degradative process in polyolefins. It initiates oxidative reactions and chain scission in PP. Free radicals formed during the irradiation process react with oxygen and form peroxide radicals, which subtract hydrogen from the main chain and decompose themselves, generating more radicals. This process known as auto-oxidation is auto-catalytic in nature, because it successively repeats itself until a terminating reaction takes place.

The effect of radiation onto PP has been analyzed by Nishimoto and Kagiya [1], Imai et al. [2], Dogue et al. [3],

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doi:10.1016/j.nimb.2007.08.057

Brostow and Gopalanarayanan [4], Spadaro and Valenza [5], etc., who studied the effects of cooling rates, morphology and surrounding media during radiation on its thermal behavior, tensile properties, EPR spectra, etc. On the other hand, Hassan et al. [6], Raja et al. [7], Gijsman and Gitton [8] evaluated the effect of radiation onto PP stabilized with different stabilizers such as PHTD (2(aminophenyl)-5-(*O*-hydroxyphenyl)-1,3,4-thiadiazole), PHMT (1-phenyl-5-(*O*-hydroxyphenyl)-2-mercapto-1,3,4-triazole), PBN (phenyl-β-naphthylamine), MDA (methylene-bis-(4,6-dimethyl)phenol), MP (2-2-methylene-bis-(4-methyl-6-*tert*-butyl)phenol), DDA (*N*,*N*′-dicumyl-*p*-phenylene diamine), phenolic and hindered amine antioxidants, etc. More recently, Alariqi et al. [9,10] studied the effects of irradiation onto an ethylene–propylene copolymer and an isotactic propylene homopolymer stabilized with phenolic and non-phenolic antioxidants (Irganox 1010, Chimassorb 944, Tinuvin 765 and Irgafos 168) at concentrations up to 0.4%. They irradiated the polymers with γ-rays and found that combinations of more than two stabilizers improved the stabilization efficiency. On the other hand, Aymes-Chodur et al. [11] analyzed the effects of two stabilizers such as Irganox 1076 and Irganox 1010 on PP irradiated in an electron beam accelerator. They found that the oxidized oligomers, as well as the degradation products, migrate towards the matrix and could induce a potential toxicity in the contact media, which was also studied by Haillant and Lemaire [12] in polypropylene stabilized with hindered amine stabilizers (HALS) in a concentration interval of 0.3–0.4% exposed to natural and artificial sources of weathering. Rivaton et al. [13] determined that a hindered phenol (Irganox 1035) and an amine (Vulkanox 4010) used as stabilizers in EPDM are rapidly consumed at γ irradiation conditions and that only the amine at concentration of 1% is observed to display a limited stabilization at 25 kGy.

Some of those reported works agree that a more effective stabilization against γ radiation for the studied polymers is based in a combination of different stabilizers. Thus, in this work the use of a stabilizer system consisting of a binary blend of a hindered phenol and a hindered amine such as butylated hydroxy toluene and poly[[6-[1,1,3,3-tetramethybutyl)amino]-1,3,5-triazine-2,4-diyl]-[2,2,6,6-tetramethyl-4-piperidinyl)imino]-1,6-hexanediyl[(2,2,6,6-tetramethyl-4-piperidinyl)imino]], (BHT, Chimassorb 994, respectively) in different ratios to protect the PP against γ irradiation at the sterilization dose was studied. Since the PP employed in this work is intended to be used as a biomedical material, the stabilizers added must be approved by the health authorities in European countries and the USA, such as the FDA (US Food and Drug Administration).

2. Experimental

A commercial PP of a MFI of 11 g/10 min supplied by Venezuelan Propilven was used. BHT (a hindered phenol) and Chimassorb 994 (Chim, a hindered amine or HALS) were the stabilizers used. BHT was added at 0.1 wt% and Chimassorb 994 at 0.2, 0.5 and 0.8 wt%. The melt-blending process was performed in an internal mixer (Rheomix at 180 °C, 60 rpm and at a total blending time of 6 min).

Films and tensile specimens were compression molded in a Carver press (model C). Then, they were irradiated at 25 and 50 kGy with γ-rays from a ^{60}Co source at room temperature in air and nitrogen atmosphere, at an average dose rate of 1.05 kGy/h. The ^{60}Co source was a MDS Nordiun (IR-216) with a Harwell-Red Perspex dosimeter (range 5–50 kGy, type 4034) located in the Venezuelan Institute for Scientific Research (IVIC).

The films and tensile specimens were molded at 190 °C, 6000–15,000 psi, during 4.5 min. The thicknesses of the specimens were 0.08 and 1 mm, respectively. Irradiated and non-irradiated films were used to obtain FTIR spectra from where the carbonyl index values (I_c) were determined. Irradiated and non-irradiated specimens were also tested in an Instron 4204 testing machine at a cross-speed of 50 mm/min. The parameters analyzed were the Young's modulus (E), elongation at break (ε_r) and tensile strength (σ_r). Differential scanning calorimetry (Mettler Toledo Star System, DSC 821) was used to study the melting and crystallization behavior of samples weighing 9 mg. The DSC equipment was calibrated using indium with a melting temperature of 156.6 °C, which resulted within ±1 °C in accuracy. Samples were weighed with a precision within ±0.02 mg. Nitrogen was used as the dragging gas (50 mL/min). To erase the previous thermal history, the samples were heated up to 200 °C and kept at that value for 5 min. Then, the first cooling and the second heating thermograms were recorded at a rate of 10 °C/min. Thermograms were recorded from samples cut out from the already mentioned tensile specimens. The melting and crystallization temperatures (T_m and T_c, respectively) and the crystallinity degree (X) were determined from the thermograms.

Melt flow index (MFI) measurements were taken from the irradiated and non-irradiated samples. A Ray Ran Advanced Melt Flow Systems with a weight of 2.16 kgf was used at 230 °C.

The molecular weights and molecular weight distributions of the samples before and after irradiation were determined through gel permeation chromatography (GPC) using a Waters Alliance 2000 equipment with a differential refractive index detector. Three columns of Waters Styragel HT6E, HT5 and HT3 of cross-linked styrene–divinylbenzene copolymer particles in a range of 10^3–10^7 g/mol were employed. The calibration curve was obtained from polystyrene standards of narrow molecular weight distributions. M_w, M_n, and the polydispersity values were recorded.

All the samples were analyzed immediately after irradiation to minimize the possible post-irradiation oxidation.

3. Results and discussion

Fig. 1 displays an increase in the I_c values of irradiated PP with the absorbed dose in the presence of nitrogen or