Effects of a Radiation Crosslinking on a Drawn Microporous HDPE Film with a Nucleating Agent

Jong-Seok Park, Sung-Jin Gwon, Youn-Mook Lim, and Young-Chang Nho*
Advanced Radiation Technology Institute, Korea Atomic Energy Research Institute, Jeollabuk-do 580-185, Korea

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Abstract: The effects of crystallinity and radiation crosslinking on the physical properties of a microporous high density polyethylene (HDPE) film with Millad3988 as a nucleating agent were investigated. The pores of the HDPE film were affected by the crystallinity. The crystallinity of the HDPE films increased with increasing Millad3988 amount up to 0.1 wt% but decreased with further addition. The mechanical characteristics of the HDPE containing Millad3988 films improved with increasing irradiation dose up to 50 kGy, but decreased at 75 kGy due to severe degradation. The thermal shrinkage behavior of the HDPE films decreased with increasing radiation dose up to 50 kGy. The porosity of the stretched HDPE/Millad3988 films after γ-ray radiation increased with increasing γ-ray radiation dose up to 50 kGy. The pores of the irradiated films were formed more easily by a stretching due to the formation of a crosslinked structure.

Keywords: microporous polyethylene, thermal-mechanical properties, porosity.

Introduction

A microporous polymer film is required to permeate high ions and be thermally stable and mechanically strong during an assembly operation.1,2 Also, the crystalline structure of the polymer is important to facilitate the formation of micropores in the stretching step because the stacked lamellae are able to open during the stretching process.3 Polyethylene (PE) is one of the most important thermoplastics due to its abundant supply, low cost, good mechanical properties and resistance to chemicals and harsh environments. Generally, the mechanical properties of PE such as its tensile strength, and storage modulus increase with a density increase.4,5 High density polyethylene (HDPE) has a very high strength due to its highly crystalline structure.6 Nucleating agents increase the number of nucleation sites, resulting in an increase in the overall crystallization rate and a decrease in the spherulite size.7 Both the number and the size of the nucleation sites may affect the crystallization process. Molecular interactions between the polymer and the surface of a nucleating agent must match so as to increase the crystallization rate.8,10 Also, the mechanical properties and thermal stability of PE can be improved by a crosslinking.4,12 The crosslinking of PE has been achieved by several methods such as an irradiation, peroxides and a silane crosslinking.13,15 In this study, we have investigated the role of a nucleating agent and a γ-ray irradiation on the crystallinity and thermal-mechanical properties of a stretched HDPE film. The mechanical properties of the stretched HDPE film were investigated using a dynamic mechanical thermal analysis and a tensile strength. Also, the effect of a γ-ray irradiation on the thermal shrinkable characteristic of the stretched HDPE film was examined. The porosity of the stretched HDPE film as a function of the stretching method was measured with a mercury porosimeter.

Experimental

Materials. A commercial grade of high density polyethylene (HDPE 5200BH) was used throughout this study and was supplied by Honam Petrochemical Corporation (Daejon, Korea). HDPE has a density of 0.964 g/cm³ and a melting index of 0.35 g/10 min. Nucleating agent Millad3988 was purchased from Milliken Chemical. The structural formula of nucleating agents Millad3988 is shown in Figure 1. Dimethylformamide (DMF) was used as the solvent and supplied by SHOWA Chemical Corporation (Tokyo, Japan).

Sample Preparation. The nucleating agent, Millad3988 was dissolved in DMF and then used to coat the surface of HDPE pellets, which were dried at 80 °C under a vacuum for 24 h. The HDPE pellets coated with Millad3988 were mixed in the extruder (Brabender D-47055). The temperatures of the three zones of the extruder were 190, 220 and 230 °C,
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respectively and the temperature of the die was 100 °C. The screw speed of the extruder was adjusted to 50 rpm. The polymer resins were melt-extruded and uni-axially drawn by roller to obtain the precursor films. Thermal ageing treatment of the HDPE/Millad3988 film was conducted to increase the crystallinity of HDPE in an oven at 125 °C in air for 40 min.

The HDPE/Millad3988 films were irradiated by γ-rays to a total dose of 25, 50 and 75 kGy at a dose rate of 5 kGy/h at room temperature. The HDPE/Millad3988 films were uni-axially stretched up to 600% in a heating chamber at 100 °C with a speed rate of 10.8 cm/sec for the formation of pores and then they were slowly cooled at room temperature. The size of the HDPE film was 6×7 cm. The mixing formulations are shown in Table I.

Measurements of the Samples. The crystallinity of the samples was measured by differential scanning calorimetry (DSC, DSCQ100 TA Instrument Company). Heating runs were conducted from 30 to 180 °C at a rate of 10 °C/min in nitrogen. The degree of crystallinity ($X_c$) can be calculated by the following equation.

$$X_c(\%) = \frac{\Delta H_m}{\Delta H_m^0} \times 100$$

Where $\Delta H_m^0=290$ J/g is the fusion enthalpy for a totally crystalline polymer and $\Delta H_m$ is the fusion enthalpy calculated from the area of the endothermic melting peak. X-ray diffractometry (XRD; D-MAX-IIIIB X-ray diffractometer, Rigaku) in the range $2\theta=5-35^\circ$, was used for a comparison of the crystalline peak of the samples. The dynamic mechanical properties were investigated with a DMA (DMA; DMA Q800, TA Instrument Company), which was varied from 30 to 150 °C at 1 Hz at a heating rate of 5 °C/min. The tensile strength was measured with an Instron443 at room temperature. The size of the specimens was 5×20 mm, the thickness was about 0.02 mm, and the head speed was 10 mm/min. Tensile strength was tested for each sample at least five times. Thermal shrinkage tests of the samples were conducted in an oven at 130 °C for 60 min in air. The percentage of shrinkage ($S_h$) can be calculated by the following equation.

$$S_h(\%) = \frac{A_o - A_a}{A_o} \times 100$$

Where $A_o$ is the original area of the samples before a heating and $A_a$ is the area of the samples after heating. The porosity of the samples was measured with a mercury porosimeter (Autopore IV 9500, Micromeritics). In the case of the porosity, at least three specimens were tested from each sample. The morphological changes of the samples were observed using a scanning electron microscope (SEM, JSM6390 JEOL Company). Specimen surfaces were coated with a thin layer of gold palladium alloy by sputtering to provide a conductive surface.

Results and Discussion

Figure 2 shows the crystallinity of the HDPE films with increasing amounts of Millad3988. The crystallinity of the HDPE films increased with the amounts of Millad3988 but decreased above the addition of 0.1 wt% of Millad3988 as shown in Figure 2. The temperature dependencies of the