Mechanical Properties of LDPE/Ethylene-1-butene Copolymer Films Crosslinked by Radiation

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Abstract: In this study, ethylene-1-butene copolymer (EBP) was blended with LDPE to improve the mechanical properties of packaging materials. After they were irradiated by an electron beam, the materials’ physical properties, such as tensile strength, elongation, modulus, peel strength, DSC, and DMA, were examined. The results showed that the addition of EBP to LDPE exerted significant effects on the mechanical properties, such as the tensile strength and peel strength. The addition of EBP led to a maximum increase in peel strength of ∼430 %. The addition of 10−25 wt% EBP in LDPE was sufficient to enhance the peel strength significantly.

Keywords: polyethylene, ethylene-1-butene copolymer, crosslinking, radiation

Introduction

Most packaging materials are based on polyolefins because they are low in price, versatile, and easy to process. Low-density polyethylene (LDPE) is especially valued for its flexibility and sealing properties [1]. In the pharmaceutical industry, ca. 50 % of solid pharmaceutical products (tablet, capsules, or powders) are now packaged in flexible materials [2]. When oxygen, aroma, and flavor protection are necessary, high-barrier materials, such as ethylene vinyl alcohol (EVOH), polyvinylidene chloride, and aluminum, are applied through a vacuum coating processes.

Ionizing radiation (gamma rays or electron beams) is used presently for sterilization of pharmaceutical and medicinal products and their respective packaging materials. The effects of ionization radiation on polymers have been investigated widely. Accelerated electrons or short-wavelength electromagnetic radiation, such as gamma rays, promote ionization and excitation to produce active species such as free radicals. The active species tend to react with neighboring atoms, resulting in crosslinking and scission.

Thermal sealing or welding is used in packaging technology to connect films. High-performance packaging materials should be obtained within the shortest possible time. However, the sealing properties of irradiated polyethylene can be reduced because of the crosslinking structure of the polymer.

In this study, ethylene-1-butene copolymer (EBP) was blended with LDPE to improve its mechanical properties, including its melt-sealing behavior. LDPE contains considerable amounts of both long- and short-chain branches. For ethylene copolymers, the distinction has to be made between heterogeneous and homogeneous copolymers. The ethylene-1-butene copolymer investigated in the present study is called a homogeneous copolymer [3] because of the way in which the comonomer is added during polymerization, which can be described by a single set of chain propagation probabilities. All of the chains have the same comonomer/monomer ratio, a relatively narrow molar mass distribution, a constant comonomer content, and the same comonomer distribution. This material is of increasing importance because of its recent commercialization, made possible by metallocene catalysis [4,5], and its potential for application, e.g. as an impact modifier or in packaging [6-8].

The objective of this research was to study the effect of electron beam irradiation on the thermal and mechanical properties of LDPE/ethylene-1-butene copolymers.

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Table 1. Characteristics of Various Resins

<table>
<thead>
<tr>
<th>Trade name</th>
<th>Density (g/cm³)</th>
<th>Melting temperature (°C)</th>
<th>Melt Index (g/10 min)</th>
<th>Company</th>
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<tbody>
<tr>
<td>LDPE 5301</td>
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<td>110</td>
<td>0.3</td>
<td>Hanwha</td>
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<tr>
<td>LDPE 5314</td>
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<td>1.3</td>
<td>Hanwha</td>
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<td>LDPE 5325</td>
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<td>111</td>
<td>4.0</td>
<td>Hanwha</td>
</tr>
<tr>
<td>EBP (Ethylene-1-butene copolymer)</td>
<td>0.880</td>
<td>60</td>
<td>0.8</td>
<td>Aldrich</td>
</tr>
</tbody>
</table>

Figure 1. Schematic diagrams of (a) heat sealing and (b) peel testing.

Experimental

Materials and Sample Preparation
LDPE and ethylene-1-butene copolymer were used as polymer matrices. Three different LDPEs were supplied by the Hanwha Chemical Corporation, Korea; their characteristics are listed in Table 1. Polyethylene-1-butene copolymer (10.7 mol% 1-butene) was supplied by the Aldrich Chemical Company; it had a density of 0.88 g/cm³ and a melt index (MI) of 0.8. LDPE and EBP were mixed in a Brabender Plastograph at 130 °C for 10 min. The composition thus produced was pressed to form a film (150×150×0.3 mm). The film was irradiated using an ELV-4 electron beam accelerator operated at a beam energy of 1 MeV and a current of 2.5 mA. Samples having dumbbell shape for tensile strength testing were cut from this film.

Gel Measurement
The gel contents of the irradiated LDPE and LDPE/PEB samples were determined by extracting the soluble components in boiling toluene for 24 h, and drying the residue at 60 °C for 24 h in a vacuum oven.

Measurements of Physical Properties
The tensile mechanical behavior of the samples was characterized using a UTM (Instron model 4443). The measurements were performed at room temperature; the cross-head speed was 100 mm/min. The reported data were obtained by averaging the results of five tests.

Differential scanning calorimetry (DSC) measurements were undertaken using a Perkin-Elmer DSC-7 instrument. The heating rate was 10 °C min⁻¹ under a 30 mL min⁻¹ N₂ flow. All of the samples were tested at temperatures from 40 to 200 °C.

The dynamic mechanical properties were investigated using a DMA 2980 dynamic-mechanical analyzer (TA Instrument Co). The samples were measured at temperatures from -50 to 100 °C at 1 Hz with a heating rate of 3 °C/min.

Peel Strength Measurement
To prepare the peeling test samples, the film (thickness: 0.3 mm) was first cut into a size of 60 × 15 mm. Two films were overlapped, and the area of 30 × 15 mm was heat-sealed at a pressure of 0.14 kg/cm² at 135 °C for 10 sec. Peel testing was performed using the Instron test machine at a crosshead speed of 50 mm/min, as shown in Figure 1. Five samples were tested for each formulation.

Results and Discussion

Crosslinking
The exposure of LDPE to high-energy radiation results in the following changes: crosslinking [9], main chain scission, evolution of hydrogen, and the formation of main chain unsaturation [10-12]. By determining the gel
content, we can obtain information regarding the molecular structure of the polymer. The gel fractions of LDPE (MI: 0.3, 1.3, 4.0) and EBP (MI: 0.8) irradiated at different doses are plotted in Figure 2. We observed that the gel content increased upon increasing the irradiation dose. The higher a polymer’s melt index, the lower its gel content. This feature can be explained by considering that crosslinking occurs readily at higher molecular weight. LDPE with an MI of 0.3 reached ca. 90% gel content at 100 kGy. Figure 3 shows the gel contents of LDPE, LDPE/EBP blends, and EBP. LDPE (MI = 4.0) had a lower gel content than EBP, while the gel content of LDPE/EBP blends depended on the composition of two polymers.

**Physical Properties**

Among the expected effects of irradiation on the mechanical properties [13], the ultimate tensile strength and ultimate elongation are of considerable technical interest. The ultimate tensile strength of the LDPE/EBP blend increased upon increasing the EBP content up to 50 wt%, and then it leveled off (Figure 4). The ultimate tensile strengths of the LDPE and LDPE/EBP blends increased slightly upon increasing the irradiation dose, regardless of the composition of the LDPE/EBP (Figure 5). The addition of EBP to LDPE led to an increase in the ultimate tensile strength of the film. Figure 6 shows the ultimate tensile strength when EBP was mixed with
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Figure 8. Elongations of various polymers plotted with respect to the irradiation dose.

Figure 9. Tensile modulus of various LDPE/EBP blends.

Figure 10. Peel strengths of various LDPE/EBP blends.

LDPE samples having the various values of MI. The tensile strength decreased upon increasing MI. The elongation at the break point of LDPE/EBP was much higher than that of LDPE. The addition of EBP to LDPE led to an increase in the elongation (Figure 7).

However, the elongations of LDPE and EBP decreased slightly upon increasing the irradiation dose because of the presence of their crosslinking networks, except for that of the LDPE (MI = 4.0) sample (Figure 8). The Young’s modulus decreased upon increasing the EBP content because of the flexible properties of EBP. However, there was no significant difference in the elongation at the break according to the MI content (Figure 9).

Figure 10 shows the effect of adding EBP on the peel strength of LDPE/EBP. The addition of EBP to LDPE resulted in an increase in the peel strength of the film. Although irradiation resulted in a decrease in the peel strength of LDPE, the EBP and LDPE/EBP blend films exhibited no significant changes after irradiation (Figure 11).

Figure 12 shows the DSC curves of LDPE, LDPE/EBP blends, and EBP. The EBP thermoanalytical curve shows a broad endothermic peak in the range 60 ~ 80 °C, while
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Figure 13. DSC thermograms of the LDPE/EBP (50/50 wt%) blend.

Figure 14. Storage moduli of various LDPE/EBP blends.

LDPE shows a main endothermic peak at ca. 111 °C. Only one endothermic peak was observed when LDPE was blended with EBP. This result shows that these LDPE/EBP blends display apparent homogeneity. Irradiation of a LDPE/EBP blend lowered its main endothermic peak because the cross-links reduced the degree of crystallinity (Figure 13).

Measurements of the optical clarity were performed using an EEL spherical haze meter. The haze percentages of LDPE (MI = 4.0) and EBP were 40 and 3, respectively; the haze values of LDPE decreased upon increasing the EBP content.

Figure 14 shows the effect of the addition of EBP on the storage modulus. The storage modulus is a parameter related to the elastic behavior of a material when it undergoes small cyclic deformations. The addition of EBP led to a decrease in the storage modulus within the temperature range from -50 to 100 °C.

Conclusions

After LDPE and LDPE/EBP had been irradiated by an electron beam, their physical properties were examined using tensile strength, elongation, modulus, peel strength, DSC, and DMA measurements. The results showed that the addition of EBP exerted significant effects on the mechanical properties of LDPE, such as the tensile strength and peel strength. The addition of EBP led to a maximum increase in peel strength of ∼430 %. The addition of 10 ∼ 25 wt% EBP in LDPE was sufficient to enhance the peel strength. However, a higher addition of EBP did not produce any additional increase in peel strength. These results show that blending of LDPE and EBP is a convenient method for improving mechanical properties such as the tensile strength and peel strength. The blending of LDPE and EBP can provide a good seal quality and high overall package performance for materials used in the medical and food industries.

References