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Physical Properties of LDPE/Ethylene-1-Butene Copolymer Film Irradiated by Electron Beam

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Abstract

In this study, ethylene-1-butene copolymer (EBP) was blended with LDPE to improve the mechanical properties as the packaging materials. After they were irradiated by electron beam, their physical properties such as tensile strength, elongation, modulus, peel strength, DSC, 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 w% EBP in LDPE was sufficient to enhance the peel strength significantly.

Key words: polyethylene, ethylene-1-butene copolymer, crosslinking, radiation

1. Introduction

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

Ionizing radiation (gamma rays or electron beams) is being used today for sterilization of pharmaceutical and medicinal products as well as respective packaging materials. Ionization radiation effects on polymers have been widely investigated. Accelerated electrons or short wavelength electromagnetic radiation such as gamma rays promotes ionization and excitation to produce active species such as free radicals. The active species tend to react with neighboring atoms, producing crosslinking and scission. Thermal sealing or welding is used in packaging technology for connecting films. The high performance of packaging should be obtained within the shortest possible time. However, the sealing property of the irradiated polyethylene can be reduced because of its crosslinking network.

In this study, ethylene-1-butene copolymer (EBP) was blended with LDPE to improve the mechanical properties including melt-sealing. LDPE exhibits a considerable amount of both long- and short-chain branches. For ethylene copolymers the distinction has to be made between heterogeneous and homogeneous copolymers. The ethyle-1-butene copolymer, investigated in the present study, is called homogeneous copolymer[2], because the way in which the comonomer is added during polymerization can be described by a single set of chain propagation probabilities. All chains have the same comonomer/monomer ratio, and have a relative narrow molar mass distribution and a constant comonomer content for all chains, while all chains have the same comonomer distribution. This material is of increasing importance because of their recent commercialization made possible by metallocene catalysis[3,4] and their potential applications, e.g., use as impact modifier, in packaging[5], etc.

The objective of this research is to study the effects of electron beam irradiation on the thermal and mechanical properties of LDPE/ethylene-1-butene copolymer.

2. Experiment

2.1. Materials and sample preparation

LDPE and ethylene-1-butene copolymer were used as polymer matrices in this work. Hanwha Chemical Corporation, Korea, supplied three different LDPEs and their characteristics are listed in Table 1. Polyethylene-1-butene copolymer (10.7 mol% 1-butene) was supplied by Aldrich Chemical Company, Inc and has density of 0.88 g/cm^3 and melt index(MI) of 0.8. LDPE and EBP were mixed in a Brabender Plastograph at 130℃ for 10 min. The composition thus produced was pressed to form a sheet(150 $\times$150$\times$0.3 mm). Samples of dumbbell shape for tensile strength were cut from this sheet.

2.2. Gel measurement

The gel content of the irradiated LDPE and LDPE/PEB samples was determined by extracting the soluble components in boiling toluene for a total of 24 h, and drying the residue at 60 ℃ for 24 h in vacuum oven.

2.3. Measurements of physical properties

The tensile mechanical behavior of samples was characterized using an UTM (Instron model 4443). The measurements were carried out at room temperature and cross head speed was 100 mm/min. The reported data were obtained by averaging the results of 5 tests.

Differential Scanning Calorimetry (DSC) measurements were done by using a DSC-7 Perkin Elmer. The heating rate was 10 ℃ min^{-1} under 30ml min^{-1} N_2 flow. All samples were run form 40 to 200 ℃

The dynamic-mechanical properties were investigated on the dynamic-mechanical analyzer (DMA 2980, TA instrument Co). The samples were measured from –50 ℃ to 100 ℃ at 1 Hz with a heating rate of 3 ℃/min.

2.4. Peel strength measurement

To prepare the peeling test sample, the film (thickness, 0.3 mm) was first cut into the 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/cm^2 at 135 ℃ for 10 s. The peel testing was carried out using the Instron test machine at 180 ° and at the crosshead speed of 50 mm/min as shown in Figure 1. A minimum five samples were tested for each formulation.

3. Results and discussion

3.1. Crosslinking

The exposure of LDPE to high energy radiation results in the following changes: crosslinking[6], main chain scission, evolution of hydrogen and formation of main chain insaturation[7-9]. By determining the gel content, we can get the information on the molecular structure of 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. It was observed that the gel content increased with increasing irradiation dose. The higher a polymer's melt index, the lower the gel content was. It can be explained that the crosslinking occur easily in the high molecular weight as the melt index is in inverse proportion to molecular weight of polymer. LDPE with 0.3 of MI reached about 90 % at 100 kGy. Figure 3 shows the gel contents of LDPE, LDPE/EBP blends and EBP. LDPE (MI = 4.0) had lower gel content than EBP, while gel content of LDPE/EBP blends depended on the composition of two polymers.

3.2. Physical properties

Among the expected effects of irradiation on mechanical properties[10], ultimate tensile strength and ultimate elongation are of considerable technical interest. Ultimate tensile strength of LDPE/EBP blend increased with EBP content up to 50 wt%, and leveled off (Figure 4). Ultimate tensile strength of LDPE and LDPE/EBP blends increased slightly with irradiation dose regardless of the composition of LDPE/EBP (Figure 5). The addition of EBP to LDPE led to the increase in the ultimate tensile strength of film. Figure 6 shows the ultimate tensile strength when EBP were mixed with LDPEs having the various MI. The tensile strength decreased with increasing MI because the high MI means the low the molecular weight of the polymer.

The elongation at the break point of LDPE/EBP was much higher than that of LDPE. The addition of EBP to LDPE led to the increase in the elongation (Figure 7). However, The elongation of LDPE and EBP decreased slightly with the irradiation dose due to their crosslinking network except LDPE of MI 4.0 (Figure 8). Young's modulus decreased with increasing EBP because of flexible properties of EBP. However, there was no significant difference in the elongation at the break according to the MI (Figure 9).

Figure 10 shows the addition effect of EBP on peel strength of LDPE/EBP blends at the irradiation dose of 50 kGy. The addition of EBP to the LDPE resulted in increase in the peel strength of film. Irradiation resulted in decrease in peel strength of LDPE; however, EBP or LDPE/EBP blends showed no significant change after irradiation (Figure 11).

Figure 12 shows the DSC curves of LDPE, LDPE/EBP blend and EBP, respectively. The EBP thermoanalytical curve shows a broad endothermic peak in the range of 60 - 80 ℃, while LDPE shows a main endothermic peak at about 111 ℃. Only one endothermic was observed when LDPE was blended with EBP. This result shows that these LDPE/EBP blends display apparent homogeneity. The irradiation of LDPE/EBP blend lowered its main endothermic peak, since cross-links reduced crystallinity (Figure 13).

Measurements of the optical clarity were made with an EEL spherical haze meter. Haze percent of LDPE (MI = 4.0) and EBP was 40 and 3, respectively, while the haze values of LDPE decreased with rising EBP contents.

Figure 14 shows the effect of EBP addition on the storage modulus. Storage modulus is the parameter related to the elastic behavior of material when undergoing small cyclic deformations. The addition of EBP led to the decrease in the storage modulus in the temperature range of –50 to 100 ℃.

4. Conclusion

After LDPE and LDPE/EBP were irradiated by electron beam, their physical properties were examined using tensile strength, elongation, modulus, peel strength, DSC, DMA. 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 w% EBP in LDPE was sufficient to enhance the peel strength. However, the more addition of EBP did not produce any additional increase in peel strength. These results show that the blend of LDPE and EBP is a convenient method for improving the mechanical properties such as tensile strength and the peel strength. The blending process of LDPE and EBP can give the seal quality and the overall package performance for materials used in medical and food industry.

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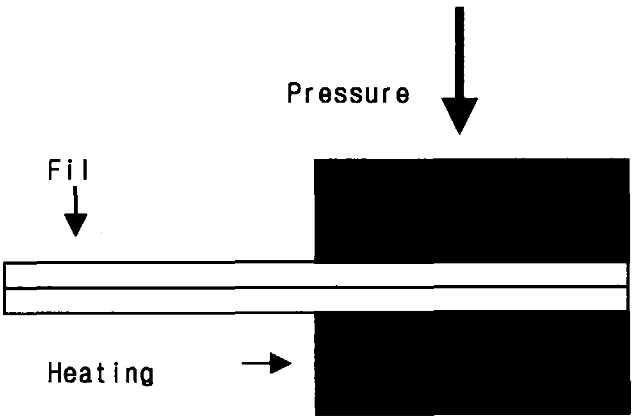
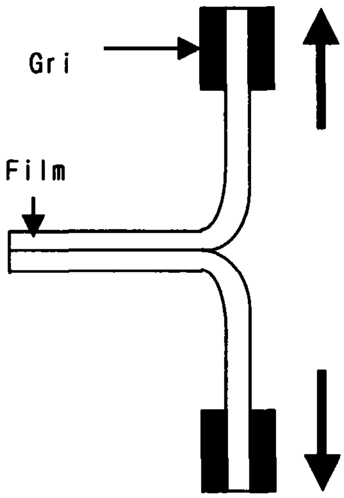
Table 1. The characteristic of various resins

Trade name	Density (g/cm^3)	Melting Temperature (℃)	Melt Index (g/10min)	Company
LDPE 5301	0.920	110	0.3	Hanwha Co.
LDPE 5314	0.923	111	1.3	Hanwha Co.
LDPE 5325	0.923	111	4.0	Hanwha Co.
EBP (Ethylene-1-butene copolymer)	0.880	60	0.8	Aldrich Co.



(a)



(b)

Figure 1. (a) Schematic diagram of heat sealing, (b) peel test.

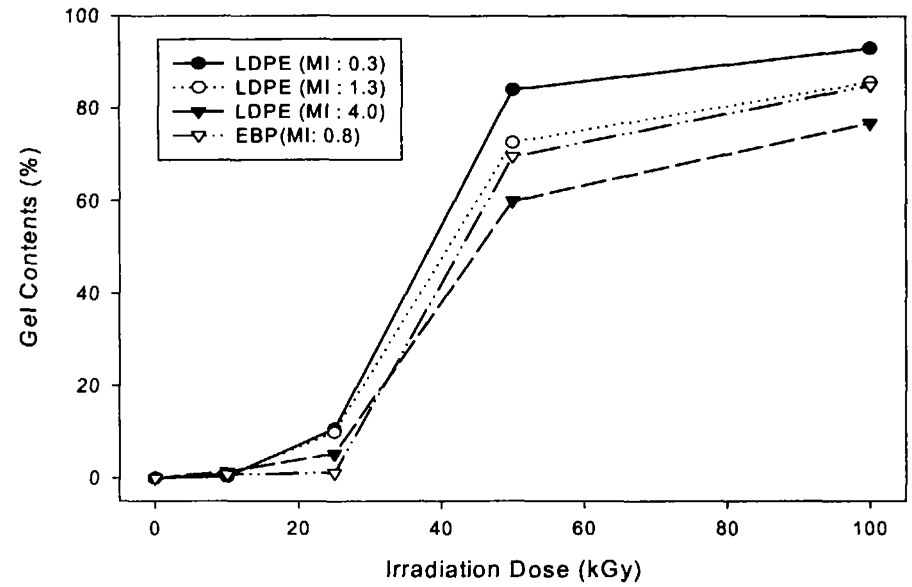


Figure 2 . Gel contents of various polymers with irradiation dose.

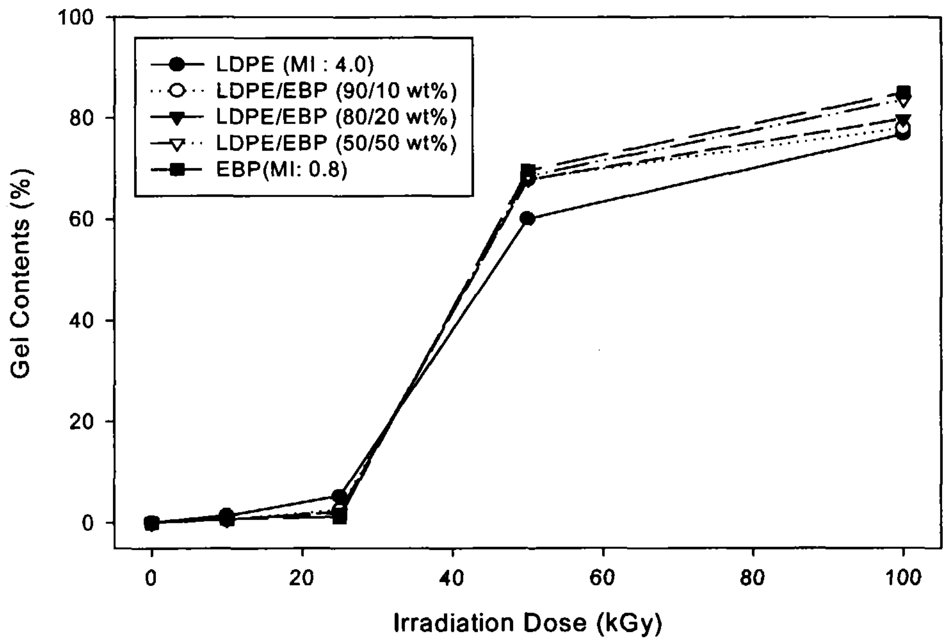


Figure 3 . Gel contents of various LDPE/EBP blends with irradiation dose.

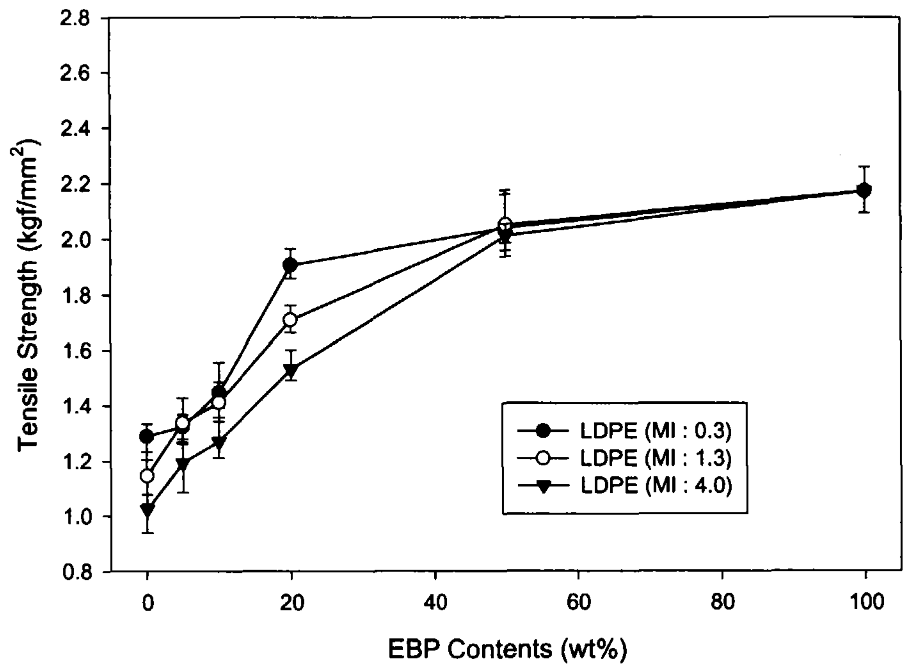


Figure 4. Tensile strength of various LDPE/EBP blends.

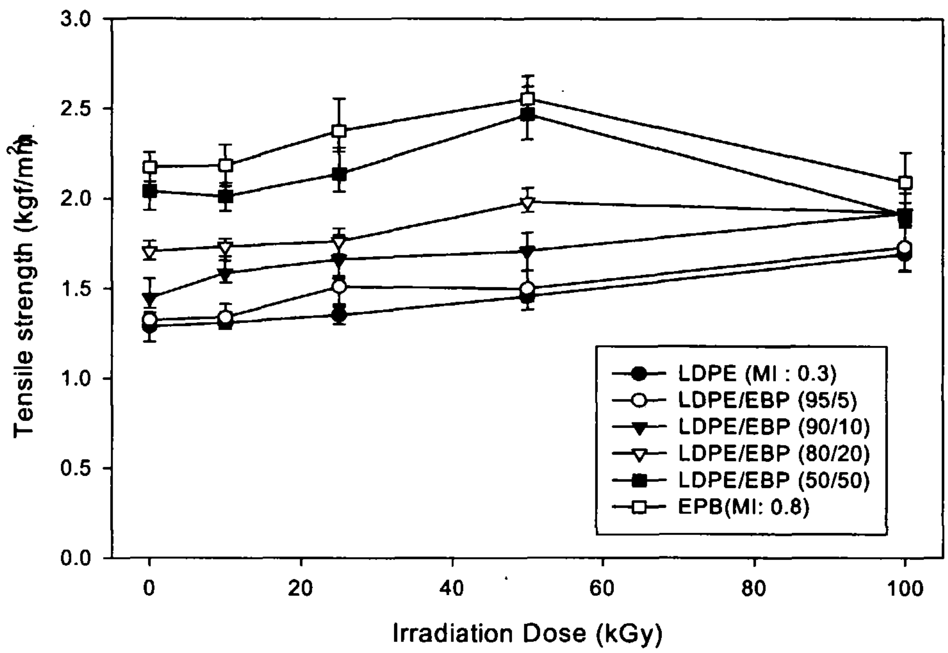


Figure 5. Tensile strength of LDPE/EBP blends with irradiation dose.

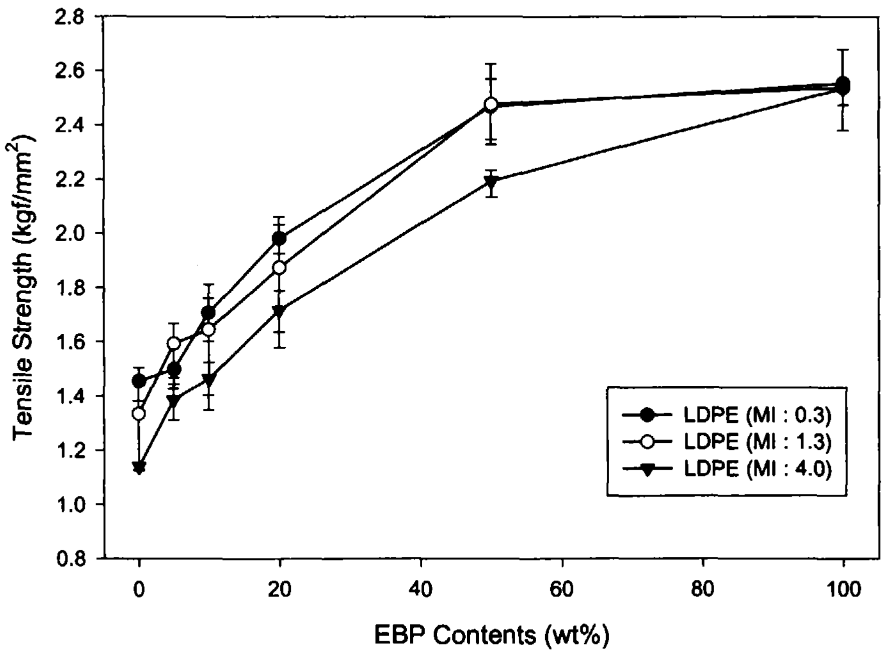


Figure 6. Tensile strength of 50 kGy-irradiated LDPE/EBP blends.

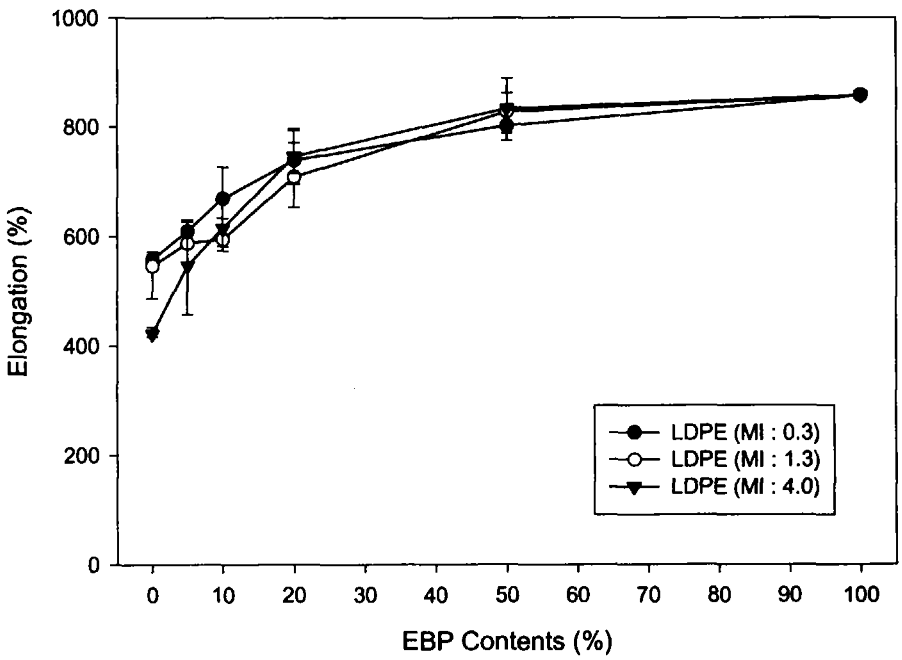


Figure 7. Elongation of various LDPE/EBP blends.

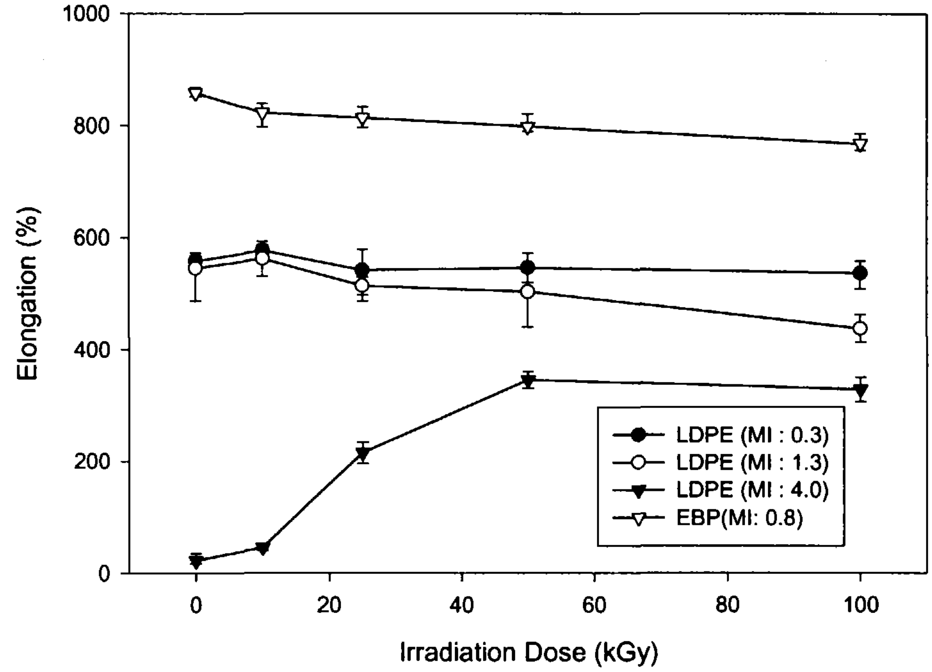


Figure 8. Elongation of various polymers with irradiation dose.

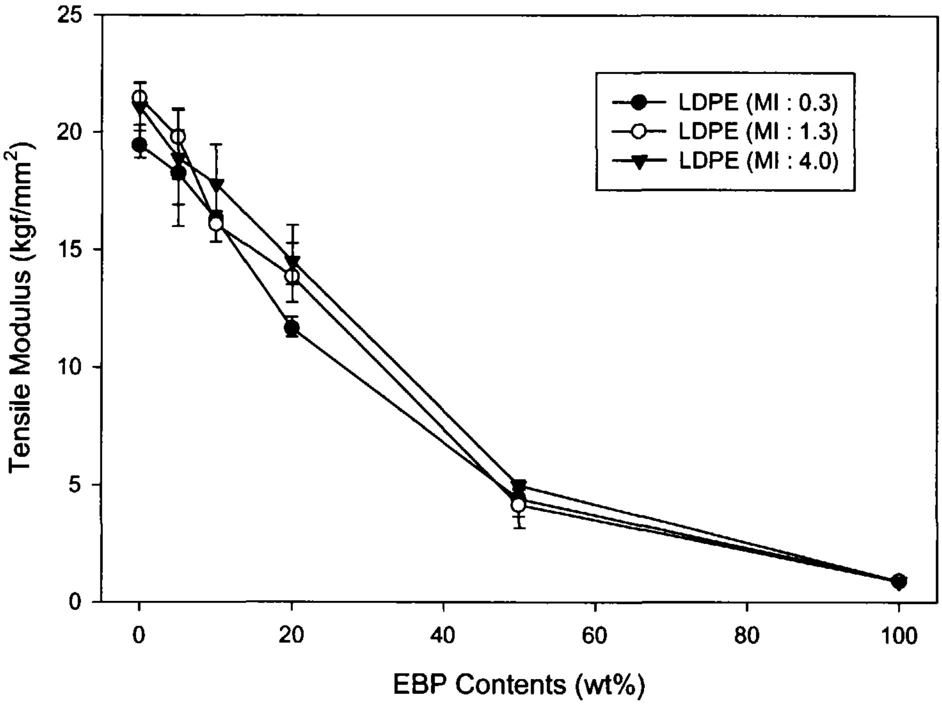


Figure 9. Tensile modulus of various LDPE/EBP blends.

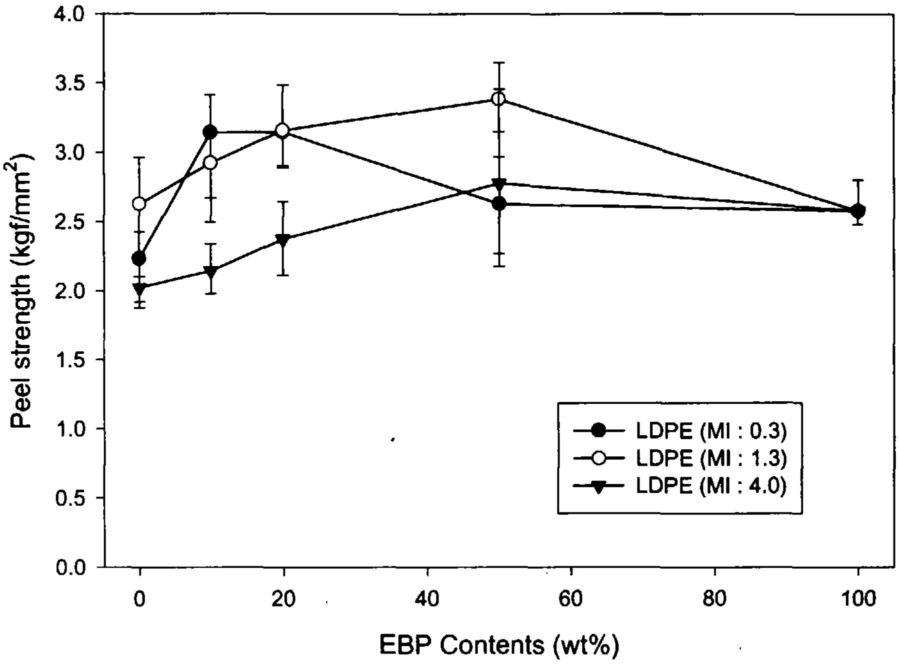


Figure 10. Peel strength of various LDPE/EBP blends.

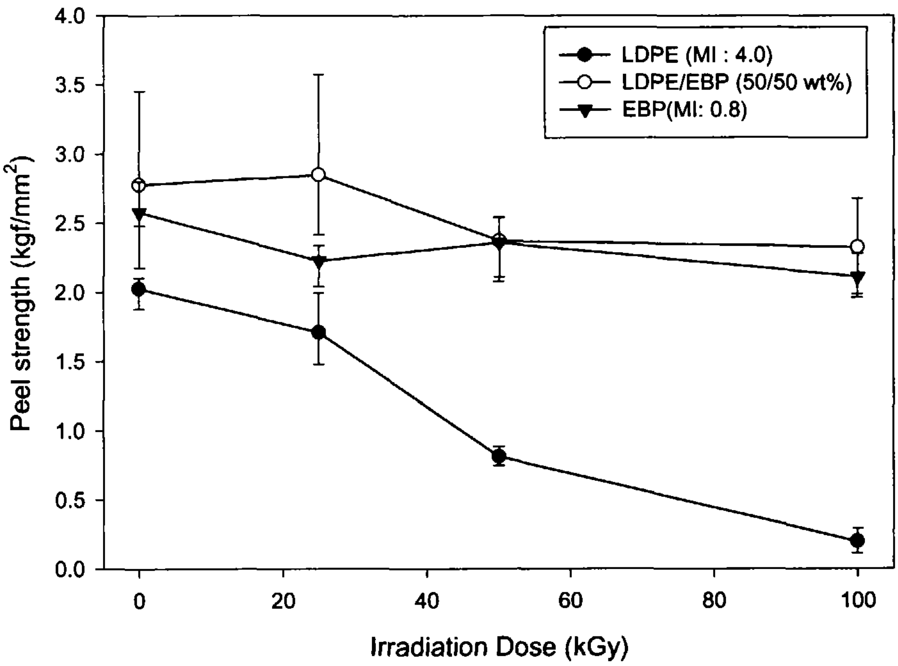


Figure 11. Peeling stress of LDPE/EBP blends with irradiation dose.

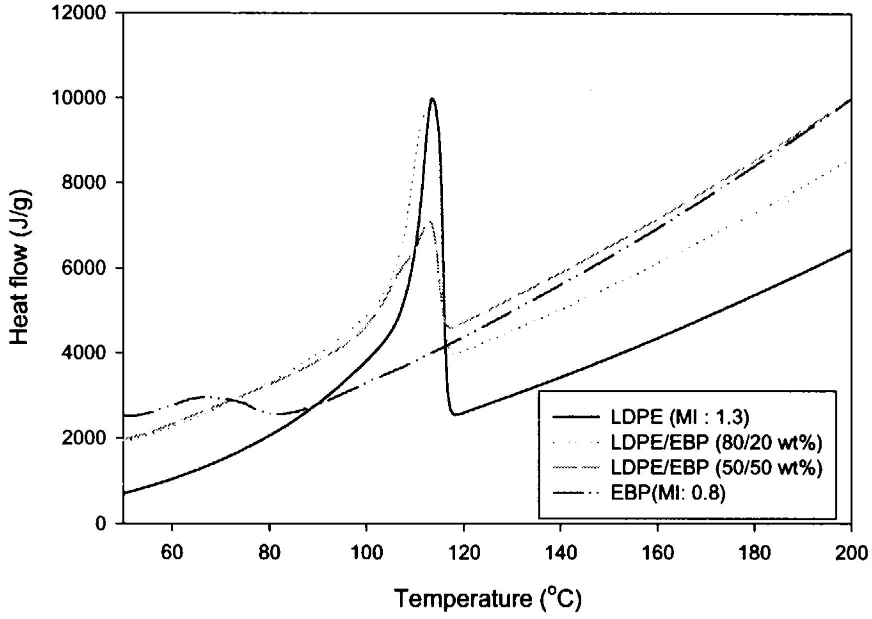


Figure 12. DSC thermograms of LDPE, LDPE/EBP blend and EBP.

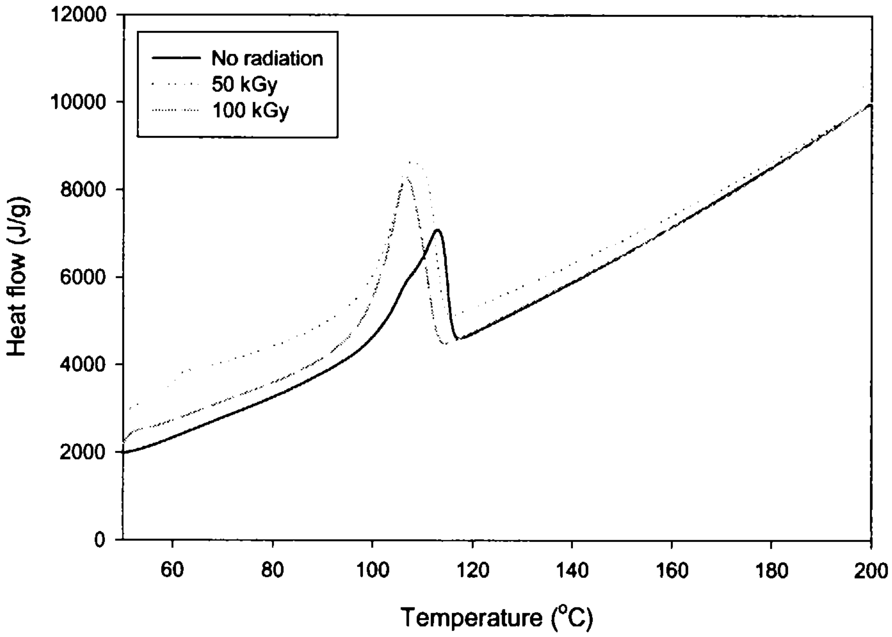


Figure 13. DSC thermograms of LDPE/EBP (50/50 wt%) blend.

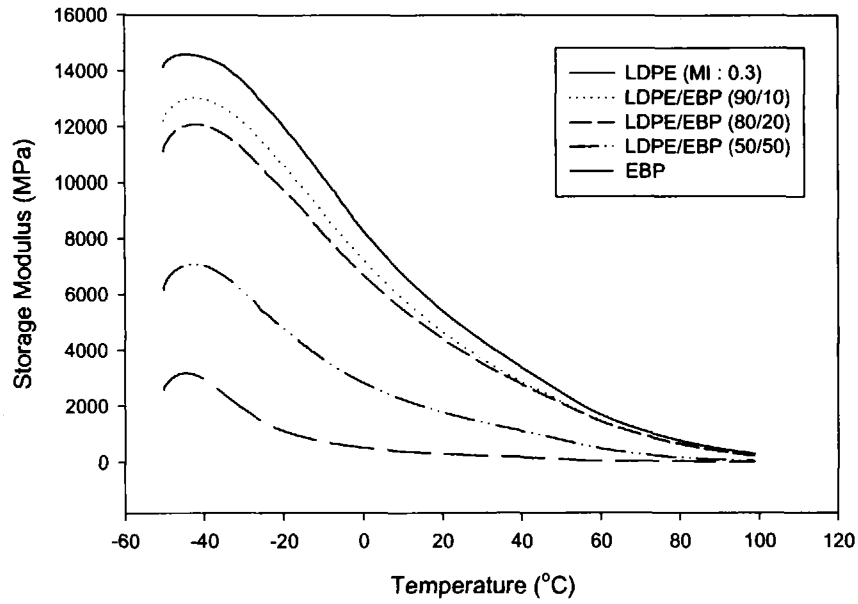


Figure 14. The storage modulus of various LDPE/EBP blends.