

Peel strength of LDPE /ethylene-1-butene copolymer film 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 as the packaging materials. After they were irradiated by an electron beam, their 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 10-25w% EBP in LDPE was sufficient to enhance the peel strength significantly.

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

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1. Introduction

Most packaging materials are based on polyolefins because they are low in price, 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 materials¹. When oxygen, aroma and flavor protection are necessary, high barrier materials such as ethylene vinyl alcohol(EVOH), polyvinylidene chloride and aluminium are applied through a vacuum coating processes.

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 promote ionization and excitation to produce active species such as free radicals. The active species tend to react with neighbouring atoms, producing crosslinking and scission.

Thermal sealing or welding is used in packaging technology to connect 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 the heterogeneous and homogeneous copolymers. The ethylene-1-butene copolymer, investigated in the present study, is called homogeneous copolymer², because the way in which the comonomer is added during polymerization can be described by a single set of chain propagation probabilities. All the chains have the same comonomer/monomer ratio, and have a relative narrow molar mass distribution and a constant comonomer content for all the chains, while all the chains have the same comonomer distribution. This material is of increasing importance because of its recent commercialization made possible by metallocene catalysis^{3,4}

and its potential applications, e.g. use as impact modifier, in packaging⁵, 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. Three different LDPEs were supplied by Hanwha Chemical Corporation, Korea and their characteristics are listed in Table 1. Polyethylene-1-butene copolymer (10.7 mole% 1-butene) was supplied by Aldrich Chemical Company, Inc and has a density of 0.88 g/cm³ and 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 (150×150×0.3mm). The film was irradiated using an ELV-4 electron beam accelerator operating at a beam energy of 1 MeV and current of 2.5mA. Samples of a dumbbell shape for tensile strength were cut from this film.

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 24h, and drying the residue at 60 °C for 24h in a vacuum oven.

2.3. Measurements of physical properties

The tensile mechanical behavior of the samples was characterized using an UTM (Instron model 4443). The measurements were carried out at room temperature and the cross head speed was 100mm/min. The reported data was 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 a $30 \text{ ml min}^{-1} \text{ N}_2$ flow. All the samples were tested from 40 to 200

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

2.4. Peel strength measurement

To prepare the peeling test sample, the film(thickness, 0,3mm) was first cut into a size of 60x15mm. Two films were overlapped, and the area of 30x15mm was heat-sealed at a pressure of 0.14 Kg/cm^2 at $135 \text{ }^\circ\text{C}$ for 10sec. The peel testing was carried out using the Instron test machine at 180 ° and at a crosshead speed of 50 mm/min as shown in Figure 1. 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: crosslinking⁶, main chain scission, evolution of hydrogen and the formation of a main chain insaturation⁷⁻⁹. 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 by increasing the irradiation dose. The higher a polymer's melt index, the lower the gel content was. It can be explained that crosslinking occurs easily at a high molecular weight. LDPE with 0.3 of MI reached about 90% at 100kGy. 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.

3.2. Physical properties

Among the expected effects of irradiation on the mechanical properties¹⁰, ultimate tensile strength and ultimate elongation are of considerable technical interest. Ultimate tensile strength of the LDPE/EBP blend increased with an EBP content up to 50wt%, and then leveled off (Figure 4). Ultimate tensile strength of the LDPE and LDPE/EBP blends increased slightly with 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 were mixed with LDPEs having the various MI. The tensile strength decreased with 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 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 the peel strength of LDPE/EBP. The addition of EBP to the LDPE resulted in an increase in the peel strength of the film. Irradiation resulted in a decrease in the 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 °C, while LDPE

shows a main endothermic peak at about 111 °C. 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 a LDPE/EBP blend lowered its main endothermic peak, since the cross-links reduced the 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 a rising EBP content.

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

4. Conclusion

After LDPE and LDPE/EBP were irradiated by an electron beam, their physical properties were examined using tensile strength, elongation, modulus, peel strength, DSC, and 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 10-25w% 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 the blend of LDPE and EBP is a convenient method for improving mechanical properties such as tensile strength and the peel strength. The blending process of LDPE and EBP can give a good seal quality and overall package performance for materials used in the medical and food industry.

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Table 1 . The characteristic of various resins

Trade name	Density (g/cm ³)	Melting temperature (°C)	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.

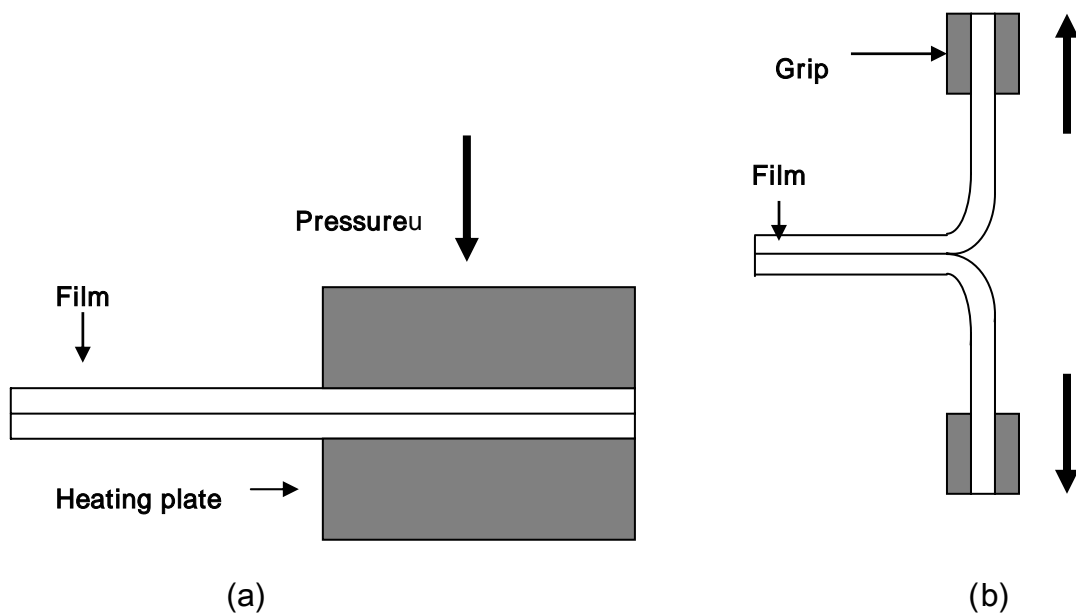


Figure 2. (a) Schematic diagram of heat sealing, (b) peel test.

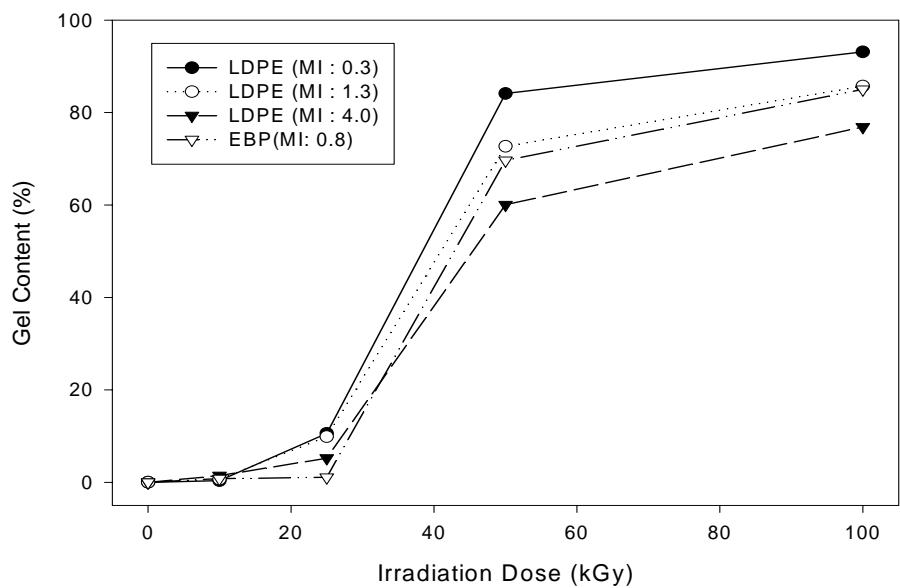


Figure 2. Gel content of various polymers with irradiation dose.

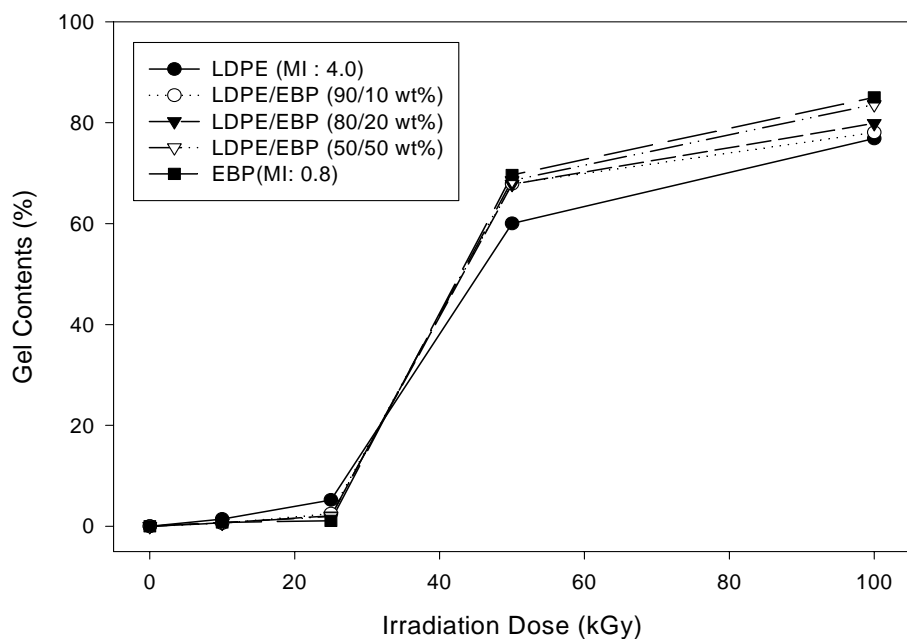


Figure 3. Gel content of various LDPE/EBP blends with irradiation dose.

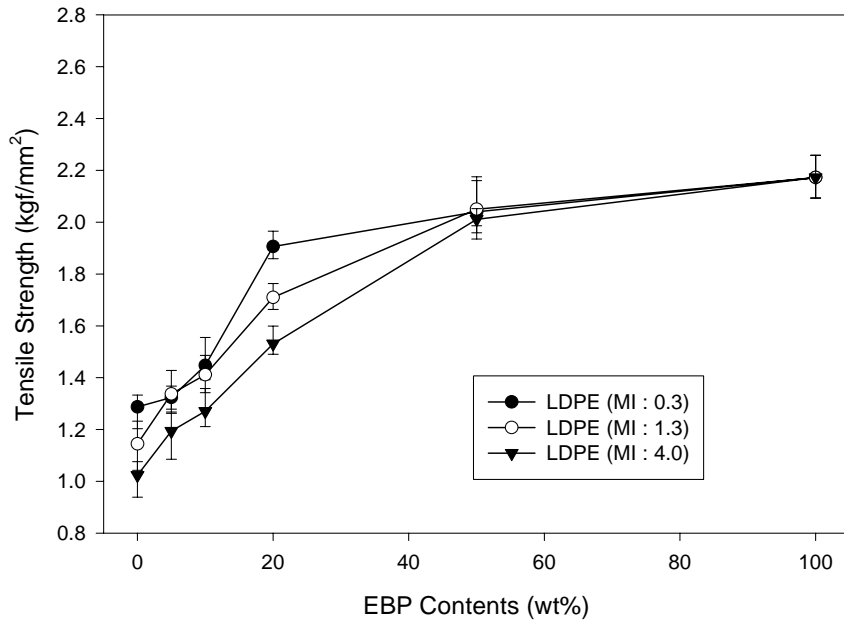


Figure 4. Tensile strength of various LDPE/EBP blends.

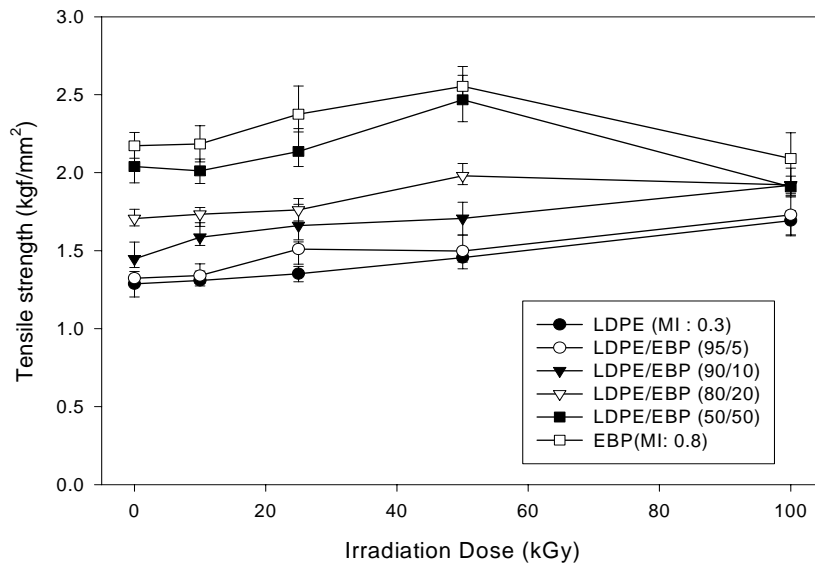


Figure 5. Tensile strength of LDPE/EBP blends with irradiation dose.

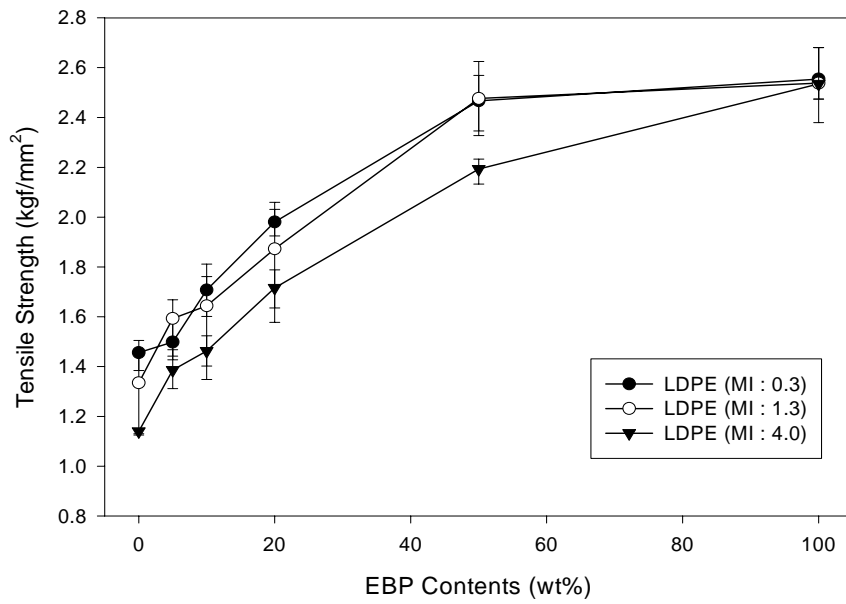


Figure 6. Tensile strength of 50 kGy-irradiated LDPE/EBP blends.

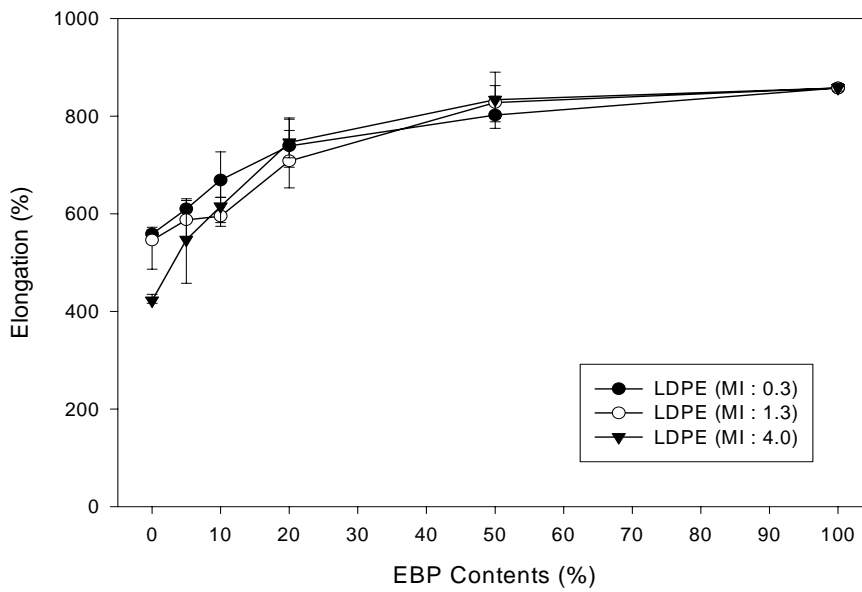


Figure 7. Elongation of various LDPE/EBP blends.

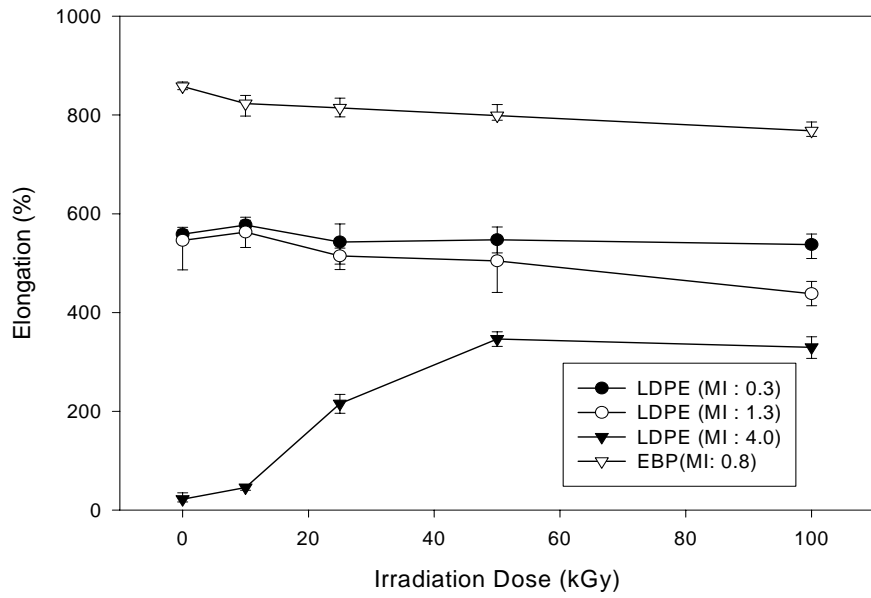


Figure 8. Elongation of various polymers with irradiation dose.

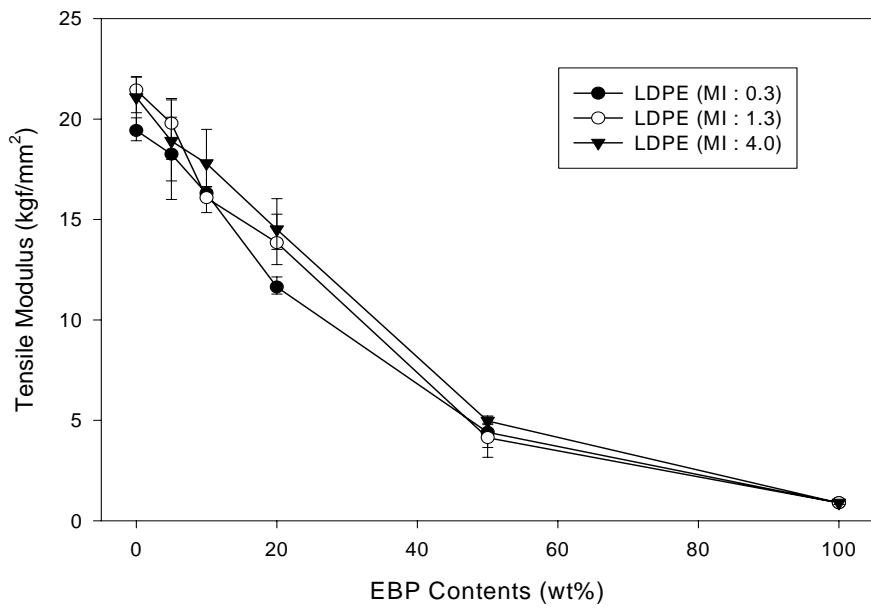


Figure 9. Tensile modulus of various LDPE/EBP blends.

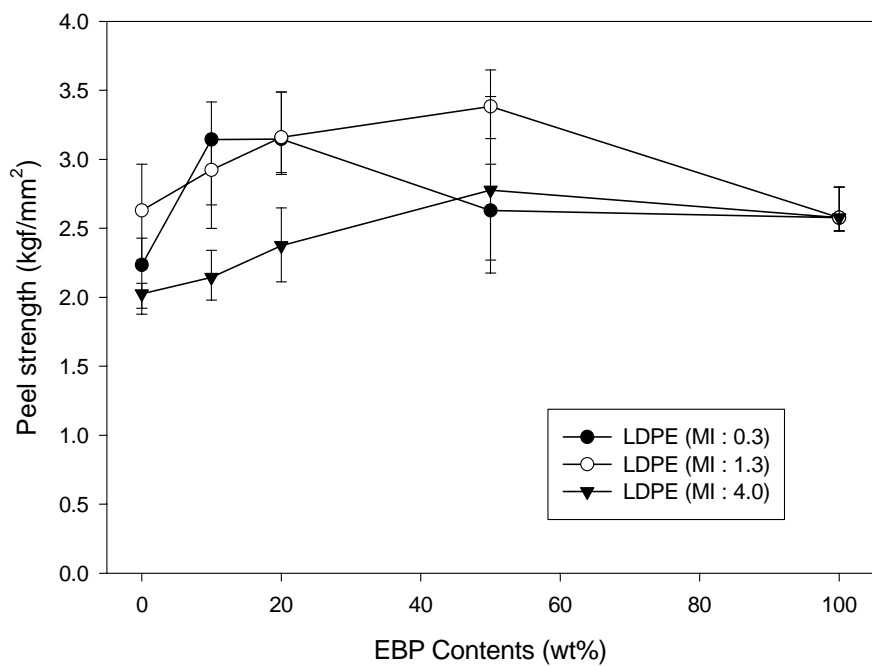


Figure 10. Peel strength of various LDPE/EBP blends.

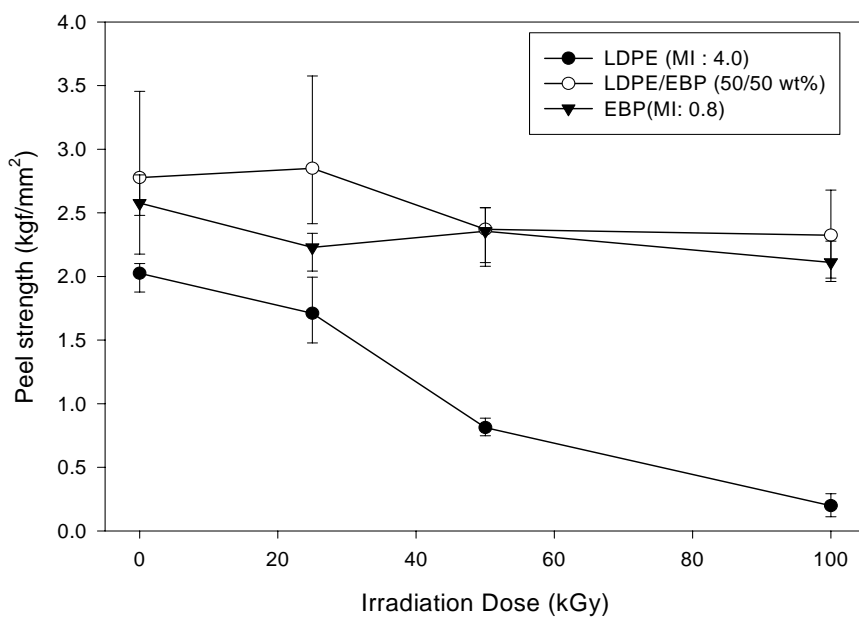


Figure 11. Peel strength of LDPE/EBP blends as a function of irradiation dose.

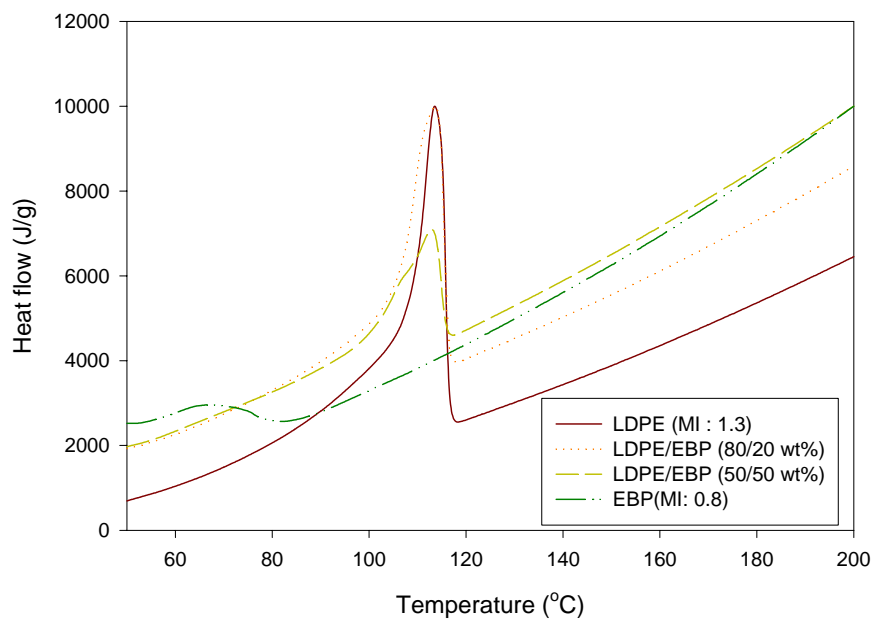


Figure 12. DSC thermograms of LDPE, LDPE/EBP blend and EBP.

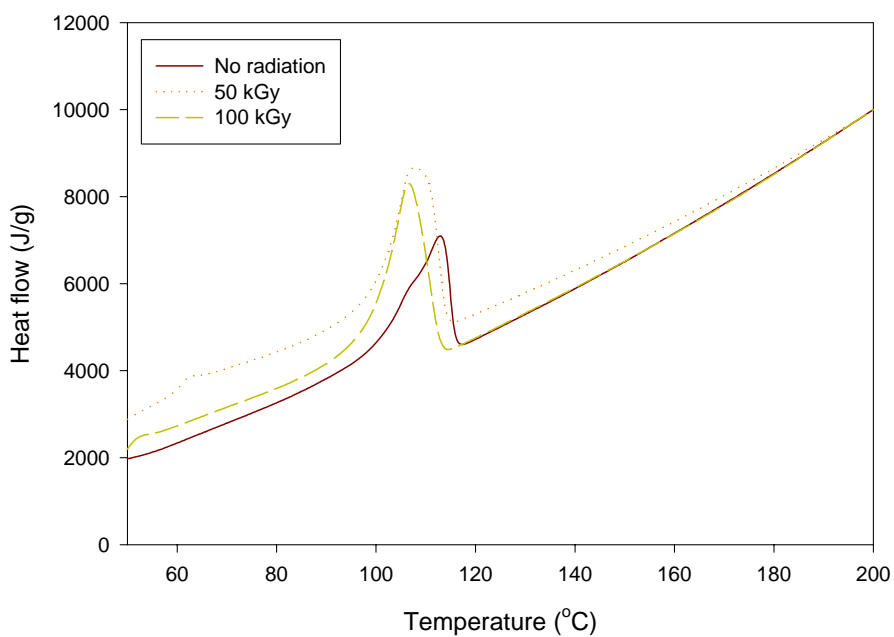


Figure 13. DSC thermograms of LDPE/EBP (50/50 wt%) blend.

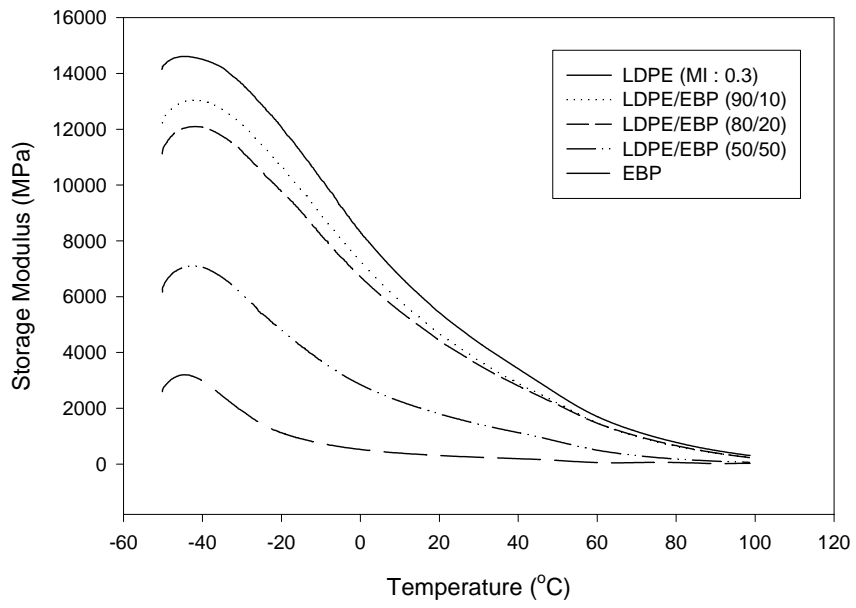


Figure 14. The storage modulus of various LDPE/EBP blends.