

Consideration on Electron Beam Cross-linked Polyethylene

Yasuyuki OKUMURA* and Yosuke TAKATA

Polyethylene (PE) is one of the polymers widely used in industry. PE is frequently used as a processing material because it is easily cross-linked by electron beam irradiation and its heat resistance is expected to be improved. This paper describes the mechanism of electron beam crosslinking of PE and its effect on PE. The property changes observed in cross-linked PE are also presented.

Keywords: electron beam irradiation, polyethylene, cross-linking, gel fraction

1. Introduction

Polyethylene (PE) is a general-purpose plastic that is widely used because of its low cost and well-balanced performance. However, due to its low melting point of approximately 120°C, PE cannot be used in high-temperature environments. Various attempts have been made to eliminate this disadvantage. As a result, cross-linking, which strengthens the properties of the material by chemically bonding polymers together to form a three-dimensional mesh structure, was found to be effective. There are several methods of cross-linking, including thermal cross-linking, silane cross-linking, and cross-linking by vulcanization. Among these, electron beam cross-linking (EB cross-linking), which uses irradiation of electron beams (EB),*¹ a form of radiation, is widely used since it requires no additives for the cross-linking and has a high processing speed.

Since the cross-linking of PE by irradiation with radiation was reported in the 1950s,⁽¹⁾ this technology has a history of more than half a century. Even in recent years, many reports have been published on the conditions and characteristics of cross-linking.⁽²⁾ In addition, innovations in material technology, such as the sophistication of PE itself, are also progressing.⁽³⁾

Thus, the technological development of PE and its EB cross-linking is progressing. This report describes the factors influencing the EB cross-linking of PE, the degree of influence, and the thermal properties of EB cross-linked PE, based on data from EB irradiation tests for PE carried out at NHV Corporation.

2. EB Irradiation Test

This chapter describes the mechanism of EB cross-linking, as well as the prerequisites and evaluation methods for EB irradiation tests.

2-1 Mechanism of EB cross-linking

When a polymer is irradiated with EB, electron energy is given to the polymer. This energy excites the polymer and breaks the bonds, producing radicals*² in the polymer chain. When the radicals produced in the polymer chains react with each other, bridging occurs between the polymer chains. This is EB cross-linking reaction. Figure 1 shows the mechanism of the EB cross-linking reaction.

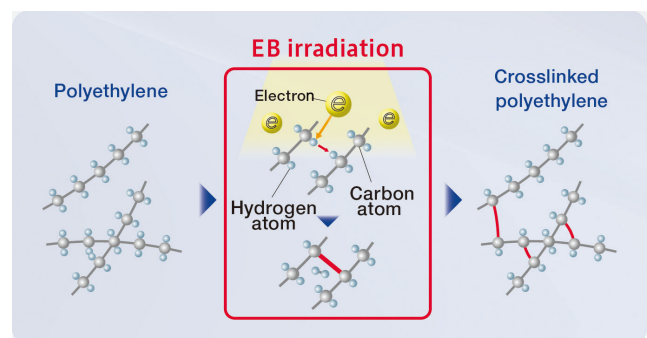


Fig. 1. Mechanism of EB Cross-linking Reaction

Cross-linked polymers have a three-dimensional network structure, and their movement is greatly restricted because they tend to maintain their structure even when the polymer chains flow as a result of melting or dissolving. This feature improves the heat resistance and chemical resistance of the polymers.

PE is a polymer that activates cross-linking reaction by EB irradiation. PE crosslinked by EB irradiation is widely used as electric wire covering material, food packaging film, and so on.

2-2 EB irradiation test method and evaluation method

In this test, high-density PE (HDPE) and low-density PE (LDPE) were formed into sheets of a given thickness by hot pressing to examine the effect of the crystallinity of PE on electron beam cross-linking. The crystallinity of the HDPE sheet was approximately 70%, and that of the LDPE sheet was approximately 40%.

In the EB irradiation test, NHV Corporation's scanning electron beam irradiator was used and the specified absorption dose*³ (hereinafter, "dose") was irradiated on the above sheets at an acceleration voltage of 750 kV. Figure 2 shows the penetrating ability*⁴ of EB when it is irradiated in common practice at an acceleration voltage of 750 kV. The maximum thickness of the sheets used for the test was 1 mm, and Fig. 2 shows that EB penetrates sufficiently into the sheets. In this test, the EB that passed through the sheets was caught by a resin plate to prevent reflection and thus to prevent irradiation of the test sheets

at doses higher than necessary. Unless otherwise described, the EB irradiation was performed at room temperature and in the atmosphere, and an irradiation dose exceeding 50 kGy was divided into 50 kGy doses to restrict the heating of the sheets due to the EB irradiation.

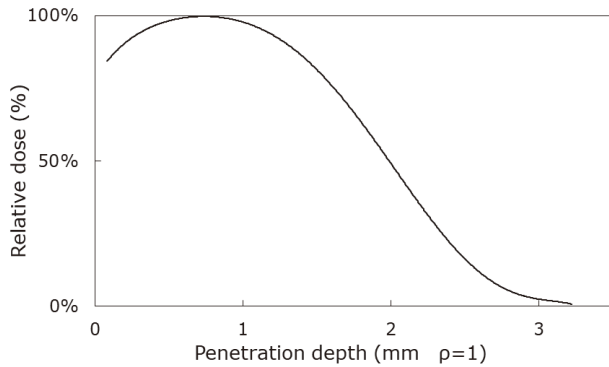


Fig. 2. Penetrating Ability of EB at Acceleration Voltage of 750 kV

As the cross-linking of PE progresses, the amount of the components (gel) insoluble in xylene and other solvents increases. Since the degree of cross-linking can be evaluated by measuring the percentage of this gel component, the gel fraction was measured to evaluate the degree of cross-linking. The method specified in JIS K 6796 was used for the measurement.

3. Analysis of Factors Affecting Electron Beam Cross-Linking

This chapter describes the factors affecting electron beam cross-linking. These factors were obtained by analyzing the results of various tests that were conducted in accordance with the EB irradiation test method and the evaluation method described in the preceding chapter.

3-1 Effect of crystallizability

In EB cross-linking, it is known that the less crystallizable the polymer is, the easier it is to cross-link. This is because the number of crosslink points generated by EB irradiation is larger in amorphous regions, where polymer

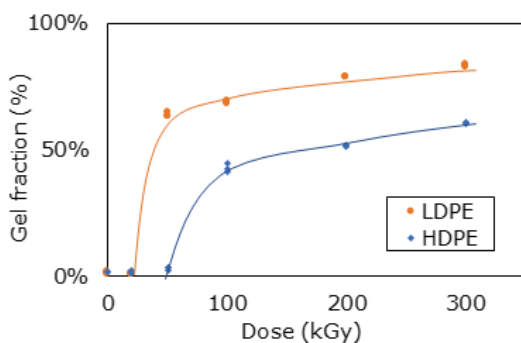


Fig. 3. Relationship between Dose and Gel Fraction in HDPE and LDPE Sheets

chains and radicals move easily, than in crystal regions where they do not.⁽⁴⁾ In order to determine the difference in cross-linking property between HDPE and LDPE, the gel fractions of 1 mm thick HDPE and LDPE sheets were measured by irradiating them with EB at doses of 20 to 300 kGy. The results are shown in Fig. 3. The LDPE sheet possessing a low crystallinity began to cross-link at a lower dose than the HDPE sheet possessing a high crystallinity, and as a whole, the LDPE sheet exhibited higher gel fractions. These results verified that PE with low crystallizability is easily cross-linked.

3-2 Effect of heating

Many chemical reactions are accelerated by heating during the reactions. In EB cross-linking, irradiation at high temperatures can also accelerate the cross-linking reaction. In this study, 1 mm thick HDPE and LDPE sheets were irradiated at room temperature and 80°C with the same doses of EB as in the test described in the preceding section, and the gel fractions were compared. The results for the HDPE and LDPE sheets are shown in Figs. 4 and 5, respectively.

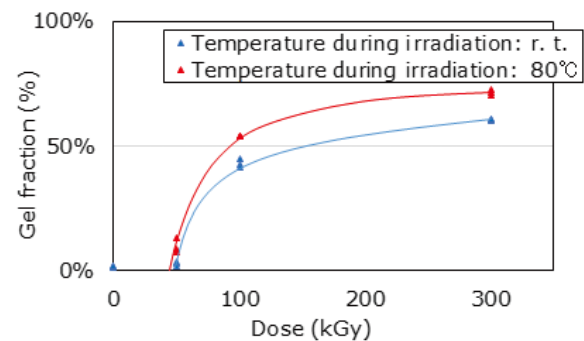


Fig. 4. Comparison of the Effect of Temperature during Irradiation (HDPE Sheet)

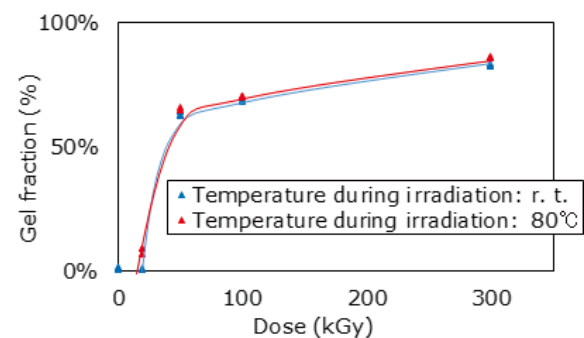


Fig. 5. Comparison of the Effect of Temperature during Irradiation (LDPE Sheet)

For the LDPE sheet, a slight cross-linking acceleration effect by high temperature was observed in an extremely low dose region, but the same effect was not observed in other dose regions (Fig. 5). On the other hand, the HDPE sheet exhibited an acceleration effect of approximately 10% at 80°C at every dose when compared to the effect at room temperature (Fig. 4). This is considered to be

attributable to the fact that the higher crystalline nature of the HDPE sheet greatly restricts the movement of polymer chains and radicals at room temperature, but the activation of their movement upon heating is greater than that of the LDPE sheet.

3-3 Inhibition of EB cross-linking by oxidation

EB irradiation is usually performed in the atmosphere, in which case the radicals generated by the EB irradiation react with oxygen in the atmosphere to form oxidized radicals. This causes an oxidized layer to form on the surface layer of the polymer, which inhibits the cross-linking reaction. In order to determine the degree of inhibition of EB cross-linking by the oxidized layer, 0.02, 0.1, and 1 mm thick LDPE sheets were irradiated with EB at the same dose as in section 3-1, and the gel fractions of these sheets were compared. The results are shown in Fig. 6. As the penetrating ability shown in Fig. 2 indicates, EB changes the relative dose after penetration when the thickness of the irradiated material changes.

In order to compare the gel fractions of LDPE sheets of different thicknesses in this test, the dose to be used was determined by calculating the average dose exposed to each sheet on the basis of penetrating ability.

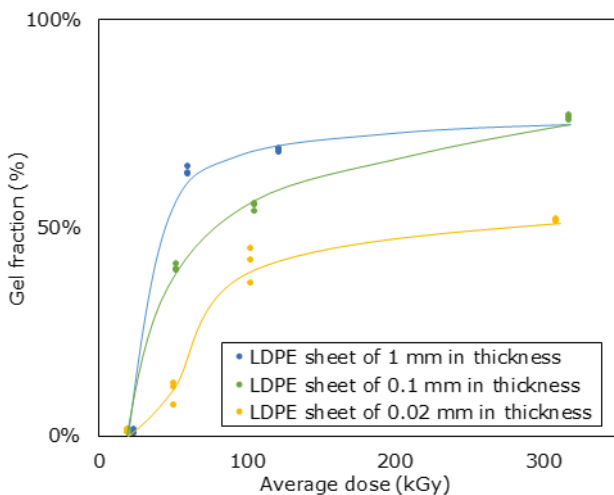


Fig. 6. Comparison of Gel Fraction between LDPE Sheets of Different

The thinner the LDPE sheet, the smaller the gel fraction at the same dose of irradiation, suggesting an increase in the effect of oxidation. In particular, the gel fraction of the 0.02 mm thick sheet was extremely small because the effect of oxidation was significantly strong. Assuming from the above result that the thickness of the oxidized layer would be constant regardless of the thickness of the sheet, an investigation was made to determine the thickness of the oxide layer formed.

As shown in Fig. 7, five 0.02 mm thick LDPE sheets were stacked on top of each other and sealed to prevent air from entering between the sheets, and the gel fraction of each sheet was measured after irradiation with 300 kGy of EB in the atmosphere.

The measurement results are shown in Fig. 8. The outer sheets ① and ⑤, which were directly exposed to the

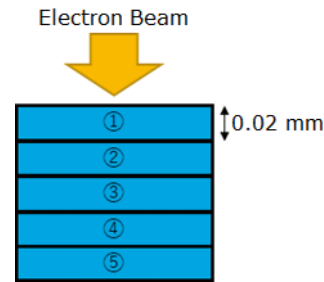


Fig. 7. EB Irradiation on Five LDPE Sheets Stacked on Top of Each Other

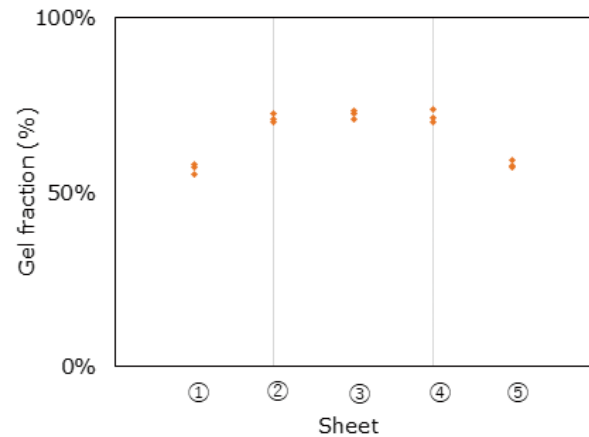


Fig. 8. Comparison of Gel Fractions between Different Sheets

atmosphere, exhibited low gel fractions, while the gel fractions of the other sheets, ② to ④, were high and almost the same. The above results suggest that the effect of oxidation was extremely small except in the case of the outer sheets. From the above, the thickness of the oxidized layer was estimated to be in the order of 1×10^{-3} mm.

3-4 EB irradiation in inert gas

As described in the preceding section, when sheets as thin as 1×10^{-3} mm are exposed to EB irradiation in the atmosphere, the cross-linking is inhibited by an oxidized layer. It was expected that EB irradiation in nitrogen, an inert gas, would be effective in avoiding the inhibition of cross-linking by preventing the formation of an oxide layer. Based on the above expectation, EB irradiation was performed in nitrogen under the same test conditions as in Fig. 6, in which LDPE sheets of different thicknesses were used. The test results are shown in Fig. 9.

Compared to the results for the 0.02 mm thick LDPE sheet irradiated in the atmosphere (see Fig. 6), the gel fraction increased significantly and the value at near 300 kGy was comparable to that of the 1 mm thick sheet. This result verified that the effect of the oxidized layer was suppressed as expected.

On the other hand, for the 1 mm and 0.1 mm thick sheets, the results did not largely differ from those obtained by irradiation in the atmosphere. At doses of nearly 300 kGy, it was estimated that the same level of cross-linking occurred regardless of the thickness of the sheets. However, the gel fraction of the 0.1 and 0.02 mm thick sheets was lower than that of the 1 mm thick sheet, especially at low

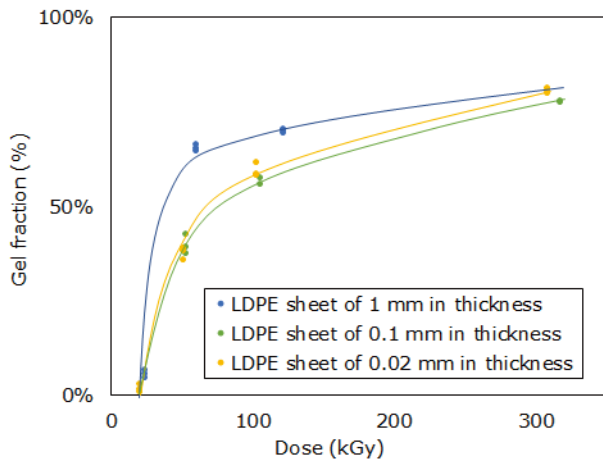


Fig. 9. Comparison of Gel Fractions between LDPE Sheets of Different Thicknesses (Irradiation in Nitrogen)

doses of 100 kGy or less. The above results suggest that other factors besides the oxidized layer interfere with cross-linking when the thickness of the material to be irradiated changes. In particular, the total number of radicals produced decreases as the sheet thickness decreases, and as a result, the total number of cross-links also decreases.

Since the effect of the thickness of the material to be irradiated on cross-linking has not been discussed in the literature on EB cross-linking, the above result is a new finding. In the future, it will be necessary to take into account the effect of the thickness of the material to be irradiated on cross-linking.

4. Thermal Property of Cross-Linked PE

This chapter describes the results of the test that was conducted to improve the heat resistance of PE, which is one of the purposes of its cross-linking. To evaluate the heat resistance, a hanging test was conducted at high temperatures. This test is schematically illustrated in Fig. 10.

First, a 1 mm thick 10 mm × 80 mm PE test piece was hung in a thermostatic chamber with a gripping distance of 50 mm. Then, a 50 g weight was attached to the bottom of

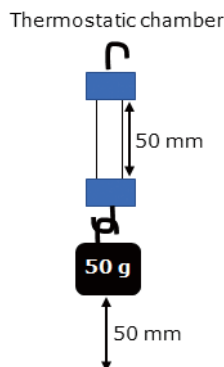


Fig. 10. Schematic Illustration of Hanging Test

the test piece, and the temperature in the thermostatic chamber was raised by 5°C every 5 minutes to measure the temperature when the gripping distance reached 100 mm (elongation rate: 100%) (hereinafter referred to as “deformation temperature”). The test results are shown in Table 1.

Table 1. Deformation Temperature Measurement Results in Hanging Test

Type of PE	Dose (kGy)	Gel fraction (%)	Deformation temperature (°C)
LDPE	0	0	100
	100	Approx. 70	118
	300	Approx. 80	Higher than 240
HDPE	0	0	128
	300	Approx. 60	217
	500	Approx. 70	Higher than 240

In the case of LDPE, when a test piece was irradiated with a dose of 100 kGy at which the gel fraction was approximately 70%, its deformation temperature was slightly different from that of an unirradiated test piece. However, when a test piece was irradiated with 300 kGy at which the gel fraction was approximately 80%, its deformation temperature increased significantly. On the other hand, when an HDPE test piece was irradiated with a dose of 300 kGy at which the gel fraction was approximately 60%, its deformation temperature increased significantly compared to that of an unirradiated test piece. In addition, increasing gel fractions with repetitive irradiation made it possible to improve the heat resistance.

The above results verified that heat resistance can be improved significantly by cross-linking, and the relationship between heat resistance and gel fraction varies greatly depending on the material.

5. Conclusion

As has been discussed in this paper, the effect of EB cross-linking differs depending on the molecular structure, crystallizability, and thickness of PE. In addition, PE for industrial use commonly contains antioxidants and other additives. Since antioxidants supplement radicals, the type and amount of the antioxidants greatly affect cross-linking. In other words, the same irradiation conditions do not always have the same cross-linking effect on every type of PE. It is therefore necessary to investigate the irradiation conditions best suited to each type of PE. The authors hope this paper will help determine optimum irradiation conditions.

Technical Terms

- *1 Electron beam: A type of radiation, occasionally referred to as “EB.” Different from γ -rays, the generation of an electron beam can be controlled by an irradiator and is used for industrial purposes.
- *2 Radical: A substance, also known as a “free radical,” produced by uniform cleavage of the chemical bonding of molecules. Since radicals are highly reactive, they are used for various purposes including polymerization reactions.
- *3 Absorption dose: The amount of energy absorbed per unit of mass by the object irradiated with radiation. The unit is the gray (Gy). One (1) Gy is equivalent to 1 J/kg.
- *4 Penetrating ability: The ability of radiation to impart energy in the direction of the thickness of the object to be irradiated. The penetrating ability of electron beams increases as the acceleration voltage increases, while it decreases as the specific gravity of the object to be irradiated increases.

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Contributors The lead author is indicated by an asterisk (*).

Y. OKUMURA*

- Ph.D.
- NHV corporation



Y. TAKATA

- NHV corporation



Source of reference

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