

Fracture Mechanics Investigation on the PP/EPDM/Ionomer Ternary Blends Using J -Integral by Locus Method

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SYNOPSIS

The fracture mechanics investigation of the polypropylene (PP)/ethylene-propylene-diene terpolymer (EPDM)/ionomer ternary blends was performed in terms of the J -integral by measuring fracture energy via the locus method. Blends were prepared in a laboratory internal mixer. The composition of PP and EPDM was fixed at a 50/50 ratio by weight. Two kinds of poly(ethylene-co-methacrylic acid) (EMA) ionomers were used. The J -integral value at crack initiation, J_c , of the PP/EPDM/EMA ionomer ternary blends were affected by the cation types (Na^+ or Zn^{2+}) and contents (5–20 wt %) of the added EMA ionomers. The ternary blend having 5 wt % of Na-neutralized ionomer showed a higher J_c value than that of any other ternary blends. The results were discussed with regard to the fracture topology by a scanning electron microscope (SEM). © 1994 John Wiley & Sons, Inc.

INTRODUCTION

The fracture toughness characterization of brittle or quasi-brittle polymers has usually followed the lead of metals characterization based on linear fracture mechanics. The utility of linear fracture mechanics, however, is inadequate for toughened polymers of multiphases, since the considerable amount of energy put into the material is dissipated, creating plastic deformation ahead of the crack tip.^{1–5}

When linear elastic fracture mechanics could not predict performance of ductile and toughened polymers, interest moved from fracture toughness characterization based on the stress intensity factor, K ,^{6–8} to the J -integral concept introduced by Rice or Begley and Landes.^{9–11} The J -integral is an energy input parameter that can be used as a criterion for crack initiation in the fracture of elastic-plastic materials. Little work, however, has been published to apply the J -integral analysis to ductile or toughened polymers.

There have been several efforts to determine the J -integral value at crack initiation, J_c , for ductile or impact-modified polymers, even though the re-

ported methodologies have been very controversial.^{12,13} Recently, a novel test technique was developed by Kim and Joe, in which a fracture test was carried out by using simple single edge-notched (SEN) tensile specimens.^{14,15} The technique was based on the locus of crack initiation points on load-displacement records. It was reported that the evaluation method of J_c was successfully applied to highly deformable materials including a thermoplastic elastomer like Santoprene¹⁴ without restricting the ratio of the initial crack length to the specimen width (a/w) or the specimen length, provided that the locus line could be located on the load-displacement record.

The object of this work was to analyze the fracture mechanics investigation on the polypropylene (PP)/ethylene-propylene-diene terpolymer (EPDM)/ionomer ternary blends using the J -integral by the locus method, along with the fracture topology. The locus method is believed to be suitable for our PP/EPDM/ionomer ternary blend systems, since the present work deals with material very similar to that used for Kim and Joe's work. In our previous work,¹⁶ we revealed that the addition of poly(ethylene-co-methacrylic acid) (EMA) ionomer, where the acid groups are partially neutralized by Na^+ or Zn^{2+} ions, significantly affected the rheological properties and morphology of a PP/EPDM binary blend. It may

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be thought that the present work will shed some light on the toughness of the ternary blends as well as of the PP/EPDM binary blend, even though the J_c by itself is not a widely accepted measure of toughness.

In the present investigation, two kinds of EMA ionomers containing different metal ions (Na^+ or Zn^{2+}) were used for comparison, and the effect of the metal component for neutralization in the ionomer and the ionomer contents in the PP/EPDM/ionomer ternary blends were discussed. The composition of PP and EPDM in the blends was fixed at a 50/50 ratio by weight. The ionomer contents were varied from 5 to 20 wt % based on the total amount of PP and EPDM.

EXPERIMENTAL

Materials

The characteristics of the polymers used in this study are summarized in Table I. The polypropylene (PP) was kindly obtained from Korea Petrochemical

Table I Materials and Their Characteristics

Material	Properties	Source
PP	$M_n = 2.83 \times 10^4$ $M_w = 2.02 \times 10^5$ MFI ^a = 6.0 $M_w/M_n = 7.14$	Korea Petrochemical Co. (PP4017)
EPDM	ν_{inh} (dL/g) ^b = 1.22 I.V. ^c : 15.2 PE/PP (mol %) ^d = 52.0/48.0 ENB type	Uniroyal (Roy. 521)
Ionomer A	Cation type: Na^+ Ethylene/methacrylic acid = 91/9 % Neutralization: 50% Specific gravity = 0.94 MFI ^a = 1.3	DuPont (Surlyn 8528)
Ionomer B	Cation type: Zn^{2+} Ethylene/methacrylic acid = 91/9 % Neutralization: 50% Specific gravity = 0.95 MFI ^a = 1.1	DuPont (Surlyn 9520)

^a Melt flow index.

^b 0.5 g/dL xylene solution at 70°C.

^c By ICl titration method.

^d By IR analysis.

Table II Blended Materials and Their Compositions

Notation	PP Contents (wt %)	EPDM Contents (wt %)	Ionomer Contents
PP50-EP50	50.0	50.0	No ionomers
PP50-EP50/IA5	47.5	47.5	5.0
PP50-EP50/IA10	45.0	45.0	10.0
PP50-EP50/IA15	42.5	42.5	15.0
PP50-EP50/IA20	40.0	40.0	20.0
PP50-EP50/IB5	47.5	47.5	5.0
PP50-EP50/IB10	45.0	45.0	10.0
PP50-EP50/IB15	42.5	42.5	15.0
PP50-EP50/IB20	40.0	40.0	20.0

Co. (PP4017 grade). The ethylene-propylene-diene terpolymer (EPDM) with ethylidene-2-norbornene (ENB) as a termonomer was supplied by Uniroyal (Royalene 521, weight-average molecular weight [M_w] = 1.80×10^5 ; ethylene content [C_2] = 52% in mol). Two kinds of EMA ionomers were supplied by Dupont. The polymers were all commercially available grades and used as received.

Blend Preparation

Binary PP/EPDM or ternary PP/EPDM/ionomer blends were prepared in a Brabender Roller Mixer (Type w50H) at 190°C and 60 rpm for 15 min. The composition of PP and EPDM was fixed at a 50/50 ratio by weight. For the ternary blends, the ionomer contents were varied from 5 to 20 wt % based on the total amount of PP and EPDM. The sample notations of blends are summarized in Table II.

Fracture Energy Determination

Many different specimen configurations are acceptable for the measurement of fracture toughness. We used single-edge-notched (SEN) tensile specimens with a constant length from compression-molded sheets. The thickness and width of the specimens were 1.0 and 20.0 mm, respectively. The length between the grips were 60.0 mm. Razor blades were used to create sharp initial cracks, which varied from 0.20 to 0.80 in terms of the ratio of the initial crack length (a) to the specimen width (w). Tensile tests were performed at a crosshead speed of 50 mm/min with an ambient temperature of 26°C and relative humidity of 35%. Load-displacement graphs were

recorded and initiation points were marked on each loading line during the test. The fracture toughness was interpreted in terms of the critical J -integral value, J_c , by the locus method developed by Kim and Joe.¹⁴

It was reported that the locus method using a tensile specimen was successfully applied to the Santoprene-like highly deformable materials when compared to the conventional method using a three-point bending specimen.^{17,18} Crack initiation points were easily observable since the crack opened widely before the crack propagated. The areas under the loading curves were calculated numerically from the data points taken from the load-displacement records. The essential energy needed for crack propagation per unit thickness, ΔU_c , vs. the initial crack length, a , was plotted. The linear least-squares fitted slope was taken as J_c .

The method determines J_c based on

$$J_c = \frac{-1}{B} \frac{\Delta U_c}{\Delta a} \quad (1)$$

where B is the thickness of the specimen; a , the initial crack length; and U_c , the enclosed area between loading line and the locus line. The total energy consumed during fracture testing includes some amount of remote energy loss as well as the energy supplied for the crack propagation. Remote plastic energy loss occurs during the loading process if plastic deformation, remote from the crack tip, exists. Several single-specimen test methods that use the relation between the essential energy U_c and the total energy absorbed, U_T , have been developed.¹⁵ The value of $\phi (= U_c/U_T)$ was known to be sensitive to the remote energy absorption. With the J_c value known, ϕ for each crack size can be determined from eq. (2):

$$\phi = \frac{J_c}{[U_T/B(w-a)]} \quad (2)$$

If crack initiation has occurred at a constant displacement and the locus of the crack initiation points continued to be a vertical line down to the displacement axis, then all the ϕ values should have been 1. It was reported that the remote energy absorption can affect the accuracy of the experimentally determined J_c values and that eliminating the remote energy term in the early stage of the procedure can help to yield consistent J_c values.¹⁴ Details of the locus method are described elsewhere.^{14,15}

Reproducibility of the fracture energy data was measured by testing different sample lengths. How-

ever, all samples were tested with the initial sample length of 100 mm unless otherwise specified. Examinations of the fractured surfaces were made using a scanning electron microscope (SEM; JEOL JSM-35CF).

RESULTS AND DISCUSSION

J_c Values

Figure 1 shows typical load-displacement records for the PP/EPDM binary blend. The bars denote the spread of observed crack initiation points. The locus line slightly deviates from a vertical line.

ΔU_c per unit thickness is plotted against each initial crack size for the PP/EPDM/ionomer ternary blends as well as for the PP/EPDM binary blend as shown in Figures 2 and 3. The slope of the least-square-fitted line yields J_c , and the resulting values are replotted against ionomer content in Figure 4.

The average correlation coefficient of the J_c test was 0.98. It is seen that linear relationships between U_c and a have been obtained for the both binary and ternary blends. The result implies that the J value at the crack initiation point, J_c , is a constant for a given thickness, which is the only assumption made in the locus method and proves its validity for our blend system.

In Figure 4, it is shown that the ionomer-added ternary blends exhibit higher J_c values than that of the PP/EPDM binary blend irrespective of the ionomer types and contents, meaning that the incor-

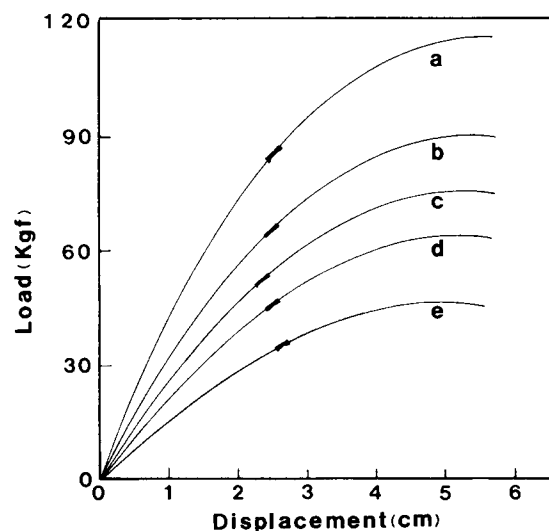


Figure 1 Load-displacement curves: the spread bars denote crack initiation points.

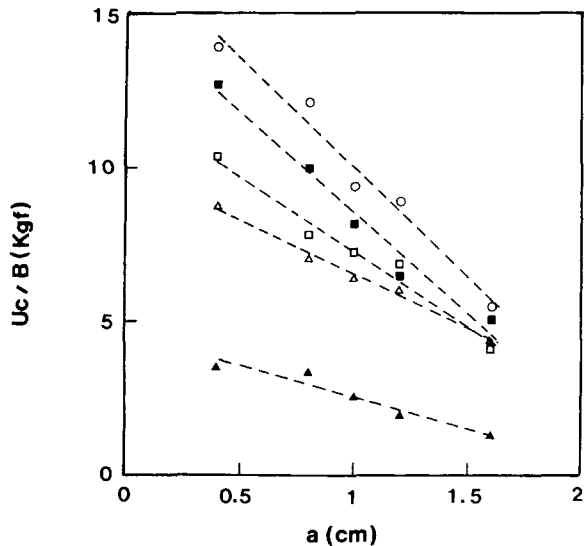


Figure 2 Variation of essential energy needed for crack initiation per unit thickness (U_c/B) with initial crack size (a). The broken lines are the least-squared ones. PP50-EP50/IA: (▲) 0 wt %; (○) 5 wt %; (□) 10 wt %; (△) 15 wt %; (■) 20 wt %.

poration of ionomer enhanced the toughness of the binary blend. In addition, it should be noted that the toughening effect by ionomer addition was most prominently observed when the contents of the ionomers were 5 wt %.

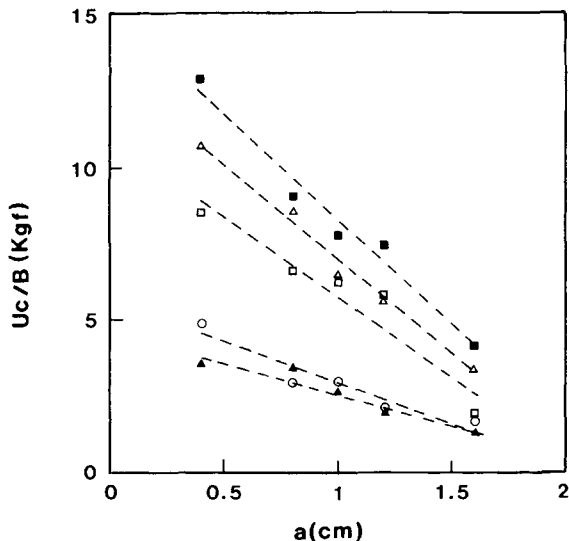


Figure 3 Variation of essential energy needed for crack initiation per unit thickness (U_c/B) with initial crack size (a). The broken lines are the least-squared ones. PP50-EP50/IB: (▲) 0 wt %; (○) 5 wt %; (□) 10 wt %; (△) 15 wt %; (■) 20 wt %.

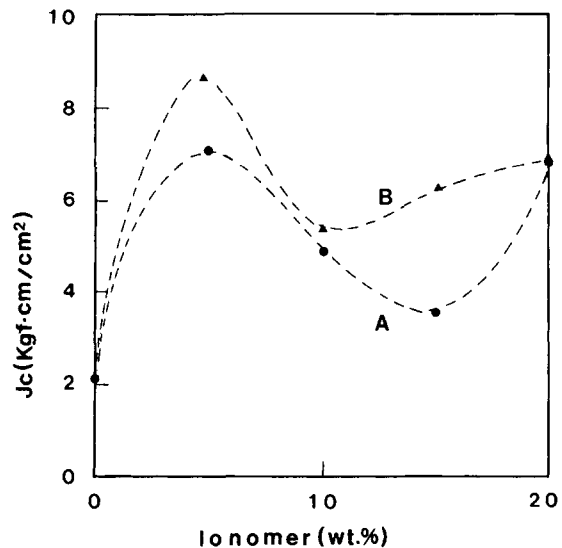


Figure 4 Effect of the added ionomer on the fracture energy J_c : (A) PP50-EP50/IA; (B) PP50-EP50/IB.

The result may be due to the compatibilization of EPDM and PP by the ionomers, as reported in our previous work.¹⁶ The difference for ionomer types are within experimental error and did not affect the J_c values.

Remote Energy Absorption

The total energy consumed during fracture testing includes some amount of remote energy loss as well as the energy supplied for the crack propagation. The remote energy absorption away from the crack tip is not negligible if the specimen length is not long.¹⁵ In this work, the specimen length is 100 mm. The remote energy absorption in determining the J_c value was also evaluated.

Figure 5 shows the effect of the ionomer addition on the ϕ values. In this plot, the ϕ value for the initial crack in length (a/w) of 0.5 was compared. The ϕ value for the PP/EPDM binary blend was less than 1.0, but that for the ternary blends was equal to or slightly larger than 1.0, regardless of ionomer types and contents. The result implies that the effect of remote energy absorption is negligible for the ionomer-added ternary blends, whereas the effect should be taken into account to estimate J_c values from our locus method for the PP/EPDM binary blend. The ϕ values for the ternary blends having 10 and 15 wt % of ionomer B are larger than any other ternary blends and are almost 1.5. This trend was because the crack initiation locus below

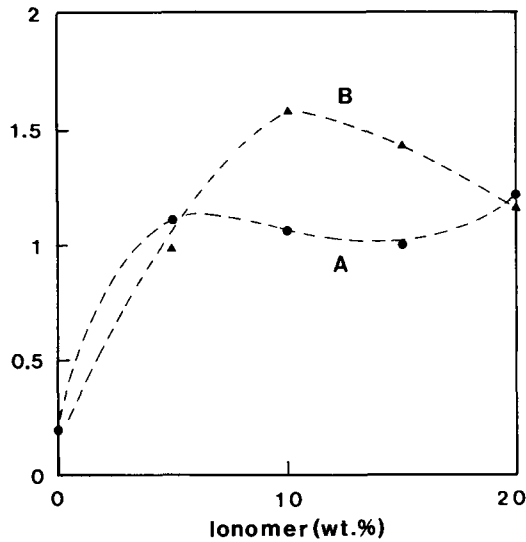


Figure 5 Effect of the added ionomer on the ratio (ϕ) of essential crack initiation energy to total energy needed for crack initiation: (A) PP50-EP50/IA; (B) PP50-EP50/IB.

the loading curve of the largest crack size has a negative slope in the load-displacement record, meaning that the critical displacements (crack initiation displacements) are larger at the same initial crack length. Thus, the J_c value determined on the locus method for the ionomer A-containing ternary blend is more accurate than that of the ionomer B-containing ternary blend. Note, however, that the sig-

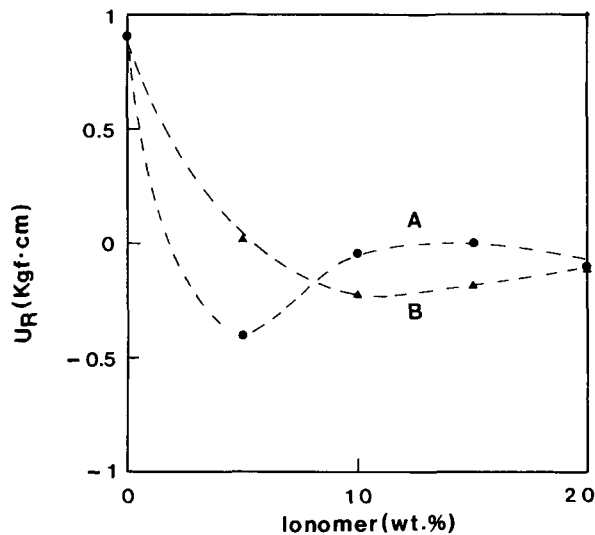


Figure 6 Effect of the added ionomer on the remote or plastic deformation energy (U_R): (A) PP50-EP50/IA; (B) PP50-EP50/IB.

Table III Fracture Energy of PP/EPDM Binary or PP/EPDM/Ionomer Ternary Blends

Sample	Fracture Energy, J_c (kgf cm/cm ²)
PP	2.90
PP50-EP50	2.08
PP50-EP50/IA5	7.13
PP50-EP50/IA10	4.88
PP50-EP50/IA15	3.49
PP50-EP50/IA20	6.82
PP50-EP50/IB5	8.62
PP50-EP50/IB10	5.30
PP50-EP50/IB15	6.22
PP50-EP50/IB20	6.91

nificance is not large and, thus, the J_c values for the ionomer B-containing ternary blend are also acceptable in our work.

The plot of remote absorption energy, U_R , against the ionomer content, as shown in Figure 6, also shows the same trend as referred to in Figure 5. For the PP/EPDM binary blend, the effect of remote energy absorption is significant ($U_R \approx 1.0$), whereas for the ionomer-added ternary blends, the effect is negligible regardless of ionomer contents and types ($U_R \approx 0.0$).

Table III shows the fracture energy data for all the blend samples investigated. Of interest is the fact that the J_c value of the PP/EPDM binary blend is lower than that of PP, whereas the J_c values of the ionomer-containing ternary blends are higher than those of PP as well as of the PP/EPDM binary blend. The result implies that the incorporation of ionomer enhances the toughness of PP and the PP/EPDM binary blend regardless of the ionomer types and contents.

Fracture Surface Topology

In our previous work, the blends showed very complicated multiphasic morphologies.¹⁶ The fracture surface topology was observed by scanning electron microscopy.

The PP/EPDM binary blend showed somewhat quasi-cleavage fracture topology,¹⁹ as shown in Figure 7. However, all the ionomer-added ternary blends showed slightly different fracture surface topologies. Figure 8 shows the SEM micrographs of the fractured surfaces taken around the crack-tip. In this case, the initial crack length was 8 mm. The ionomer-added ternary blend shows the typical fracture surface topology of tough materials. Careful

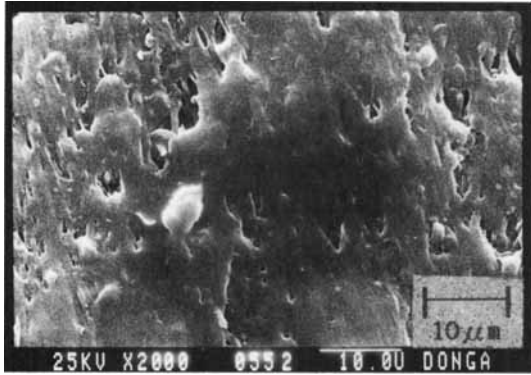


Figure 7 SEM microfractograph of the PP/EPDM binary blend. The initial crack length is 8 mm.

inspection of Figures 7 and 8 shows that the fracture surface of the 5 wt % ionomer-added ternary blends has clearer dimple fracture topology, exhibiting tougher characteristics than that of the 10 wt % ionomer-added ternary blends, regardless of ionomer type.

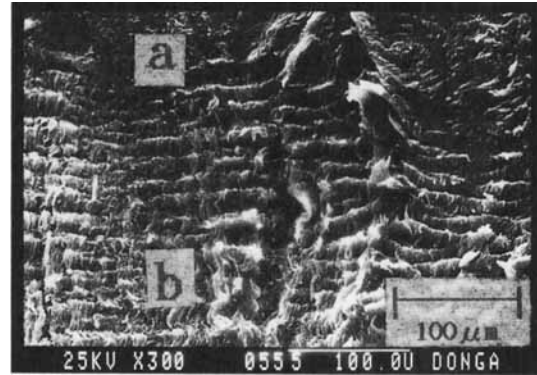


Figure 9 SEM microfractograph of the PP50-EP50/IA5 ternary blend at a lower magnification of 300X. The initial crack length is 8 mm. (a) is a notched region and (b) is an initiation region.

Figure 9 shows a lower magnification of the fractured surface of the 5 wt % ionomer A-added ternary blends. The micrograph clearly reveals dimple rupture topology, which is usually observed in tough

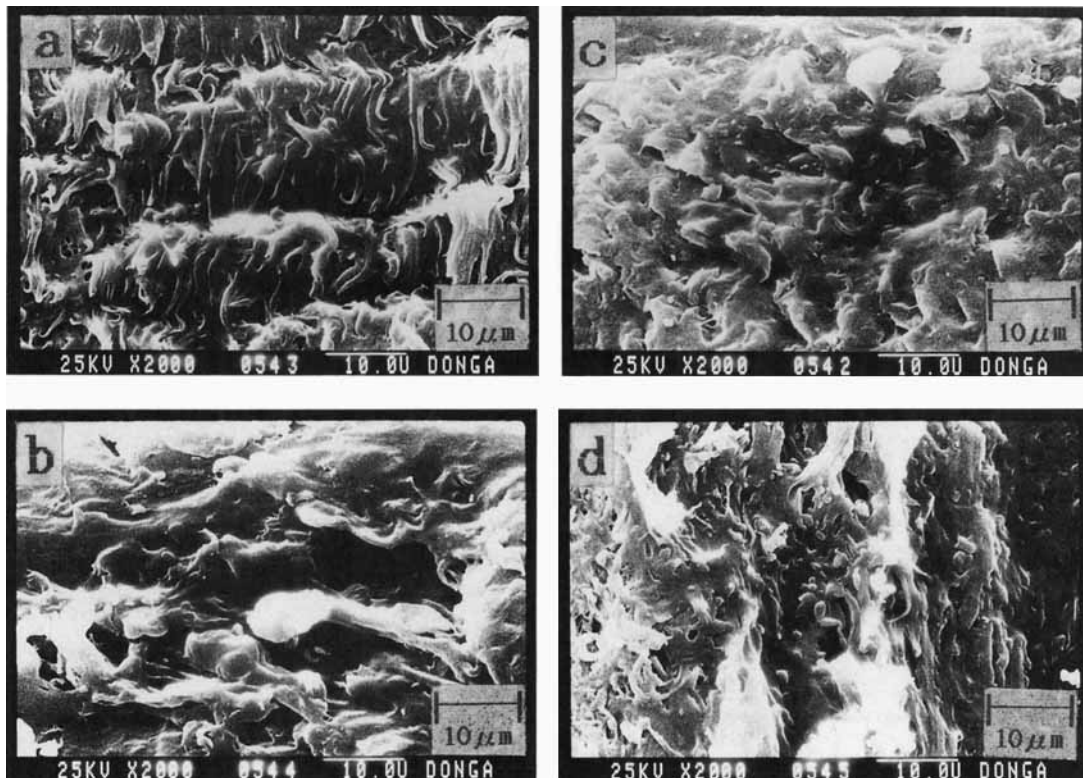


Figure 8 SEM microfractographs of the PP/EPDM/ionomer ternary blends: (a) PP50-EP50/IA5; (b) PP50-EP50/IA10; (c) PP50-EP50/IB5; (d) PP50-EP50/IB10. The initial crack length is 8 mm.

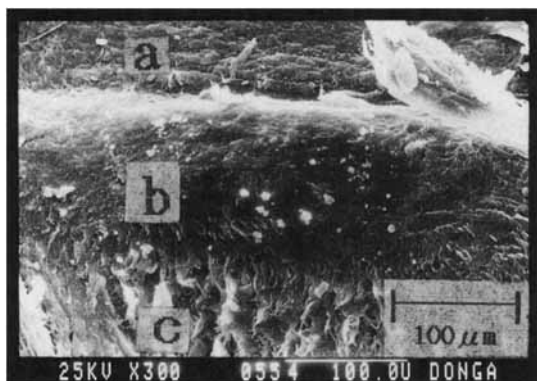


Figure 10 SEM microfractograph of the PP50-EP50 binary blend at a lower magnification of 300 \times . The initial crack length is 8 mm. (a)–(c) are the same as referred to in legend to Figure 11.

materials. When the samples with an initial crack are subjected to load, they initially resist crack propagation, but on exposure to high load, they finally undergo spontaneous failure. When a material is tough enough to resist crack propagation, the material will stretch over long distances until it reached failure. We call the distances between the initial crack region and the end band region an initiation region.

The SEM micrograph of Figure 10 shows a majority of the fractured surface of the PP/EPDM binary blend. In these micrographs, A, B, and C represent the initial crack tip, initiation region, and end band region, respectively. The direction of crack travel is from top to bottom. The side view of a fractured sample is schematically shown in Figure 11.

Table IV shows the length of the initiation region for each sample. It is seen that the ternary blends containing ionomers showed larger initiation regions than did the binary blend without ionomers, regardless of ionomer types and contents.

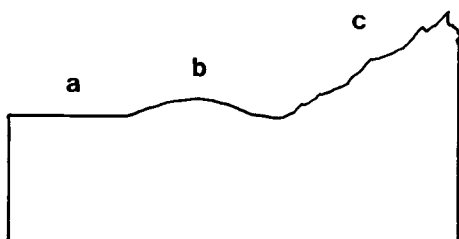


Figure 11 Schematic diagram of a fractured specimen from a sideview, where (a), (b), and (c) are a notched region; an initiation region, i.e., stretched zone; and an end band region, i.e., rapid destroyed region, respectively.

Table IV Crack Initiation Length of Blends, d (mm)

Sample	Crack Initiation Length, d (mm)
PP50-EP50	0.124
PP50-EP50/IA5	0.363
PP50-EP50/IA10	0.148
PP50-EP50/IB5	0.379
PP50-EP50/IB10	0.152

CONCLUDING REMARKS

Several conclusions can be drawn from the above results concerning the fracture mechanics investigation of the PP/EPDM/ionomer ternary blends by using the J_c integral via the locus method: (1) PP/EPDM blends containing ionomer showed higher J_c values than those of the PP/EPDM binary blend as well as of PP itself. (2) The J_c values were highest for the ternary blends containing 5 wt % of ionomer, regardless of the ionomer types. (3) The ternary blend containing ionomer showed negligible remote absorption energy, which manifests the validity of the evaluation of J_c values by the locus method.

The second conclusion will be discussed with reference to our previous work.¹⁶ In our previous work,¹⁶ we revealed that the ionomer enhanced the miscibility of PP and EPDM and the effect was most prominent at a 5 wt % concentration. The rheological and morphological studies revealed that ionomer A showed more of a compatibilizing effect between PP and EPDM than did ionomer B at the same concentration.

In our present investigation, ternary blends containing ionomer B showed higher J_c values over the entire ionomer concentration investigated. This may be due to the inherent higher toughness of the added ionomer B than that of the added ionomer A, according to the manufacturer's data. Even though the compatibilization by ionomer A is larger than that by ionomer B, the effect of ionomer addition on the J_c values was very similar. The miscibility will surely affect the fracture mechanics behavior of polymer blends. More detailed research should be carried out to investigate the relationship of miscibility and fracture toughness, since there is some controversy as to whether J_c by itself is an accepted measure of toughness.

It can be concluded, however, that the incorporation of a small amount of ionomer increased J_c

values, probably enhancing the fracture toughness of the PP/EPDM blend and the enhancing effect is most prominently observed at a certain concentration (in this case, 5 wt %) and the effect is irrespective of the ionomer types. Note also that the evaluation of J_c integrals, using a simple single-edge notched specimen, was successfully applicable to investigate the fracture behavior of the PP/EPDM/ionomer ternary blends.

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