Mechanism of Toughening for Polypropylene Blended with Ethylene–Propylene–Diene Rubber Following Selective Crosslinking

MASARU ISHIKAWA,[1,*] MASATAKA SUGIMOTO,[1] and TOSHIO INOUNE[2]

[1]Department of Material Engineering, Faculty of Engineering, Yamagata University, Jonan 4-3-16, Yonezawa-shi, Yamagata 992, and [2]Nippon Petrochemicals Company Ltd., Plastics Laboratory, 2-3-2 Yako, Kawasaki-Ku, Kawasaki 210, Japan

SYNOPSIS

Toughening mechanism of polypropylene (PP) blended with ethylene–propylene–diene rubber (EPDM) following selective crosslinking was examined in comparison with that of blends of PP before crosslinking. The yield stress, strength of craze, and density of void which are dominant factors for enhancing toughness in PP blends were evaluated and the deformation and fracture mechanism was discussed. It was concluded that toughness of PP blended with EPDM is improved by selective crosslinking, since the improvement of the craze strength is greater than the drop in the release of the constraint of strain. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

It has been well known that enhancement of toughness in polymers is widely achieved commercially by blending. Several examinations have been proposed to account for the toughening mechanism of polymer blends,[1–4] but most of these investigations were phenomenalistic studies. It is obvious that the problem of deformation and fracture mechanism for polymer blends, in which the modifier (such as rubber) is dispersed in a matrix polymer, belongs to the category of the mechanics of composite materials which are based on the deformation and fracture mechanics for composed materials. We[5–7] have already pointed out that the development of many voids at modifier leads to releasing the constraint of strain which is the origin of the stress concentration. Therefore the brittle–ductile transition takes place when the stress ahead of the local plastic zone developed from the notch tip decreases below the strength of craze due to the release of the constraint of strain. As a result, the toughness is improved in the polymer blend.

The toughening mechanism of polypropylene (PP) blended with an elastomer such as ethylene–propylene rubber (EPR) has been previously reported by many authors.[8–15] We suggested that the toughening mechanism of the EPR/PP blend is the release of constraint of strain because the density of void increases with increased content of the modifier.[16,17] Recently, Inoue[18–20] pointed out that the toughness of PP blended with ethylene–propylene–diene rubber (EPDM) is improved by selective crosslinking at EPDM. In this case, the morphology of the modifier is similar to that of the PP blend before crosslinking. According to the author's opinion,[5] the relaxation of stress concentration due to Poisson's contraction between the voids which are nucleated at modifier is a basis for the toughening of polymer blends. In general, the elastomer which has low modulus and low cohesive strength is used as a modifier, therefore the yield stress and strength of craze decreases with increasing modifier content. In these blends, if the maximum stress is adjusted to lower stress than the strength of craze by the release of the constraint of strain or decrease of yield stress, then the toughness may be improved.

The purpose of this study is to examine yield stress, strength of craze, and density of void of PP blended with EPDM following selective crosslinking,

---

[*] To whom correspondence should be addressed.

Journal of Applied Polymer Science, Vol. 62, 1495–1502 (1996)
CCC 0021-8995/96/101495-08

and to discuss the essential factors for enhancing toughness in this polymer blend.

EXPERIMENTAL

Materials

The materials used in this study were commercial grades of PP (Nihon Petrochemical Co. Ltd, Kawasaki, Japan) with MFR = 1.8 g/10 min as matrix polymer, and EPDM with Moony viscosity of 88 (373 K), content of propylene of 28, and an iodine value of 15 as modifier. The parent PP was blended with EPDM at the ratios resulting in the volume fraction from 5 to 30 vol %. The crosslink system comprised *N-N'-m*-phenylenebismaleimido as a crosslink agent, and polyerized (2,2,4-trimethyl-1,2-dihydroquioline) as accelerator. Selective crosslinking was carried out under twin-screw extrusion with a radius of 30 mm at 503 K. Table I shows the MFR and degree of crosslinking as a function of EPDM content before and after crosslink.

Preparation of Specimens

To estimate the elastic modulus and yield stress, sheets of 2-mm thickness for the tensile test were prepared by compression molding. The pellets were melted at 473 K for 10 min and then cooled to 293 K. A test specimen with the width of 10 mm and length of 150 mm was cut from the sheet. A 1-mm-thick sheet which was molded by compression at the same conditions as above was used to estimate the strength of craze. In this case, the specimen width was 6 mm.

For a three-point bending test, rectangular bars with width of 12.4 mm and thickness of 6 mm were prepared by an injection-molding machine. A round notch with radius of 0.5 mm was shaped by machining with the convex milling cutter. The ligament thickness was 4 mm. The specimens were cooled with water during machine processing in order to prevent the rise of temperature.

Mechanical Testing

The initial longitudinal elastic modulus and upper yield stress were estimated from the stress–strain curves by the uniaxial tensile test of rectangular sheets. Poisson's ratio was calculated from the change of both width and length during uniaxial tensile deformation. The contraction of width was measured by a Laser equipment (Keyence, LS-3100) and extensional strain was measured by a extension meter with strain gauge (Shimadzu SG-50-100). Tests were carried out at a strain rate of 0.15/min at 296 K in a servohydrulic testing unit (Servo Pulsar, Shimadzu EHF-EB5-10L). The strengths of fibrillar bundles in the craze were estimated from the strength of the oriented region formed by necking on the uniaxial tensile test.[21] In this experiment, the strain rate was 0.4/min.

The toughness of specimen was evaluated by the three-point bending test of a U-notched bar. The specimens were loaded at a bending rate of 125 mm/s with a span length of 40 mm in a servohydrulic testing unit. The impact strength was measured by Izod impact test using a V-notched specimen in accordance with ASTM D 256.

Morphologic Analysis of Deformation Mode

To discuss the deformation processes of U-notched bars in the three-point bending test under plane strain, thin sections of about 25 μm were cut perpendicular to the plane of initial notch using a conventional microtome. The morphologies of crazes

Table I MFR and Degree of Crosslink for PP Blended with EPDM

	MFR [230°C/2.16 kg):(g/10 min)]		Degree of Crosslinking (%)	
PP/EPDM	Before Crosslink	After Crosslink	Before Crosslink	After Crosslink
95/5	2.4	4.7	—	—
90/10	2.1	3.9	—	—
85/15	1.9	3.3	—	26
80/20	1.7	2.2	—	54
75/25	1.4	1.6	—	65
70/30	1.4	1.4	—	56

Crosslink system: PN/PTMQ = 0.2/0.3; PN, *N,N'-m*-phenylenebismaleimido; PTMQ, polymerized (2,2,4-trimethyl-1,2-dihydroquioline). PP, MFR (melt flow rate) = 1.8 homopolymer; EPDM: M1 + 4 (100°C) = 88, C3 = 28%, IV = 15.

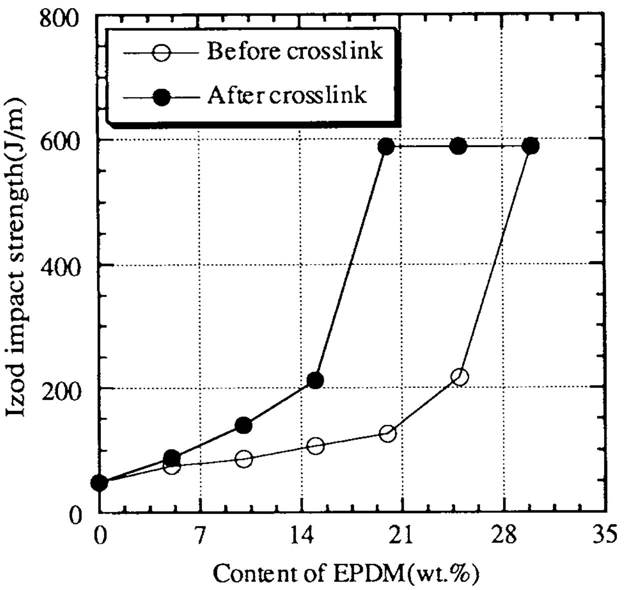

Figure 1 Izod impact strength of PP blended with EPDM following selective crosslinking in comparison with that of PP blend before crosslink.

and plastic deformations were studied with an optical microscope for the microtomed sections.[21] The microstructure of the plastic deformation zone was observed with a scanning electron microscope for the surfaces of cryogenically fractured samples. Samples which were subjected to the bending test were first immersed in a liquid nitrogen bath for 5 min, and broken normal to the plane of the notch immediately after removal. Because strain recovery on unloading significantly influences the morphology of the deformation zone, the deformation by three-point bending was fixed by casting in epoxy resin, which consisted of 100 parts per hundred (phr) of bisphenoal-A epoxy resin (weight per epoxide equivalent: 190 g/eq) and 60 phr of polyaminoamide (Ankamide 506).[21] Specimens were treated with ion spatter to give an adhesiveness to the interfaces.[21]

RESULTS

Impact Strength and Toughness

Figure 1 shows Izod impact strength of PP blended with EPDM following selective crosslinking in comparison with that of the PP blend before crosslink.[20] The content of EPDM required to improve the impact strength of the PP blend before crosslink was above 30 wt %. On the other hand, in the blend of PP after crosslink, the impact strength was improved by an increase of 20 wt %. It is suggested that the efficiency of the improvement of impact strength of PP blended with EPDM is increased by the selective crosslinking. Because the pendulum speed of an Izod impact tester changes after impacting on a specimen, the mechanism of deformation and fracture is complex. Figure 2 shows the variation of toughness with increase in modifier content in the three-point bending test on U-notched specimens at a constant speed. The bending rate was a high speed of 125 mm/s. The bending moment–displacement curves show that the mode of fracture of the PP blend is brittle with slight ad-

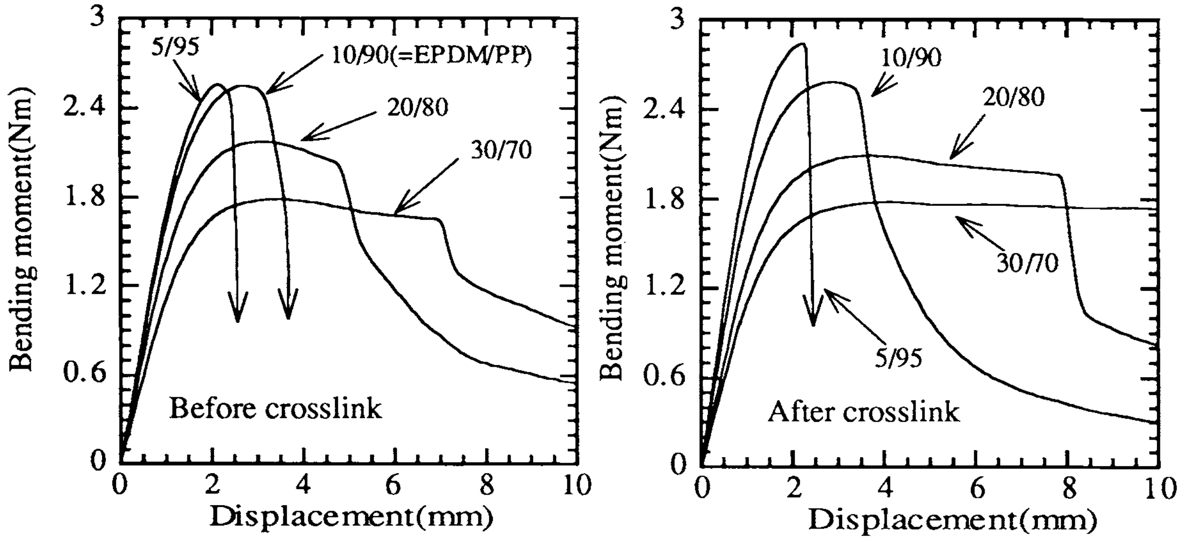

Figure 2 Variation of bending moment–displacement curves of the round notched bar of PP blended with EPDM with increases in EPDM content.

dition of modifier. It was indicated that the mode of deformation changes from brittle fracture to ductile deformation, showing general yielding when the addition of modifier is over a critical content. For the blend of PP before crosslink, as much modifier as 10 to 20 wt % was required for the mode of deformation to change to ductile deformation; and for the blend of PP after crosslink, its content was about 5 to 10 wt %. The modifier content required to change the mode of deformation from brittle fracture to ductile deformation depends on the bending rate. The brittle-to-ductile transition takes place with slight addition of modifier at low bending rate. The addition for brittle-to-ductile transition increases with increasing bending rate. In Izod impact testing, the speed of a pendulum is about 3 m/s at the position just before impacting against the specimen. The speed is one order of magnitude faster than that in high-speed three-point bending testing. The content required to change the mode of deformation in the three-point bending test is close to that in the Izod impact test. Therefore it is suggested that in Izod impact testing, the actual average speed of deformation exerted on the specimen is slower than that just before impact.

Morphology of Plastic Zone

We have already detailed the suggested morphology of the plastic zone of PP developed from the notch tip.[21,23,24] Figure 3 shows the microphotographs of the plastic zone of PP immediately before the brittle fracture. The plastic zone containing the microcrazes was observed. When the size of the plastic zone reaches a critical extent and fulfills the unstable condition of the deformation, the macrocraze developed.[22] The brittle fracture occurred from this macrocraze by the rupture of fibrillar bundles extending in the direction of principal stress.

The addition of a large amount of EPDM leads to the relaxation of the stress concentration due to the release of constraint of strain by Poisson's contraction between voids nucleated at the modifier, similar to that of PP blended with EPR. As a result, the nucleation of catastrophic crack at the craze is suppressed and the toughness is improved. Figure 4 shows microphotographs of the plastic zone of PP blended with EPDM of 20 wt % before crosslink. The plastic zone containing voids or microcrazes was observed. Figure 5 shows microphotographs of the plastic zone after crosslink for PP blended with EPDM of 20 wt %. The smaller voids than those of blends of PP before crosslink were uniformly distributed.

Strength of Craze and Yield Stress

It was already pointed out[5] that both yield stress (which is resistance to plastic deformation) and strength of fibril (which constitutes the craze) are characteristic values for brittle fracture of ductile polymer.[5,25-28] Figure 6 shows the yield stress and strength of craze estimated by the uniaxial tensile test of oriented polymer blend as a function of content of EPDM. It was found that in either case the characteristic value decreases with increasing con-

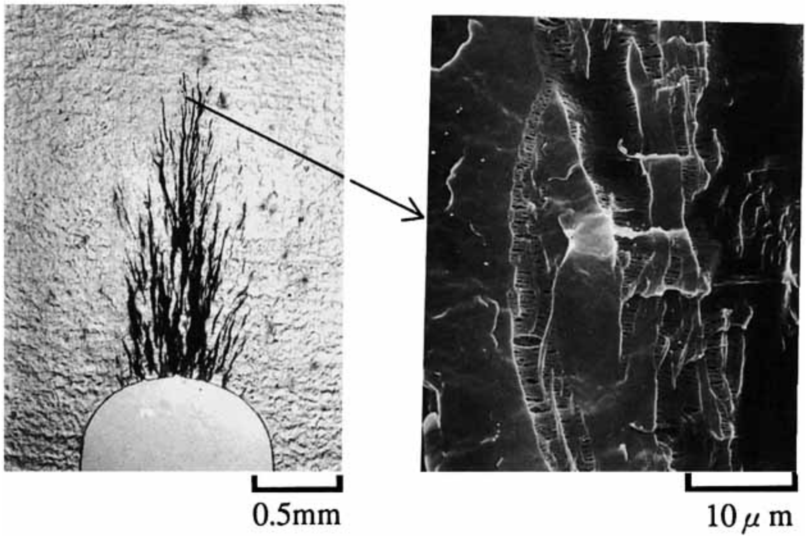

Figure 3 Microphotographs of the plastic zone of PP immediately before the brittle fracture.

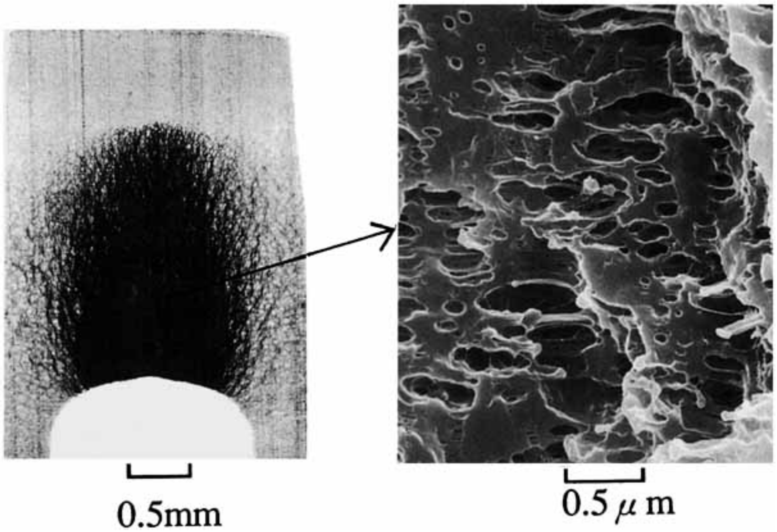

Figure 4 Microphotographs of the plastic zone of PP blended with EPDM of 20 wt % before crosslink.

tent of modifier. The magnitude of the decrease of craze strength in the blend of PP after crosslink is smaller than that in the blend of PP before crosslink. On the other hand, it seems likely that the shear yield stress decreases slightly with crosslinking.

Volumeric Expansion and True Stress–Strain Curve

The effect of the release of the constraint of strain on the improvement of toughness can be found from the volumeric expansion.[7] The condition of plastic instability for the nucleation of craze can also be evaluated by the true stress–strain curve for an essential condition and by the ratio of shear yield stress to shear modulus for a sufficient condition.[29,30] Figure 7 shows the volumeric strain against the longitudinal strain in the uniaxial tensile test of PP blended with EPDM of 20 wt %. It was found that the volumeric expansion due to development of voids is suppressed by the selective crosslinking in the polymer blend. Figure 8(a) shows the true stress–strain curves in same sample. The strain hardening was observed above the yield strain on PP blended with EPDM following selective crosslinking, although the true stress decreased above the yield

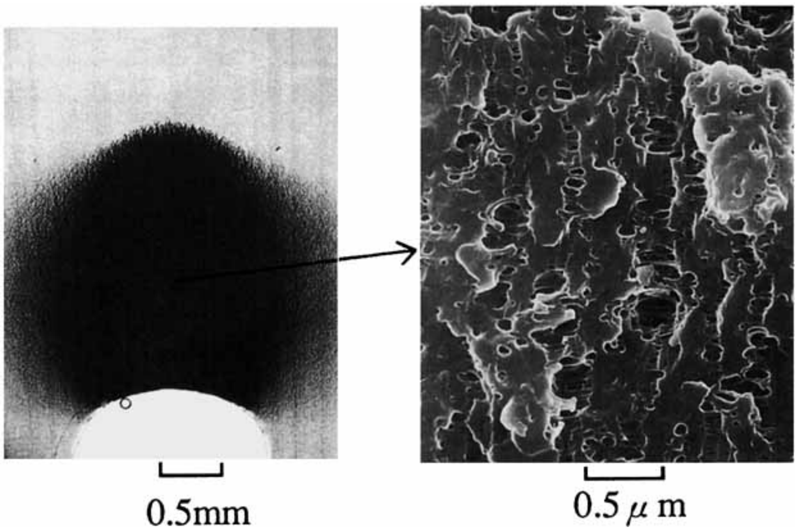

Figure 5 Microphotographs of the plastic zone of PP blended with EPDM of 20 wt % after crosslink.

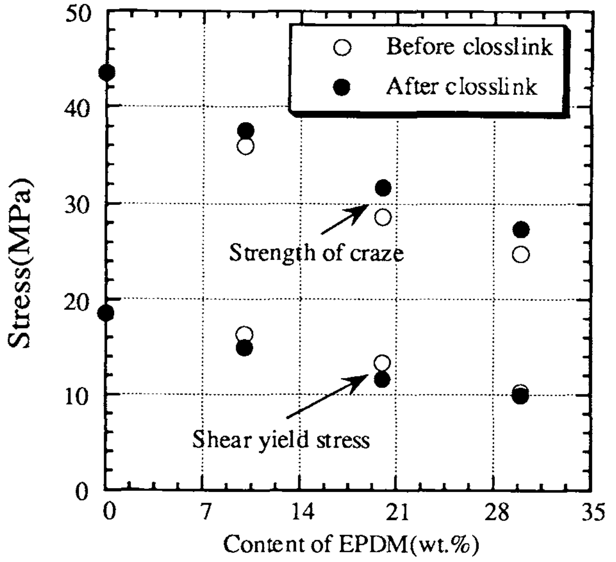

Figure 6 Yield stress and strength of craze estimated by the uniaxial tensile test of oriented PP blended with EPDM as a function of EPDM content.

strain on the blend of PP before crosslink. Figure 8(b) shows the ratio of shear yield stress to shear modulus as a function of EPDM content. This ratio was nearly constant, independent of the EPDM content and the crosslinking.

DISCUSSION

We have already examined in detail the mechanism of the brittle fracture of PP initiated from the notch.[21,23,24] Figure 9 shows the stress distribution of the local plastic zone developed from the notch tip. It is known from the mechanics of plasticity that there is a maximum stress at the tip of the local plastic zone which spreads across the ligament thickness ahead of a round notch under the plane strain. When the stress ahead of the plastic zone reaches a critical stress by extending the plastic zone, the development of the macroscopic craze, in which the plastic strain is locally concentrated between neighboring microcrazes, occurs at the tip of the local plastic zone. If the stress ahead of the local plastic zone reaches the strength of craze, then the microrupture of the fibrils of craze leads to the catastrophic brittle fracture. Under the condition in which fracture occurs by such mechanism as mentioned above, there are two ways to improve the toughness: improve the strength of craze, and suppress the concentrated stress due to constrained plasticity below the fibril strength.[5]

In the case of materials containing elastomer with reduced cohesion as modifier, the increase of applied load causes the preferential formation of void. The breeding of void proceeds to a sufficient densely crowded condition and Poisson's shrinkage occurs between voids. Under such conditions, the strain is released from restriction to reduce the stress concentration. The toughness is improved by suppression of brittle fracture when the general yielding takes place before the stress ahead of the plastic zone reaches the strength of craze, as shown in Figure 9. The validity of such mechanism for the toughening of polymer blends has been discussed elsewhere.[5-7] The strength of craze for the blend of PP before crosslink decreases with increasing the addition of EPDM. In this case, the improvement of toughness suggests that the release of constrained strain due to void formation sufficiently compensates the decrease in the strength of craze.

In order to reveal the mechanism of toughening due to selective crosslinking, it is necessary to examine the effect of selective crosslinking on the strength of craze and release of the constraint of strain. The strength of craze increases as shown in Figure 6 because the interfacial adhesion between the EPDM particles and PP matrix increases by the graft copolymer and/or the strength of EPDM particles is improved after the crosslink reaction. On the other hand, the yield stress decreases because it seems that the growth of crystal is suppressed due to the crosslink reaction. The mechanics of plasticity indicates that the size of the plastic zone spreads

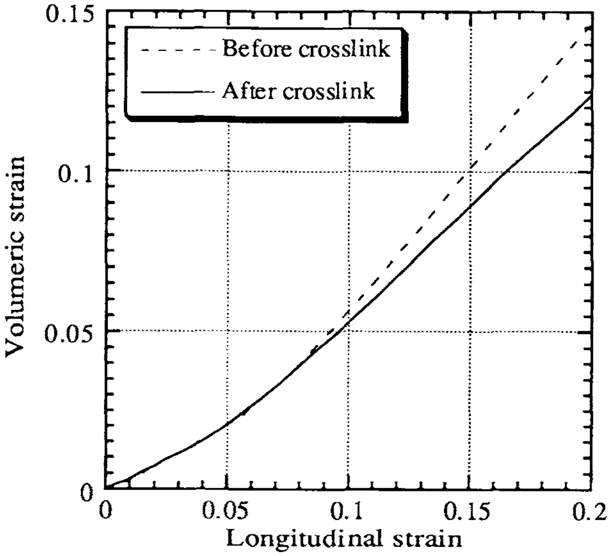

Figure 7 Volumetric expansion against the longitudinal strain of PP blended with EPDM of 20 wt % in uniaxial tensile test.

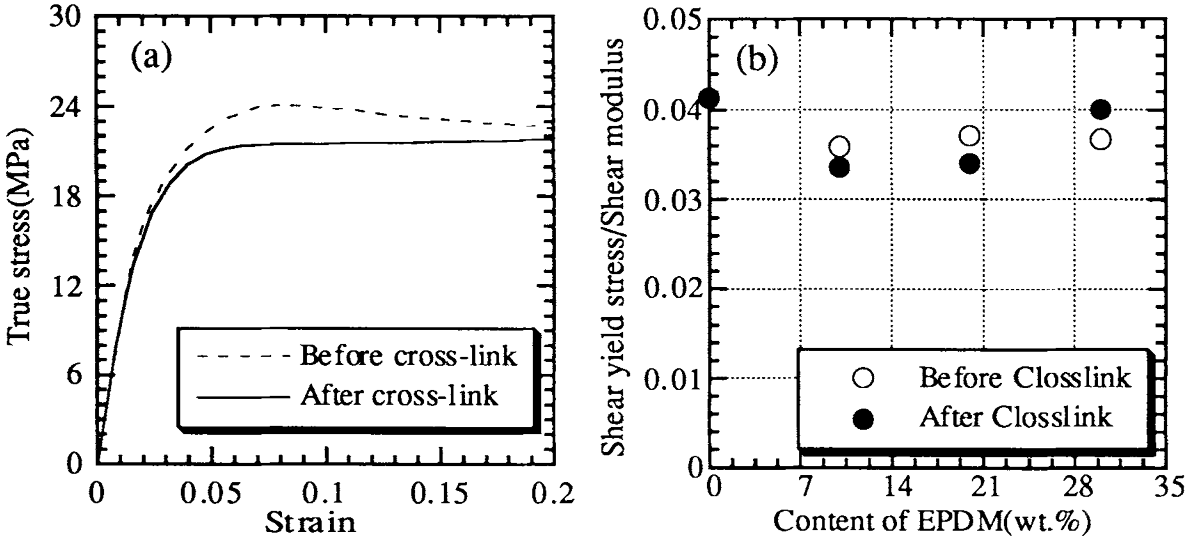

Figure 8 (a) True stress–strain curves of PP blended with EPDM of 20 wt %, and (b) ratio of shear yield stress to shear modulus as a function of EPDM content.

out until the fracture of craze is proportional to the ratio of strength of craze to yield stress.[25-28] Figure 10 shows the ratio of strength of craze to yield stress calculated from Figure 6 as a function of content of EPDM. This ratio of the blend of PP after crosslink increases with increasing the content of EPDM, although its ratio of the blend of PP before crosslink is independent of the addition of modifier. It is known that the size of the plastic zone at general yielding depends on both boundary condition and yield criterion.[31] The large ratio indicates that the plastic zone is largely extended until the fracture initiates at the tip of the plastic zone; therefore the general yielding takes place at the slight addition of modifier on the blend of PP after crosslink. In contrast, the density of voids, which relates to the release of the constraint of strain, is decreased by the selective crosslinking as shown in Figure 7 since the strength of EPDM is improved. To summarize these discussions, we concluded that toughness is im-

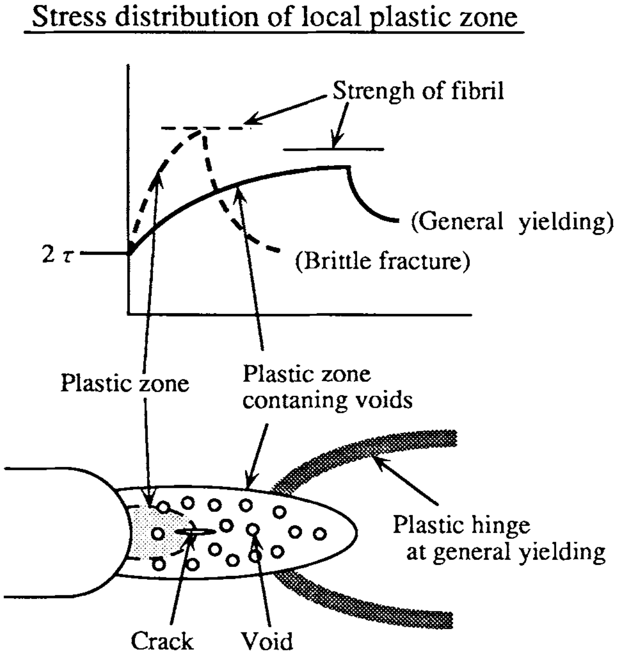

Figure 9 Stress distribution of the local plastic zone developed from the notch tip.

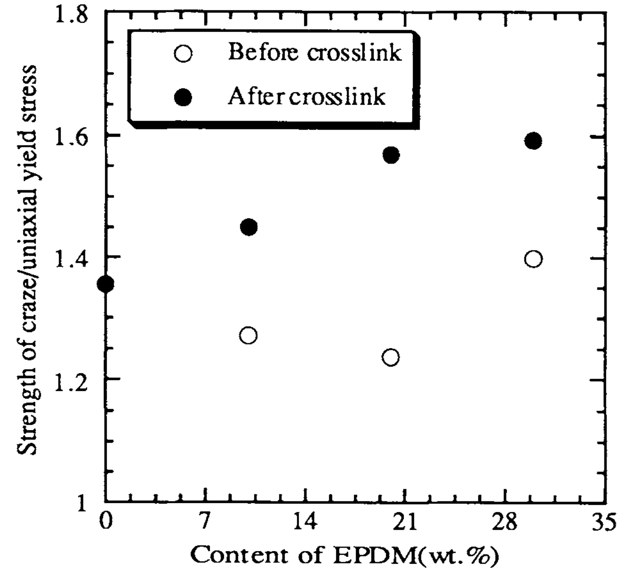

Figure 10 Ratio of strength of craze to yield stress calculated from Figure 6 as a function of EPDM content.

proved for PP blended with EPDM following selective crosslinking since the improvement of the strength of craze is greater than the drop in the release of the constraint of strain.

It is found on the true stress–strain curves shown in Figure 8 that unloading, which is an essential condition for concentration of plastic strain, is inhibited by the crosslinking; and the ratio of shear yield stress to shear modulus, which is a sufficient condition, is independent of the crosslinking as shown in Figure 8(b). Therefore, it is understood that the nucleation of macrocraze is suppressed by crosslinking.

CONCLUSION

The yield stress, strength of craze, and density of void for PP blended with EPDM following selective crosslinking was examined in comparison with the blend of PP before crosslink, and the essential factor for enhancing toughness of this polymer blends was discussed. It was concluded that toughening is improved for PP blended with EPDM following selective crosslinking since the improvement of the strength of craze is greater than the drop in the release of the constraint of strain.

REFERENCES

1. C. Bucknall, *Toughened Plastics,* Applied Science, London, 1977.
2. A. J. Kinoch and R. J. Young, *Fracture Behavior of Polymer,* Applied Science, London, 1983.
3. H. J. Sue and A. Yee, *J. Mater. Sci.,* **24,** 1447 (1989).
4. S. Y. Hobbes and M. E. J. Dekkers, *J. Mater. Sci.,* **24,** 1316 (1989).
5. M. Ishikawa, *Kobunshi Ronbunshu,* **47,** 83 (1990).
6. M. Ishikawa and I. Chiba, *Polymer,* **31,** 1233 (1990).
7. M. Ishikawa, *Polymer,* **36,** 2203 (1995).
8. R. Greco, E. Martuscell, and G. Ragosta, *J. Mater. Sci.,* **23,** 4307 (1988).
9. L. D. Orazio, C. Mabcarella, E. Martuscelli, and G. Sticotti, *J. Mater. Sci.,* **26,** 4033 (1991).
10. R. Greco, C. Manacarella, E. Martuscelli, and G. Ragosta, *Polymer,* **28,** 1929 (1987).
11. L. D'Orazio, C. Manacarella, E. Martuscelli, and F. Polato, *Polymer,* **32,** 1186 (1991).
12. L. D'Orazio, C. Manacarella, E. Martuscelli, and G. Sticotti, *Polymer,* **34,** 3671 (1993).
13. J. Chou, K. Vijayan, D. Kirby, A. Hiltner, and E. Baer, *J. Mater. Sci.,* **23,** 2521 (1988).
14. J. Chou, K. Vijayan, D. Kirby, A. Hiltner, and E. Baer, *J. Mater. Sci.,* **23,** 2533 (1988).
15. K. C. Dao, *J. Appl. Polym. Sci.,* **27,** 4799 (1982).
16. M. Ishikawa, M. Sugimoto, and K. Hatada, *Kobunshi Ronbunshu,* **53,** 1 (1996).
17. M. Ishikawa, M. Sugimoto, and K. Hatada, *Kobunshi Ronbunshu,* **53,** 8 (1996).
18. T. Inoue, *J. Appl. Polym. Sci.,* **54,** 709 (1994).
19. T. Inoue, *J. Appl. Polym. Sci.,* **54,** 723 (1994).
20. T. Inoue, T. Suzuki, T. Takahashi, and M. Miyazaki, *Polym. Prepr.* (Japan), **42,** 3926 (1993).
21. M. Ishikawa, M. Sugimoto, K. Hatada, and T. Tanaka, *Kobunshi Ronbunshu,* **52,** 134 (1995).
22. M. Ishikawa and H. Takahashi, *J. Mater. Sci.,* **26,** 1295 (1991).
23. M. Ishikawa, M. Sugimoto, K. Hatada, and T. Tanaka, *Kobunshi Ronbunshu,* **52,** 149 (1995).
24. M. Sugimoto, M. Ishikawa, and K. Hatada, *Polymer,* **36,** 3675 (1995).
25. M. Ishikawa, I. Narisawa, and H. Ogawa, *J. Polym. Sci., Polym. Phys. Ed.,* **15,** 1977 (1977).
26. M. Ishikawa, H. Ogawa, and I. Narisawa, *J. Macromol. Sci., Phys.,* **B19,** 421 (1981).
27. M. Ishikawa and I. Narisawa, *J. Mater. Sci.,* **18,** 1974 (1983).
28. M. Ishikawa and I. Narisawa, *J. Mater. Sci.,* **18,** 2826 (1983).
29. M. Ishikawa and Y. Kobayashi, *Kobunshi Ronbunshu,* **52,** 141 (1995).
30. A. S. Argon, *The Solid State of Polymers,* Marcel Dekker, New York, 1974, p. 573.
31. R. Hill, *Mathematical Theory of Plasticity,* Oxford University Press, England, 1950.

Received October 23, 1995
Accepted March 18, 1996