Synthesis of Poly(chloroprene-co-isobutyl methacrylate) and Its Compatibilizing Effect in Polychloroprene/ Poly(isobutyl methacrylate) Blends

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SYNOPSIS

A copolymer of chloroprene (CP) and isobutyl methacrylate (iBMA) [poly(CP-co-iBMA)] was prepared in benzene by radical copolymerization. For comparison, the graft copolymer of iBMA onto polychloroprene (CR) [poly(CR-g-iBMA)] was also prepared. The glass transition temperature of the poly(CP-co-iBMA) was about $-32.4°C$. The monomer reactivity ratios determined by the Finneman–Ross method were given as r_1 (CP) = 1.80 and r_2 (iBMA) = 0.74 in the copolymerization of CP and iBMA, respectively. Miscibility of blends of CR and poly(isobutyl methacrylate) (PiBMA), prepared by casting from tetrahydrofuran (THF) solution, was investigated by their glass transition temperature behaviors and morphologies. Although the blends of CR and PiBMA were incompatible, the addition of poly(CP-co-iBMA) or poly(CR-g-iBMA) enhanced miscibility between the two base polymers. It was found that the extent of partial miscibility becomes larger when adding poly(CP-co-iBMA) than poly(CR-g-iBMA) as a third component to the CR/ PiBMA blend of 50/50 wt % composition. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

Polychloroprene (CR) is one of the most commonly used synthetic rubbers in adhesives and in the automotive and energy industries because of its high mechanical strength, good resistance to hydrocarbon oils and chemicals, and adequate low-temperature behavior.[1-6] However, its poor heat resistance and weatherability limit its outdoor use. To improve the poor performance, the introduction of a second monomer into the CR backbone or the use of appropriate fillers for compounding has been widely investigated.[1,2,7-14]

Compatibilizers or interfacial agents in polymer blends have attracted much interest from theoretical and practical standpoints.[15-19] Moreover, the use of a copolymer, especially a block or graft copolymer, as a compatibilizer in incompatible homopolymer/ homopolymer blends has been also one of the main research themes in the field of polymer blends.

In this work, we obtained a copolymer of chloroprene and isobutylmethacrylate. The copolymer was characterized with IR and ^{1}H-NMR spectroscopies. The effect of the addition of the copolymer in blends containing each homopolymer, CR and poly(isobutyl methacrylate), was investigated. For comparison, a graft copolymer of isobutyl methacrylate onto CR was also prepared. The miscibility of blends was discussed in terms of their glass transition temperature behaviors and morphologies using differential scanning calorimetry (DSC) and scanning electron microscopy (SEM), respectively.

EXPERIMENTAL

Materials

Isobutyl methacrylate (Aldrich) and benzene (Aldrich) were purified by the standard methods. 2,2'-Azobisisobutyronitrile (AIBN) was purified by re-

crystallization in dehydrated ethanol. 3,4-Dichloro-1-butene (DCB) (Aldrich), tetrahydrofurfuryl alcohol (THFA; Junsei), and sodium hydroxide (NaOH; Junsei) were used as received without further purification.

Synthesis of Chloroprene (2-Chloro-1,3-butadiene)

Chloroprene (CP) was prepared by reacting DCB in an aqueous solution of sodium hydroxide in the presence of THFA at 60°C by the same method described as in our previous work.[19] The mol ratio of DCB/NaOH/THFA/H_2O was 1/1.3/1.5/1.5. Dehydrochlorination of DCB was carried out in 250 mL of a four-necked flask equipped with condenser, separable funnel, stirrer, and thermometer. The product was filtered to remove sodium chloride and the supernatant was dried with $CaCl_2$ and distilled in argon under reduced pressure. The fraction collected at 25°C and 160 mmHg was retained for copolymerization. The purity of CP was confirmed to be 99.5% by gas chromatography and the yield of CP was 85%. CP was used as soon as possible after distillation because it was polymerized slowly during storage, even at low temperature. The structure of CP was identified by IR spectrophotometry (Perkin-Elmer 1330) and ^{1}H-NMR spectroscopy (Bruker 300 CW).

Synthesis of Polychloroprene and Poly(isobutyl methacrylate)

The polychloroprene (CR) and poly(isobutyl methacrylate) (PiBMA) were obtained in a glass ampule by polymerizing 0.2 mol of CP or iBMA with 0.2 mol % of AIBN as an initiator at 50°C in 100 mL of benzene for 10 h. After reaction, the reaction mixture was poured into a large amount of methanol. The product of CR or PiBMA recovered from methanol was dried under vacuum at 30°C to remove all volatiles.

Synthesis of Poly(chloroprene-co-isobutyl methacrylate) [poly(CP-co-iBMA)]

The copolymer of CR and isobutyl methacrylate (iBMA) was obtained by the same method as described for CR. For the determination of monomer reactivity ratios, a series of polymerizations in which the feed ratio was varied for CP (M_1) to iBMA (M_2) in benzene (ranging from 0.43 to 2.33) yielded copolymers; copolymerization was adjusted to make conversion below 10% by controlling reaction time.

To make a copolymer with $M_1/M_2 = 1$, e.g., 0.20 mol of CP and 0.20 mol of iBMA were radically polymerized with 0.2 mol% AIBN as an initiator at 50°C in 100 mL of benzene.

Poly(CP-co-iBMA) was identified by FTIR spectroscopy (Mattson Galaxy Series 6030). The FTIR spectrum of poly(CP-co-iBMA) exhibited characteristic peaks of a stretching vibration of a vinyl C — H bond at 3020 and 3100 cm^{-1}. The peaks of the C — Cl bond, C — O bond, C=O bond, and C=C double bond appeared at 600–800, 1250, 1750, and 1660 cm^{-1}, respectively (see Fig. 1).

Synthesis of Poly(chloroprene-g-isobutyl methacrylate) [poly(CR-g-iBMA)]

The graft copolymerization of iBMA onto CR was carried out in an 100 mL glass tube. One gram of CR was dissolved in 10 mL of benzene, and 0.20 mol of iBMA was dissolved in 20 mL of benzene and then added to 0.20 mol % of AIBN. The tube was sealed after charging with argon and the reaction was carried out for 10 h. The precipitate from methanol was filtered and dried in vacuum to constant weight. The poly(CR-g-iBMA) was also characterized by its FTIR spectrum.

Blends of CR/PiBMA, CR/PiBMA/Poly(CP-co-iBMA), and CR/PiBMA/Poly(CR-g-iBMA)

The blends were prepared by dissolving the component polymers in THF. The 15 wt % of component solutions in THF were cast on glass plates and most of the solvents were allowed to evaporate slowly in the air at room temperature. The films obtained were
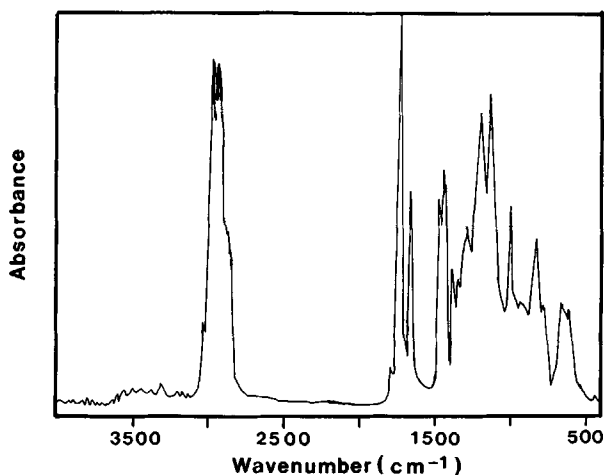

Figure 1   FTIR spectrum of poly(CP-co-iBMA).

completely dried in vacuum at 30°C to constant weight. The compositions of the blends and the sample notations are listed in Table I.

Measurements

Molecular Weight

The molecular weight of the polymers was measured by gel permeation chromatography (GPC) using PS standards. THF was used as an effluent.

Glass Transition Temperature

The glass transition temperature (T_g) was measured using differential scanning calorimetry (DSC, DuPont Model 2100). The thermograms of the blends were obtained at a heating rate of 10°C/min. All the reported T_g's were recorded at the onsets of the heat capacity jumps on the second runs.

Morphology

Scanning electron micrographs (SEM) were obtained using a JEOL JSM35-CF SEM. Samples were cryogenically fractured in liquid nitrogen and metallized by gold coating prior to the installation in the SEM chamber.

RESULTS AND DISCUSSION

Characterization

The molecular weight of poly(CP-*co*-iBMA) was determined as $\bar{M}_n$ = 52,500 and $\bar{M}_w$ = 78,000. In this case, the copolymer has the composition ratio of 1/1 by weight in feed. This copolymer was used for the investigation of miscibility of blends containing CR as well as for the determination of glass transition temperature. The molecular weight of poly(CR-*g*-iBMA) was determined as $\bar{M}_n$ = 67,000 and $\bar{M}_w$ = 126,000. For reference, the molecular weights of CR and PiBMA were determined as $\bar{M}_n$ = 81,000 and $\bar{M}_w$ = 194,000 (CR), and $\bar{M}_n$ = 74,000 and $\bar{M}_w$ = 134,000 (PiBMA), respectively.

Figure 2 shows DSC thermograms of CR, PiBMA, poly(CR-*g*-iBMA), and poly(CP-*co*-iBMA). The T_g's of homopolymers were 46.4 and −45.7°C for PiBMA and CR, respectively. The copolymer has a T_g of −32.4°C, which is higher by about 13°C than that of CR. The CR exhibited a melting peak around at 52.8°C, but the copolymer does not show any melting peak, meaning that the CR has some degree of crystallinity, whereas the copolymer is amorphous. The graft copolymer, poly(CR-*g*-iBMA), showed a T_g of −40.3°C.

Table I Sample Notations

| Sample Notations | Composition by Wt | | | |
	CR	PiBMA	Poly(CP-*co*-iBMA)	Poly(CR-*g*-iBMA)
C100	100	—	—	—
C90B10	90	10	—	—
C80B20	80	20	—	—
C70B30	70	30	—	—
C60B40	60	40	—	—
C50B50	50	50	—	—
C40B60	40	60	—	—
C30B70	30	70	—	—
C20B80	20	80	—	—
C10B90	10	90	—	—
B100	—	100	—	—
CB-C1	50	50	10	—
CB-C2	50	50	20	—
CB-C3	50	50	30	—
CB-C4	50	50	40	—
CB-G1	50	50	—	10
CB-G2	50	50	—	20
CB-G3	50	50	—	30
CB-G4	50	50	—	40
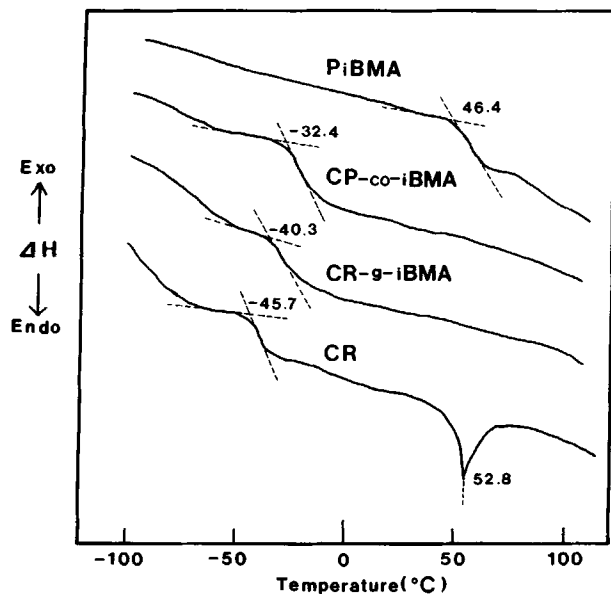
Figure 2 DSC thermograms of various samples.

Figure 3 Feed–copolymer composition curve for poly(CP-co-iBMA). f_1, mol fraction of CP in the feed; F_1, mol fraction of CP in the copolymer.

Monomer Reactivity Ratios

To determine monomer reactivity ratios, all radical copolymerizations of CP and iBMA were carried out in the presence of AIBN as an initiator in benzene at 50°C, and their conversions were adjusted to be less than 10%. The monomer ratios in feed, [iBMA]/[CP], were varied from 0.43 to 2.33. The copolymer compositions (F_1), determined by using ^{1}H-NMR spectroscopy (Bruker 300 CW), were plotted as a function of the monomer composition in feed (f_1) in Figure 3. The monomer reactivity ratios were determined as r_1 (CP) = 1.80 and r_2 (iBMA) = 0.74, respectively, in copolymerization of CP (M_1) and iBMA (M_2), using the Finneman-Ross method with the data in Table II.

Miscibility of CR/PiBMA Blends

Figure 4 shows typical DSC thermograms of CR/PiBMA blends, and Figure 5 shows the glass tran-
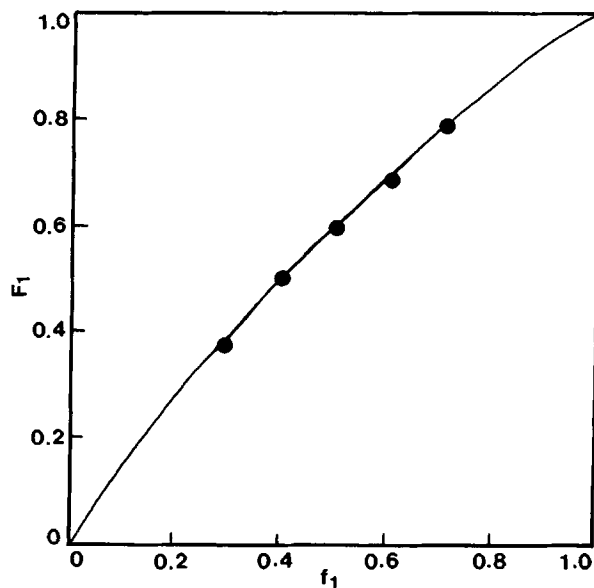
sition temperatures of each component against their compositions by weight % for the blends. The glass transition temperatures are nearly constant regardless of PiBMA contents. This result means that CR and PiBMA are incompatible.

Figures 6 and 7 show the changes of the glass transition temperatures of CR and PiBMA in the presence of poly(CP-co-iBMA) and poly(CR-g-iBMA) for the 1/1 CR/PiBMA blend, respectively. Table III also shows the glass transition temperatures of CR/PiBMA/poly(CP-co-iBMA) and CR/PiBMA/poly(CR-g-iBMA) ternary blends. In this case, the composition of the blends was fixed at 50/50 by weight and the content of copolymers ranged from 10 to 40 phr based on the CR/PiBMA mixture. The T_g's of CR and PiBMA were shifted inward to those of each homopolymer to larger extents as the contents of the added poly(CP-co-iBMA) or poly(CR-g-iBMA) increase. It should be noted that

Table II   Determination of Monomer Reactivity Ratios for the Copolymerization of CP (M_1) and iBMA (M_2)

Sample	$F = [M_2]/[M_1]$	$f = m_2/m_1$	F^2	$f - 1$	$(f - 1)/F$	f/F^2
CB-1	0.43	0.26	0.1849	−0.74	−1.72	1.41
CB-2	0.67	0.44	0.4489	−0.56	−0.84	0.98
CB-3	1.00	0.70	1.0	−0.30	−0.30	0.70
CB-4	1.50	1.08	2.25	0.08	0.05	0.48
CB-5	2.33	1.70	5.4289	0.70	0.30	0.31

Figure 4   DSC thermograms of CR/PiBMA blends.

Figure 6   Changes of the glass transition temperatures (O) of CR and (●) of PiBMA in the presence of various contents of poly(CR-co-iBMA) for the 1/1 CR/PiBMA blends.
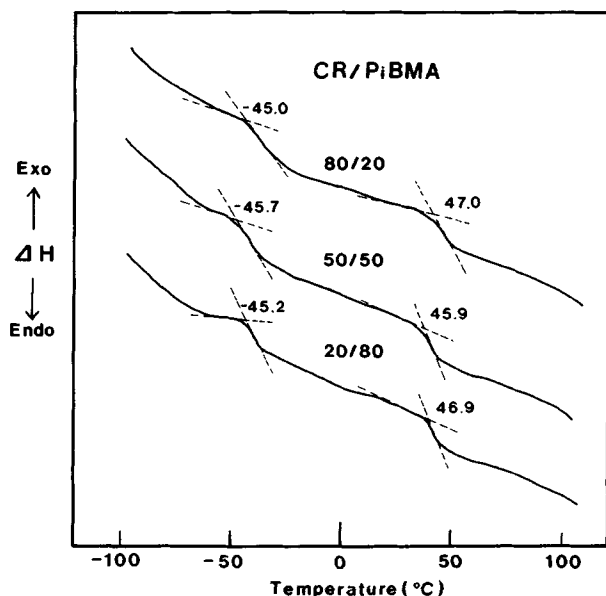
when the copolymers were added to the binary CR/PiBMA blend with the amount of more than 30 phr, the T_g's of the blend significantly shifted inward to those of each homopolymer, even though the ternary blends consisting of each homopolymer and the copolymer show two separate T_g's.

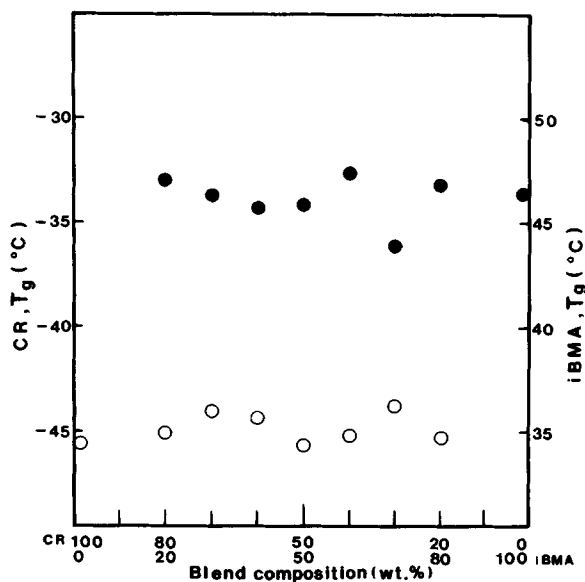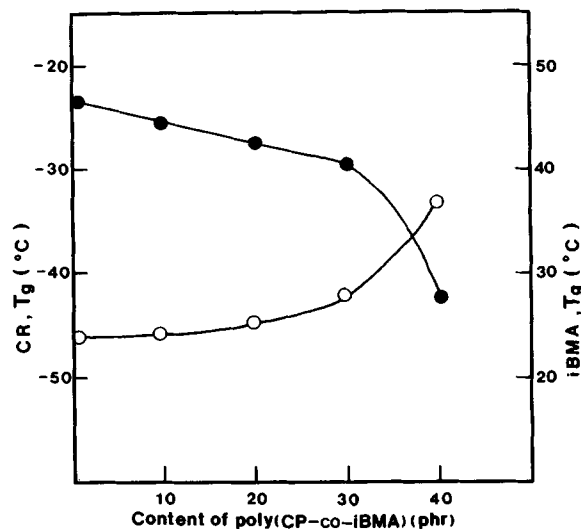The results imply that the poor miscibility of the CR/PiBMA blend of 50/50 composition by weight

was improved in the presence of both the copolymer and graft copolymer. Careful inspection of Table III, however, shows that the addition of poly(CP-co-iBMA) is slightly more effective to increase the extent of partial miscibility for the 50/50 CR/PiBMA blend than is the addition of poly(CR-g-iBMA), even though the difference is not large.
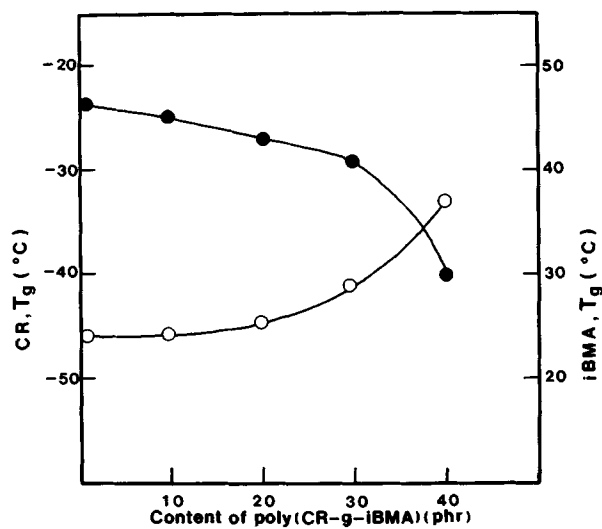

Figure 5   Glass transition temperatures of each component vs. for the CR/PiBMA blend composition by weight.

Figure 7   Changes of the glass transition temperatures (O) of CR and (●) of PiBMA in the presence of various contents of poly(CR-g-iBMA) for the 1/1 CR/PiBMA blends.

Table III   Effect of Poly(CP-*co*-iBMA) and Poly(CR-*g*-iBMA) Content on the Glass Transition Temperature of the 50/50 CR/PiBMA Blend

	Contents (phr)	T_g, CR (°C)	T_g, iBMA (°C)
Poly(CR-*g*-iBMA)	0	−45.7	46.4
	10	−45.1	44.6
	20	−44.3	43.4
	30	−41.2	41.3
	40	−33.3	29.2
Poly(CP-*co*-iBMA)	0	−45.7	46.4
	10	−44.9	44.2
	20	−43.3	42.3
	30	−41.3	40.7
	40	−32.1	27.8

The enhancement of the miscibility in the 50/50 CR/PiBMA blend was also confirmed by the morphological studies. The morphologies of CR/PiBMA, CR/PiBMA/poly(CP-*co*-iBMA), and CR/PiBMA/poly(CR-*g*-iBMA) blends were analyzed by scanning electron microscopy (SEM). Figure 8(a) shows the SEM micrograph of the CR/PiBMA blend of 50/50 composition by weight. It can be seen that the CR/PiBMA blend is incompatible and the phase is grossly separated. When 30 phr of poly(CR-*g*-iBMA) or poly(CP-*co*-iBMA) was added to the binary blend, the morphology changes [see Fig. 8(b) and (c)].

The SEM micrograph of the ternary blend consisting of poly(CR-*g*-iBMA) [Fig. 8(b)] shows a finer domain structure than that of the binary blend without the graft copolymer. It is clearly seen that the ternary blend (c) consisting of poly(CP-*co*-iBMA) shows much finer domain structure than that of the ternary blend (b) consisting of poly(CR-*g*-iBMA) as well as the binary blend (a). The result again implies that the addition of poly(CP-*co*-iBMA) is slightly more effective to enhance the miscibility of CR and PiBMA than is poly(CR-*g*-iBMA).

CONCLUSIONS

In this work, the copolymerization of chloroprene (CP) and isobutyl methacrylate (iBMA) was carried out and the effect of the addition of the resulting copolymer was investigated on the miscibility of the

CR/PiBMA blends. For comparison, poly(CR-*g*-iBMA) was also prepared. The conclusions are as follows:

1. The monomer reactivity ratios were given as r_1 (CP) = 1.80 and r_2 (iBMA) = 0.74 in the copolymerization of CP and iBMA.
2. The copolymer, poly(CP-*co*-iBMA), was amorphous and has a glass transition temperature of −32.4°C, whereas CR has a T_g of −45.7°C and a melting temperature of 52.8°C.
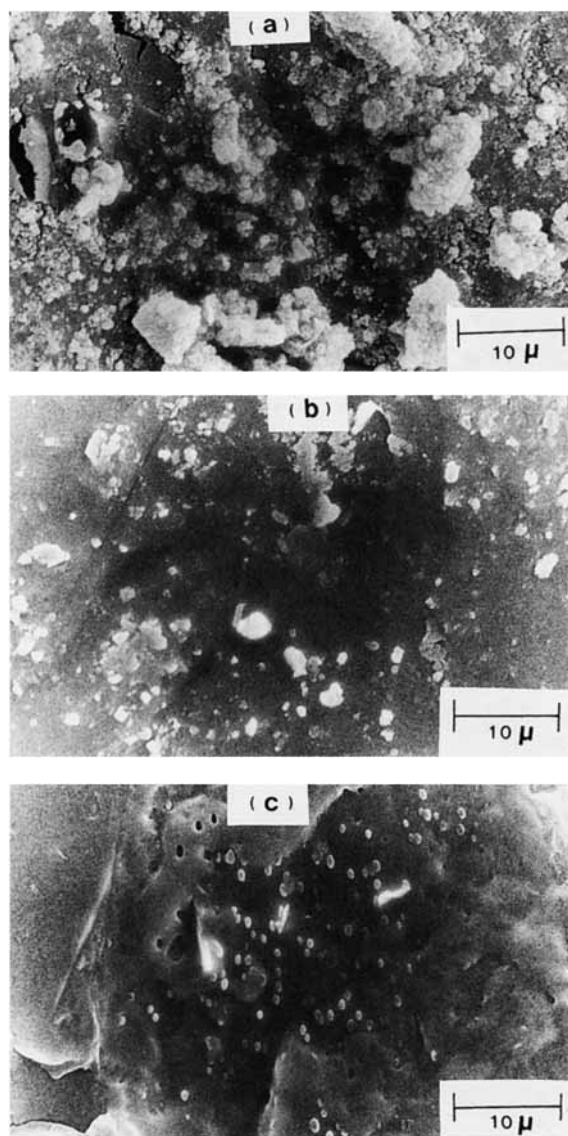

Figure 8 SEM micrographs of samples: (a) 50/50 CR/PiBMA blend; (b) 50/50 CR/PiBMA blend + 30 phr poly(CR-*g*-iBMA); (c) 50/50 CR/PiBMA blend + 30 phr poly(CP-*co*-iBMA).

3. CR and PiBMA were incompatible. The addition of poly(CR-g-iBMA) as well as poly(CP-co-iBMA), however, increased the extent of partial miscibility of CR and PiBMA.

4. The addition of poly(CP-co-iBMA) was slightly more effective in enhancing miscibility between CR and PiBMA in the CR/PiBMA blend of 50/50 composition by weight than was poly(CR-g-iBMA).

REFERENCES

1. R. S. Graff, in *Rubber Technology*, 3rd ed., M. Morton, Ed., Van Nostrand, New York, 1989, Chap. 12.
2. C. A. Stewart, Jr., T. Takeshita, and M. Coleman, in *Encyclopedia of Polymer Science and Technology*, 2nd ed., H. F. Mark and C. G. Overberger, Eds., Wiley, New York, 1985, Vol. 4, p. 522.
3. K. Itoyama, M. Dohi, and K. Ichikawa, *J. Jpn. Soc. Adhes.*, **20**(6), 268 (1984).
4. T. Okada and M. Otsuru, *J. Appl. Polym. Sci.*, **23**, 2215 (1979).
5. E. G. Brame and A. A. Khan, *Rubber Chem. Tech.*, **50**, 272 (1976).
6. A. A. Khan and E. G. Brame, *J. Polym. Sci. Polym. Phys. Ed.*, **14**, 165 (1976).
7. T. Okada, M. Izuhara, and T. Hashimoto, *Polym. J.*, **7**, 1, 1 (1975).
8. N. G. Gaylprdard and B. K. Patnaik, *J. Polym. Sci. Polym. Chem. Ed.*, **13**, 837 (1975).
9. S. K. Choi, C. S. Ha, and W. J. Cho, *Polymer (Korea)*, **15**(5), 539 (1991).
10. J. R. Ebdon, *Polymer*, **15**, 782 (1974).
11. A. Masaki, M. Yasui, and I. Yamashita, *J. Macromol. Sci.-Chem.*, **A6**(7), 1285 (1972).
12. Y. Iwakura, T. Kurosaki, and N. Nakabyashi, *Markromol. Chem.*, **44**, 570 (1961).
13. K. S. V. Srinivasan, N. Radhakrishnan, and H. K. Pillai, *J. Appl. Polym. Sci.*, **37**, 1551 (1989).
14. K. Itoyama, M. Dohi, and K. Ichikawa, *J. Adhes. Soc. Jpn.*, **20**(6), 268 (1984).
15. D. R. Paul and S. Newman, *Polymer Blends*, Academic Press, New York, 1978, Vols. I and II.
16. D. R. Paul, C. E. Locke, and C. E. Vinson, *Polym. Eng. Sci.*, **13**, 202 (1973).
17. C. E. Locke and D. R. Paul, *J. Appl. Polym. Sci.*, **17**, 2597 (1973).
18. D. R. Paul, C. E. Locke, and C. E. Vinson, *Polym. Eng. Sci.*, **12**, 157 (1972).
19. C. H. Choi, C. K. Park, C. S. Ha, B. K. Kim, and W. J. Cho, *Polymer (Korea)*, **16**(2), 344 (1992).