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클로로프렌과 에틸메타크릴레이트 공중합체의 합성과 상용화 효과

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Synthesis and Its Compatibilizing Effect of Poly(chloroprene-co-ethylmethacrylate)

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요 약 : 클로로프렌(CP)과 에틸메타크릴레이트(EMA) 공중합체(Poly(CP-co-EMA))를 라디칼 용액 중합으로 합성하였다. 본 연구에서 제조된 공중합체는 무정형이었고, 유리전이온도는 −34.5℃이었다. 공중합체의 단량체 상대반응성비는 r_1(CP)은 2.11이었고, r_2(EMA)는 0.27이었다. 폴리클로로프렌(CR)과 폴리에틸메타크릴레이트(PEMA)를 각각 THF에 녹여 블렌드를 얻었고, 이들 블렌드의 상용성을 유리전이온도와 모폴로지로서 조사하였다. 또한, 무게비 50/50 조성의 CR과 PEMA 블렌드에 Poly(CP-co-EMA)와 클로로프렌에 EMA를 그라프트시킨 공중합체 (Poly(CR-g-EMA))를 각각 10～50phr 첨가했을 때의 상용성을 조사하였다. CR/PEMA 블렌드는 서로 상용성이 없었지만, 첨가된 Poly(CP-co-EMA) 혹은 Poly(CR-g-EMA)의 존재하에서는 상용성 향상효과가 현저하게 나타났으며, Poly(CP-co-EMA)이 Poly(CR-g-EMA)에 비해 양호한 효과를 나타내었다.

Abstract : A copolymer of chloroprene(CP) and ethylmethacrylate(EMA) (poly(CP-co-EMA)) was prepared by radical solution copolymerization. The copolymer was amorphous and had glass transition temperature of about −34.5℃. The monomer reactivity ratios were given as r_1(CP)=2.11 and r_2(EMA)=0.27 in the copolymerization of CP and EMA, respectively. Miscibility of blends of polychloroprene(CR) and polyethylmethacrylate (PEMA), prepared by casting from tetrahydrofuran(THF), were investigated by their glass transition temperature behavior and morphologies. Compatabilization effect of poly(CP-co-EMA) was also studied for the CR/PEMA blend of 50/50 wt.% composition. For comparision, the graft copolymer of EMA onto CR (poly(CR-g-EMA)) was also prepared. The blends of CR and PEMA were incompatible. The addition of Poly(CP-co-EMA) or poly(CR-g-EMA) enhanced miscibility between CR and PEMA. The compatibilizing effect of Poly(CP-co-EMA) was more prominent in the blends consisting of each homopolymer than poly(CR-g-EMA).

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INTRODUCTION

Polychloroprene(CR) is one of the most commonly used synthetic rubbers in adhesives and the automotive or energy industries because of high mechanical strength, good resistance to hydrocarbon oils and polar solvents and chemicals, adequate low-temperature behavior, and compatibility with other rubbers.[1~5] However, its poor heat resistance and weatherability limit the outdoor use. The preparation of copolymers of chloroprene or graft copolymers of CR has been studied extensively.[6~13] To improve the poor performances, the introduction of a second monomer into the CR backbone or the use of appropriate fillers for compounding has been widely investigated.[1,2]

Compatibilizers or interfacial agents in polymer blends have been attracted much interests from theoretical and practical standpoints.[14~17] Moreover, the use of a copolymer, especially 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 ethylmethacrylate. The copolymers were charaterized with IR and ^{1}H-NMR spectroscopies. The compatibilizing effect of the copolymer in blends containing each homopolymer, CR and poly(ethylmethacrylate), was investigated. For comparision, a graft copolymer of ethylmethacrylate onto CR was also prepared. The miscibility of blends was discussed in terms of their glass transition temperature behavior and morphologies using differential scanning calorimetry(DSC) and scanning electron microscopy(SEM),respectively.

EXPERIMENTAL

Materials

Ethylmethacrylate(Aldrich) and benzene(Aldrich) were purified by the standard methods. 2,2'-azobisisobutylonitrile(AIBN) was purified by recrystallization 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 purifications.

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

Chloroprene(CP) was prepared by reacting DCB in aqueous solution of sodium hydroxide in the presence of THFA at 60℃ by the same method described as in our previous work.[18] The mole ratio of DCB/NaOH/THFA/H_2O was 1/1.3/1.5/1.5. Dehydrochlorination of DCB was carried out in 250ml of three-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 and the fraction collected at 25℃ and 160 mmHg was retained for copolymerization. The purity of chloroprene was confirmed to be 99.5% by gas chromatography and the yield of chloroprene was 85%. Chloroprene was used as soon as possible after distillation because it was polymerized slowly during storage,even at low temperature. The structure of chloroprene was identified by IR spectrophotometry(Perkin Elmer 1330) and ^{1}H-NMR spectroscopy(Bruker 300 CW).

Synthesis of Polychloroprene and Polyethylmethacrylate

The polychloroprene(CR) and polyethylmethacrylate (PEMA) were obtained in a glass ampoule by polymerizing 0.2 mole of CP or EMA with 0.2 mole% of AIBN as an initiator at 50℃ in 100ml of benzene for 10 hours.

After reaction, the reaction mixture was poured into a large amount of methanol. The product of CR or PEMA recovered from metanol was dried under vacuum at 30℃ to remove all volatiles.

Synthesis of Poly(chloroprene-co-ethylmethacrylate)(poly(CP-co-EMA))

The copolymer of chloroprene and ethylmethacrylate 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 EMA(M_2) in benzene(ranged 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, for example, 0.20 mole of chloroprene and 0.20 mole of EMA were radically polymerized with 0.2 mole% AIBN as an initiator at 50℃ in 100ml of benzene.

Poly(CP-co-EMA) was identified by FT-IR spectroscopy(Mattson Galaxy series 6030). The FT-IR spectra of CR, polyethylmethacrylate(PEMA) and poly(CP-co-EMA) were illustrated in Figs. 1, 2 and 3, respectively. The FT-IR spectrum of poly (CP-co-EMA) exhibited characteristic peaks of stretching vibration of vinyl C-H bond at 3020 and 3100 cm^{-1}. The peaks of C-Cl bond, C=O bond and C=C double bond were appeared at 600~800, 1750, and 1660 cm^{-1},respectively.

Synthesis of Poly(chloroprene-g-ethylmethacrylate)(poly(CR-g-EMA))

The graft copolymerization of EMA onto CR was carried out in 100ml of a glass tube. 1 g of CR was dissolved in 10 ml of benzene. 0.20 mole of EMA was dissolved in 20ml of benzene and then added 0.20 mole% of AIBN. The tube was sealed after charging with argon and the reaction was carried out for 10 hrs. The precipitate from methanol was filtered and dried in vacuum to constant weight.

The FT-IR spectrum of poly(CR-g-EMA), as shown in Fig. 4, exhibited characteristic peaks of C=O bond at 1750 cm^{-1}, C=C double bond at 1660 cm^{-1} and C-Cl bond at 600~800 cm^{-1}.

Blends of CR/PEMA,CR/PEMA/Poly(CP-co-EMA) and CR/PEMA/Poly(CR-g-EMA)

The blends were prepared by dissolving the component polymers in THF. The 15 wt.% of component solutions in THF were casted on a glass plates and most of the solvents were allowed to evaporate slowly in the air at room temperature. The films obtained were completely dried in vacuum at 30℃ to constant weight. The compositions of the blends and the sample notations are listed in Table 1.

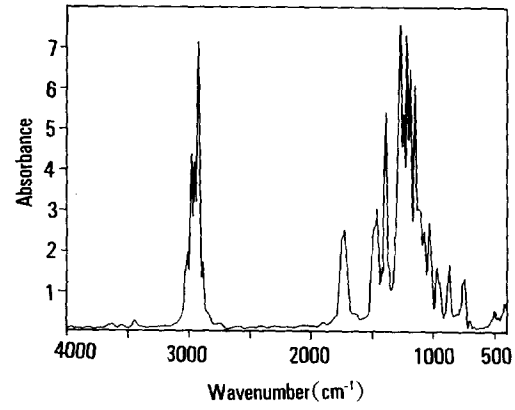

Fig. 2. FT-IR spectrum of polyethylmethacrylate (PEMA).

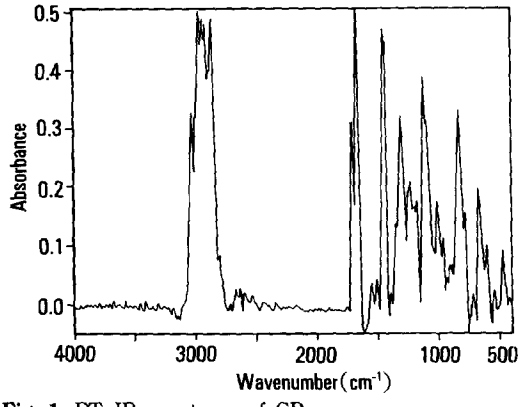

Fig. 1. FT-IR spectrum of CR.

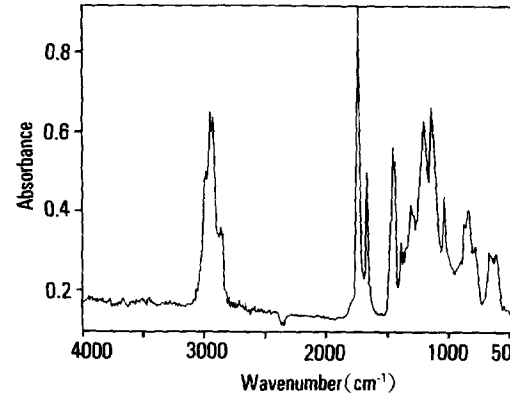

Fig. 3. FT-IR spectrum of poly(CP-co-EMA).

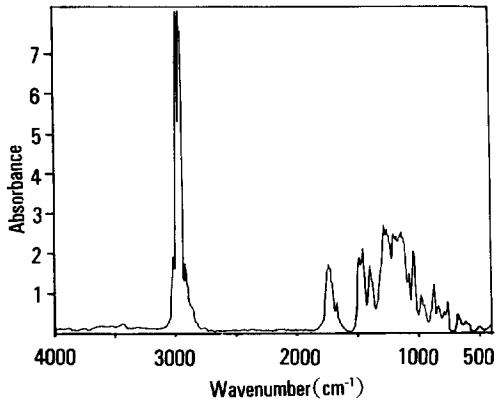

Fig. 4. FT-IR spectrum of poly(CR-g-EMA).

Table 1. Sample Notation

Sample notation	Composition by wt. CR	PEMA	Poly (CP-co-EMA)	Poly (CR-g-EMA)
C100	100	–	–	–
C90E10	90	10	–	–
C80E20	80	20	–	–
C70E30	70	30	–	–
C60E40	60	40	–	–
C50E50	50	50	–	–
C40E60	40	60	–	–
C30E70	30	70	–	–
C20E80	20	80	–	–
C10E90	10	90	–	–
E100	–	100	–	–
CE-C1	50	50	10	–
CE-C2	50	50	20	–
CE-C3	50	50	30	–
CE-C4	50	50	40	–
CE-C5	50	50	50	–
CE-G1	50	50	–	10
CE-G2	50	50	–	20
CE-G3	50	50	–	30
CE-G4	50	50	–	40
CE-G5	50	50	–	50

Measurements

Molecular weight; The molecular weight of polymers were 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 a differential scanning calorimetry(DSC ; DuPont 2100). The thermograms of the blends were obtained at a heating rate of 10℃/min.

Morphology ; Scanning electron micrographs (SEM) were obtained by 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-EMA) was determined as $\overline{M}_n$=58,300, $\overline{M}_w$=71,000. 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-EMA) was determined as $\overline{M}_n$=74,000 and $\overline{M}_w$=166,000. For reference, the molecular weights of CR and PEMA were determined as $\overline{M}_n$ = 81,000 and $\overline{M}_w$=194,000(CR) ; $\overline{M}_n$=190,000 and $\overline{M}_w$=283,000(PEMA).

Fig. 5 shows DSC thermograms of CR, PEMA, poly(CR-g-EMA) and poly(CP-co-EMA). The T_g's of homopolymers were 57.5℃ and −45.0℃ for PEMA and CR, respectively. The copolymer has T_g of −34.5℃ , which is higher by about 10℃ than that of CR. The CR exhibited a melting peak around at 52.8℃ but the copolymer does not show any melting peak, meaning that the CR has some degree of crystallinity whereas the copolymer is amorphous. This kind of thermal characteristic of a chloroprene-containing copolymer was also oberseved in the case of poly(chloroprene-co-maleic anhydride).[18] However, the graft copolymer, poly (CR-g-EMA) showed T_g of −42.3℃ with a small degree of crystallinity, exhibiting a melting peak at 51.9℃.

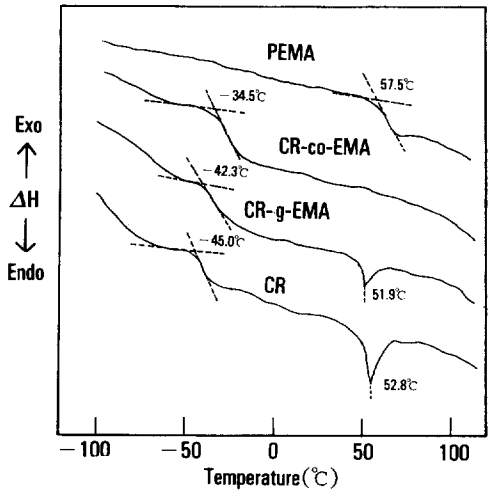

Fig. 5. DSC thermograms of various samples.

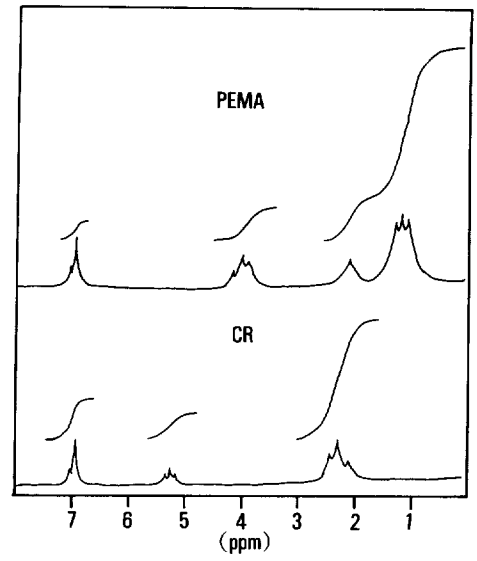

Fig. 6. ^{1}H-NMR spectra of CR and PEMA.

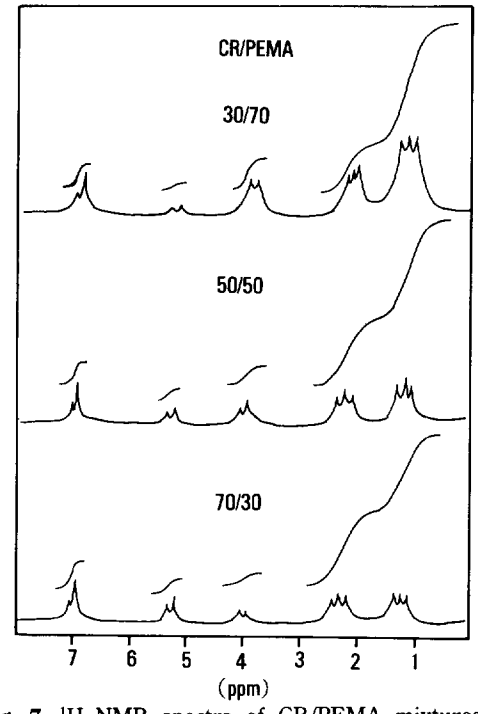

Fig. 7. ^{1}H-NMR spectra of CR/PEMA mixtures of three different compositions, 30/70, 50/50, and 70/30 by weight %.

Monomer Reactivity Ratios

To determine monomer reactivity ratios, all radical copolymerizations of CP and EMA were carried out in the presence of AIBN as an initiator in benzene at 50℃, and their conversions were adjusted to be less than 10%. The monomer ratios in feed, [EMA]/[CP], were varied from 0.43 to 2.33.

The compositions of poly(CP-co-EMA) were determined by using ^{1}H-NMR spectroscopy(Bruker 300 CW). Fig. 6 shows ^{1}H-NMR spectra of CR and PEMA. The resonance peaks of the methine and methylene protons of CR were appeared at δ=5.1~5.5 and 2.0~2.8 ppm, respectively. Those of OC_2H_5, methylene, and $-CH_3$ protons of PEMA were appeared at δ=3.8~4.2, 2.0~2.8, and 0.8~1.3 ppm, respectively. The $-CH_3-$ protons appeared in PEMA only were used to determine the copolymer compositions. In Fig. 7, Typical ^{1}H-NMR spectra of CR/PEMA mixtures of three different compositons, i.e. 30/70, 50/50, and 70/30 by weight % were illustrated, where the resonance peaks of the methine, methylene, OC_2H_5 and $-CH_3$ protons of the homopolymer mixtures were appeared at δ=5.1~5.5, 2.0~2.8, 3.8~4.2 and 0.8~1.3 ppm, respectively.

From the integrated areas at the resonance peaks due to $-CH_3$ protons in CR/PEMA mixtures having various compositions, a calibration curve was obtained to determine compositions of poly

(CP-co-EMA). The mole fractions of CP and EMA, thus obtained, were tabulated in Table 2. From the data, the Finneman-Ross plot in copolymerization of CP(M_1) and EMA(M_2) could be drawn , as shown in Fig. 8.

In Fig. 8, the monomer reactivity ratios are determined as r_1(CP)=2.11 and r_2(EMA)=0.27 in the copolymerization of CP and EMA.

Miscibility of CR/PEMA Blends

Fig. 9 shows typical DSC thermograms of CR/PEMA blends. The glass transition temperatures are nearly constant regardless of PEMA contents. This result means that CR and PEMA is incompatible.

Table 3 shows the glass transition temperatures of CR/PEMA/Poly(CP-co-EMA) and CR/PEMA/Poly(CR-g-EMA) 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 50 phr based on the CR/PEMA mixture. The T_g's of CR and PEMA were not significantly changed when the content of the graft copolymer added was below 40 phr. However, when the graft copolymer was added to the binary CR/PEMA

Table 2. Determination of Monomer Reactivity Ratios for the Copolymerization of CP(M_1) and EMA(M_2)

Sample	$F=\frac{[M_2]}{[M_1]}$	$F=\frac{m_2}{m_1}$	F^2	$F-1$	$\frac{(f-1)}{F}$	f/F^2
CE-1	0.43	0.18	0.185	-0.82	-1.90	0.97
CE-2	0.67	0.27	0.449	-0.73	-1.09	0.60
CE-3	1.00	0.37	1.00	-0.63	-0.63	0.37
CE-4	1.50	0.52	2.25	-0.48	-0.32	0.23
CE-5	2.33	0.75	5.43	-0.25	-0.11	0.14

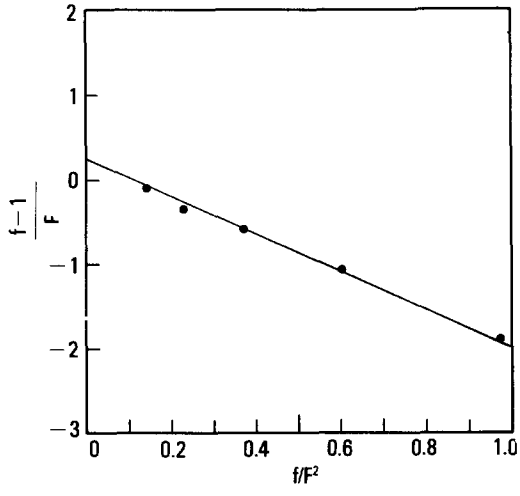

Fig. 8. Finneman-Ross plot for copolymerization of chloroprene(r_1=2.11) and ethylmethacrylate(r_2=0.27) at 50℃.

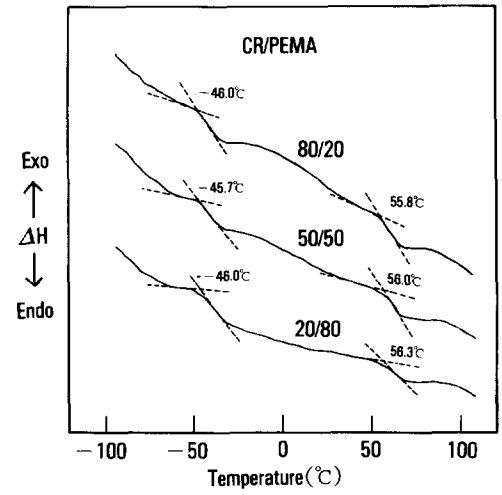

Fig. 9. DSC thermograms of CR/PEMA blends.

Table 3. Effect of Poly(CP-co-EMA) and Poly(CR-g-EMA) Content on the Glass Transition Temperatures of 50/50 CR/PEMA Blends

	Contents (phr)	Tg, CR (℃)	Tg, PEMA (℃)
Poly	0	−45.7	56.0
(CR-g-EMA)	10	−45.0	56.0
	20	−44.8	55.8
	30	−44.8	55.0
	40	−44.6	45.0
	50	−43.8	27.0
Poly	0	−45.7	56.0
(CP-co-EMA)	10	−43.5	53.0
	20	−42.6	47.0
	30	−41.0	29.8
	40	−32.7	26.2
	50	−30.9	23.2

blend with the amount of more than 40phr, the T_g's of the blend significantly shifted inward to those of other homopolymers.

Such trend was more clearly seen in the case of poly(CP-co-EMA) addition to the 50/50 CR/PEMA blend. When more than 20 phr of the copolymer were added to the binary blend, the T_g's of each homopolymer change considerably, even though the ternary blend consisting of each homopolymer and the copolymer show two separate T_g's. One can see that compatibilization was achieved in the CR/PEMA blend of 50/50 composition by weight in the presence of both the copolymer and graft copolymer. The T_g's of the ternary blends increased with increasing poly(CP-co-EMA) or poly(CR-g-EMA) contents. It should be noted that the addition of poly(CP-co-EMA) showed better compatibilizing effect for the 50/50 CR/PEMA blends than the addition of poly(CR-g-EMA).

The enhancement of the miscibility in the 50/50 CR/PEMA blend by those copolymers was also confirmed by the morphological studies. The morphologies of CR/PEMA, CR/PEMA/Poly(CP-co-EMA) and CR/PEMA/Poly(CR-g-EMA) blends were analyzed by scanning electron microscopy (SEM). In these SEM micrographs, it was observed that PEMA always formed continuous phases and thus exhibited brittle fracture behaviors due to the glassy matrices in liquid nitrogen temperature.

Fig. 10(a) shows the SEM micrograph of the CR/PEMA blend of 50/50 composition by weight. It can be seen that the CR/PEMA blend is incompatible and the phase is grossly separated. When 40 phr of poly(CR-g-EMA) or poly(CP-co-EMA) was added to the binary blend, the morphology changes(see Fig. 10(b) and (c)). The SEM micrograph of the ternary blend consisting of poly (CR-g-EMA)(Fig. 10-b) shows finer domain structure than the binary blend without the graft copolymer. It is cleary seen that the ternary blend(c) consisting of poly(CP-co-EMA) shows much finer domain structure than the ternary blend(b) consisting of poly(CR-g-EMA) as well as the binary blend(a). The result again implies that the addition of poly(CP-co-EMA) was more effective to enhance the miscibility of CR and PEMA than poly (CR-g-EMA).

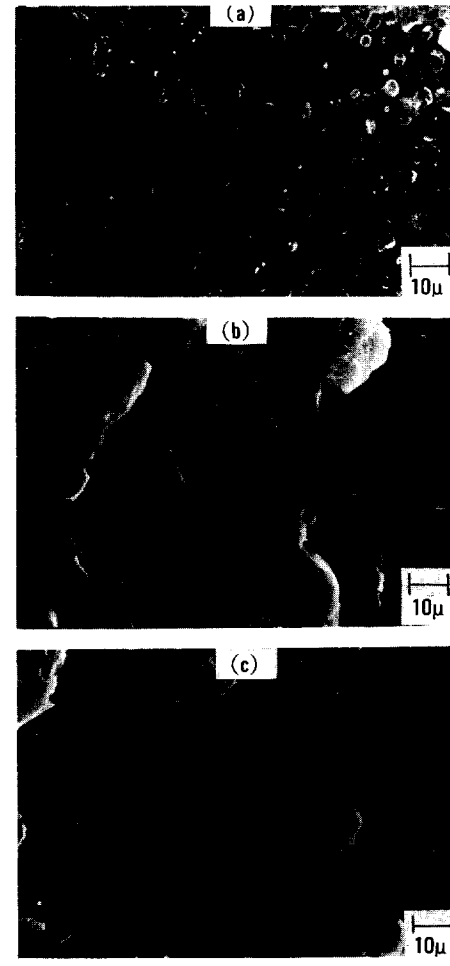

Fig. 10. SEM micrographs of samples : (a) 50/50 CR /PEMA blend ; (b) 50/50 CR/PEMA blends+40phr Poly(CR-g-EMA) ; (c) 50/50 CR/PEMA blends+40 phr poly(CP-co-EMA).

CONCLUSIONS

In this work, the copolymerization of chloroprene(CP) and ethylmethacrylate(EMA) was carried out and compatibilizing effect of the resulting

copolymer was investigated in CR/PEMA blends. For comparision, poly(CR-g-EMA) was also prepared. Conclusions follow ;

1. The monomer reactivity ratios were given as $r_1(CP)=2.11$ and $r_2(EMA)=0.27$ in the copolymerization of CP and EMA.

2. The copolymer, poly(CP-co-EMA) was amorphous and has glass transition temperature of $-34.5℃$, whereas CR has T_g of $-45.0℃$ and melting temperature of 52.8℃.

3. CR and PEMA was incompatible. The addition of poly(CR-g-EMA) as well as poly(CP-co-EMA), however, enhanced miscibility of CR and PEMA.

4. The addition of poly(CP-co-EMA) was more effective to enhance miscibility between CR and PEMA in the CR/PEMA blend of 50/50 composition by weight than poly(CR-g-EMA).

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