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폴리클로로프렌/폴리글리시딜메타크릴레이트 블렌드의 상용성과 Poly(chloroprene-co-glycidylmethacrylate) 첨가의 영향

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Miscibility of Polychloroprene/Polyglycidylmethacrylate Blends and Effects of Poly(chloroprene-co-glycidylmethacrylate) Addition

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요 약 : 폴리클로로프렌(CR)과 폴리글리시딜메타크릴레이트(PGMA)를 각각 THF에 녹여서 블렌드 물을 만들고, 이들 블렌드의 상용성을 유리전이온도 측정과 모폴로지 관찰로서 조사하였고, X-ray Diffractometer를 통해 이들의 결정성을 관찰하였다. 또한 무게비 50/50 조성의 CR-PGMA 블렌드에 클로로프렌-글리시딜메타크릴레이트 공중합체(poly(CP-co-GMA))를 10～40 phr 첨가했을 때의 상용성을 조사하였으며, 클로로프렌에 GMA를 그라프트시킨 공중합체(poly(CR-g-GMA))를 동일한 방법으로 첨가하였을 때의 상용성과 비교하였다. CR/PGMA 블렌드는 서로 상용성이 없었지만, poly(CP-co-GMA) 혹은 poly(CR-g-GMA)를 첨가하였을 때는 상용성 효과가 현저하게 나타났으며, poly(CP-co-GMA)는 poly(CR-g-GMA)에 비해 더욱 양호한 효과를 나타내었다. 또한, CR/PGMA 블렌드에 대해 공중합체 혹은 그라프트 공중합체 첨가가 블렌드의 결정화도 및 결정구조에 미치는 영향을 고찰하였다.

Abstract : Miscibility of blends of polychloroprene(CR) and polyglycidylmethacrylate(PGMA), prepared by casting from tetrahydrofuran(THF), was investigated by their glass transition temperature behaviors and morphologies. Crystalline structure of the blends was investigated using an X-ray diffractometer. Compatibilization effect of a copolymer of chloroprene(CP) and glycidylmethacrylate(GMA) (poly(CP-co-GMA)) was studied for the CR/PGMA blend of 50/50 wt.% composition. For comparison, the graft copolymer of GMA onto CR, (poly(CR-g-GMA)) was also prepared. The blends of CR and PGMA were incompatible. The addition of poly(CP-co-GMA) or poly(CR-g-GMA) enhanced miscibility between CR and PGMA. The compatibilizing effect of poly(CP-co-GMA) was more prominent in the blend consisting of each homopolymer than poly(CR-g-GMA). The effects of the copolymer or the graft copolymer on the crystalline structure and the degree of crystallinity of the blend were also dicussed.

Miscibility of Polychloroprene/Polyglycidylmethacrylate Blends and Effects of Poly(chloroprene-co-glycidylmethacrylate) Addition

INTRODUCTION

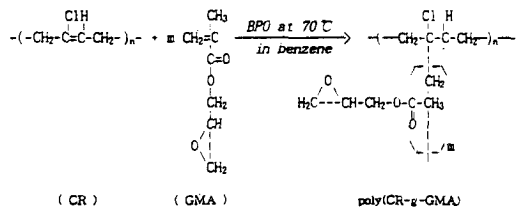
The use of a copolymer or a graft copolymer as a compatibilizer or interfacial agent in incompatible homopolymer/homopolymer blends have been attracted much interest from both the theoretical and practical standpoints in the field of polymer blends.[1~3] To improve the compatibility in incompatible binary polymer blends containing polychloroprene(CR), copolymers or graft copolymers of chloroprene have been studied extensively.[4~9] In our earier reports,[10~12] we synthesized copolymers of chloroprene(CP) with ethylmethacrylate (EMA), isobutylmethacrylate(iBMA) and maleic anhydride(MAH), (poly(CP-co-EMA), poly(CP-co-iBMA) and poly(CP-co-MAH), respectively) and their corresponding graft copolymers of EMA, iBMA, and MAH onto CR(poly(CR-g-EMA), poly (CR-g-iBMA) and poly(CR-g-MAH), respectively). A copolymer of chloroprene with glycidylmethacrylate(GMA)(poly(CP-co-GMA)) was prepared by the same method described as in our previous work.[13] For comparison, the graft copolymer of GMA onto CR(poly(CR-g-GMA)) was also prepared.

In this work, we obtained blends of polychloroprene(CR) and polyglycidylmethacrylate(PGMA) by casting from THF. The compatibilizing effects of the copolymer or the graft copolymer in blends containing each homopolymer, CR and PGMA, were investigated. The miscibilities of blends were discussed in terms of their glass transition temperature behaviors and morphologies using differential scanning calorimetry(DSC) and scanning electron microscopy(SEM), respectively. The crystalline structure of the CR/PGMA blends was studied by X-ray diffractometry.

EXPERIMENTAL

Materials. Glycidylmethacrylate(Aldrich) and benzene(Aldrich) were purified by the standard methods. 2,2'-Azobisisobutylonitrile(AIBN) and benzoyl peroxide(BPO) were purified by recrystallization in dehydrated ethanol. 3,4-Dichloro-1-butene(DCB)(Aldrich), tetrahydrofurfuryl alcohol (THFA)(Aldrich), sodium hydroxide(NaOH) (Junsei), dioxane(Junsei), and isopropyl alcohol (IPA)(Junsei) were used as received without further purifications.

Synthesis of Polymers. Polychloroprene(CR) and polyglycidylmethacrylate(PGMA) were obtained by the same method described as in our previous work.[13] Preparation of the poly(chloroprene-co-glycidylmethacrylate)(poly(CP-co-GMA)) is described elsewhere.[13] Poly(chloroprene-g-glycidylmethacrylate)(poly(CR-g-GMA)) was synthesized by graft copolymerization of GMA onto CR with BPO as an initiator at 70℃ in benzene for 10 hours. In this reaction, CR of a commercial grade (Denka A-90 ; $\overline{M}_n = 23{,}000$, $\overline{M}_w = 55{,}000$), supplied from Denka Co.(Japan), was used. After reaction, the reaction mixture was poured into a large amount of methanol. In the case of the graft copolymerization, the product recovered from methanol was poured once more into a large amount of isopropyl alcohol(IPA) to separate PGMA, and a large amount of dioxane to separate CR in the reaction mixture, respectively. The product of CR and PGMA recovered from methanol was dried under vacuum at 30℃ to remove all volatiles. The structures of polymers were confirmed by FT-IR examination(Mattson Galaxy series 6030). The reaction scheme of poly(CR-g-GMA) is as follows.



The grafting ratio and grafting efficiency of the graft copolymer were determined as 160% and 52 %, respectively, which were estimated from the following equations,[14]

$$\text{grafting ratio}(\%) = \frac{\text{weight of polymer in grafts}}{\text{weight of substrate}} \times 100$$

$$\text{grafting efficiency}(\%) = \frac{\text{weight of polymer in grafts}}{\text{total weight of polymer formed}} \times 100$$

Blends of CR/PGMA, CR/PGMA/Poly(CP-co-GMA) and CR/PGMA/Poly(CR-g-GMA). 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 completely dried in vacuum at 30℃ to constant weight. The compositions of the blends and the sample notations are listed in Table 1.

Measurements

Molecular Weight : The molecular weight of polymers was measured by gel permeation chromatography(GPC ; Water 244) 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. The T_g value was taken as the initial onset of the change of slope in the DSC curve on the second run.

X-ray Diffractometry : X-ray diffraction patterns were obtained by an X-ray diffractometer(Rigaku Denki) using nickel filtered CuK_α radiation(30 kV, 20 mA).

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.

Table 1. Sample Notation

Sample notation	Composition by wt.%			
	CR	PGMA	Poly(CP-co-GMA)*	Poly(CR-g-GMA)*
C100	100	–	–	
C80G20	80	20	–	
C70G30	70	30	–	
C60G40	60	40	–	
C50G50	50	50	–	–
C40G60	40	60	–	–
C30G70	30	70	–	–
C20G80	20	80	–	–
G100	–	100	–	–
CG-C1	50	50	10	–
CG-C2	50	50	20	–
CG-C3	50	50	30	–
CG-C4	50	50	40	–
CG-G1	50	50	–	10
CG-G2	50	50	–	20
CG-G3	50	50	–	30
CG-G4	50	50	–	40

* Units in phr based on the 50/50 CR/PGMA mixture

RESULTS AND DISCUSSION

Characterization. Polychloroprene(CR), polyglycidylmethacrylate(PGMA), and poly(CP-co-GMA) were identified by FT-IR spectroscopy as already reported by the authors.[13] The molecular weights of CR, PGMA and poly(CP-co-GMA) were reported as $\overline{M}_n$=81,000, $\overline{M}_w$=194,000(CR) ; $\overline{M}_n$=77,000, $\overline{M}_w$=126,400(PGMA) ; $\overline{M}_n$=45,600, $\overline{M}_w$=74,200(poly(CP-co-GMA)), respectively.

Poly(CR-g-GMA) was identified by FT-IR spectroscopy(Mattson Galaxy series 6030). The FT-IR spectrum of poly(CR-g-GMA), as shown in Fig. 1, 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}. The FT-IR spectrum of poly(CR-g-GMA) exhibited also characteristic peaks of stretching vibration of vinyl C-H bond at 3020 and 3100 cm^{-1}. The peaks of epoxy groups for the poly(CR-g-GMA) were appeared at 1100~1200 cm^{-1}. The molecular weight of poly(CR-g-GMA) was determined as $\overline{M}_n$=63,000, $\overline{M}_w$=128,000.

Fig. 2 shows DSC thermograms of CR, PGMA, poly(CP-co-GMA) and poly(CR-g-GMA). The T_g's

of homopolymers were 63.7℃ and −45.7℃ for PGMA and CR, respectively. The copolymer has T_g of −16.4℃, which is higher by about 36.4℃ 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. The graft copolymer, poly(CR-g-GMA) showed two T_g's ; T_g of −29.7℃ for CR, which is higher by about 17.7℃ than that of CR, and is lower by about 13.3℃ than that of poly(CP-co-GMA), and T_g of 45.3℃ for PGMA, which is lower by about 18.4℃ than that of PGMA, respectively.

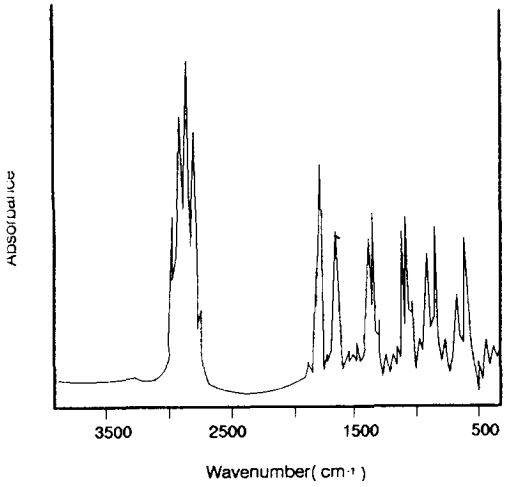


Fig. 1. FT-IR spectrum of Poly(CR-g-GMA).

Fig. 3 shows the X-ray diffractograms of CR, PGMA, poly(CP-co-GMA), and poly(CR-g-GMA). The X-ray diffractogram of the CR shows four sharp crystalline reflection peaks in the region of the Bragg angle(2θ) between 10° and 40°. Those diffraction peaks of CR are located at the diffraction angles 2θ of 19.7, 21.9, 26.2 and 28.4°, respectively. The diffraction pattern of the PGMA shows double peaks at 2θ values of 18.0~20.0°. It is quite interesting to note that the poly(CP-co-GMA) did not show any crystalline peaks, in accord with the DSC result mentioned above, while the diffraction peaks of poly(CR-g-GMA) shows four crystalline reflection peaks at 2θ of 20.0, 21.8, 26.0 and 28.8°, respectively.

It should be noted that the poly(CR-g-GMA) exhibits crystalline structure, even though the crystalline melting temperature was not detected in DSC measurement. The result implies that the graft copolymer has some degree of crystallinity, although that is much smaller compared to that of CR, while the poly(CP-co-GMA) was purely amorphous.

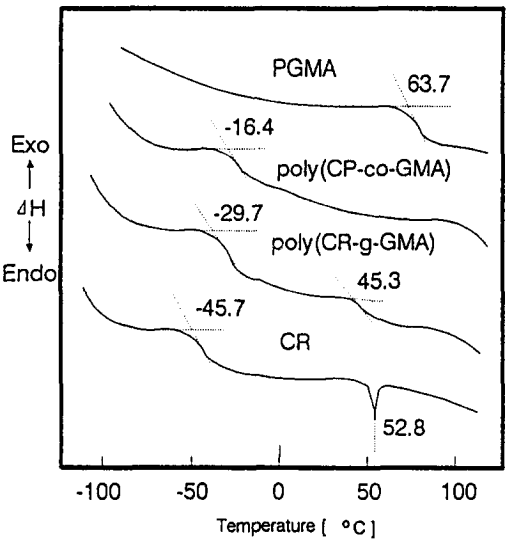


Fig. 2. DSC thermograms of the various samples.

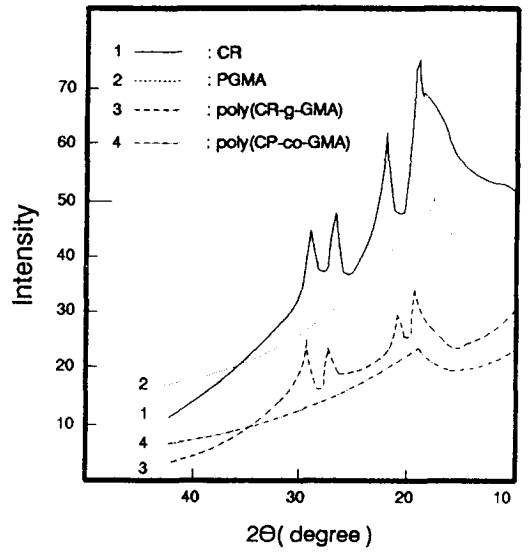


Fig. 3. X-ray diffractograms of various samples.

Miscibility of CR/PGMA Blends. Fig. 4 shows typical DSC thermograms of CR/PGMA blends. The glass transition temperatures of CR/PGMA binary blends over the entire blend concentrations are also listed in Table 2. The blends show two separate glass transition temperatures, which are nearly identical with those of each homopolymer regardless of the blend concentrations. This result means that CR and PGMA are incompatible. It was reported that the homologous polymethacrylates are usually miscible with other chlorine containing polymers, such as polyvinylchloride or chlorinated polyethylene, because of the molecular interaction between ether group in the polymethacrylates and the Cl group in chlorine-containing polymers.[15~17] It has been also reported, however, that the miscibility becomes weaker as the chlorine contents becomes smaller in the chlorine-containing polymers.[18] The CR used in this work has ca. 35 wt.% of chlorine. Thus, it is not surprising that the CR was not miscible with polyglycidylmethacrylate in spite of their chlorine in the chain.

In Figs. 5 and 6, the glass transition temperatures of CR and PGMA in ternary blends containing poly(CP-co-GMA) or poly(CR-g-GMA) are plotted against the weight concentrations of the copolymers. 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/PGMA mixture. When either the copolymer or the graft copolymer was added to the CR/PGMA binary blend, the T_g's of each homopolymer change considerably, even though the ternary blends consisting of each homopolymer and the copolymers show two separate T_g's.

Those results imply that compatibilization was achieved in the CR/PGMA blends of 50/50 composition by weight in the presence of both the co-

Table 2. Glass Transition Temperatures of Polychloroprene and Polyglycidylmethacrylate in the CR/PGMA Blends

Sample notation	contents (wt. %)	T_g, CR (℃)	T_g, PGMA (℃)
C100	100 : 0	−45.7	−
C80G20	80 : 20	−44.3	61.4
C70G30	70 : 30	−44.3	59.7
C60G40	60 : 40	−44.6	61.4
C50G50	50 : 50	−44.7	63.7
C40G60	40 : 60	−44.3	62.8
C30G70	30 : 70	−44.8	63.7
C20G80	20 : 80	−44.0	63.3
G100	0 : 100	−	63.7

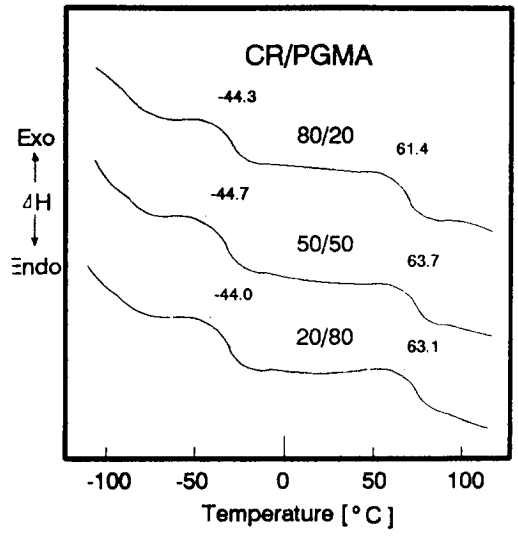


Fig. 4. DSC thermograms of CR/PGMA blends.

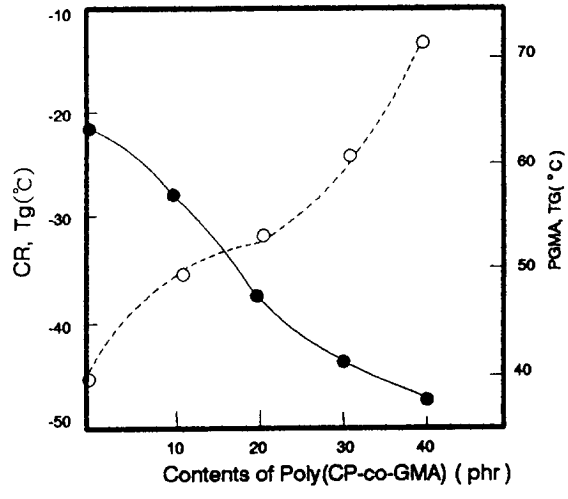


Fig. 5. Changes of the glass transition temperatures of CR(○), and of PGMA(●) in the presence of poly (CP-co-GMA) in the 1/1 CR/PGMA blends.

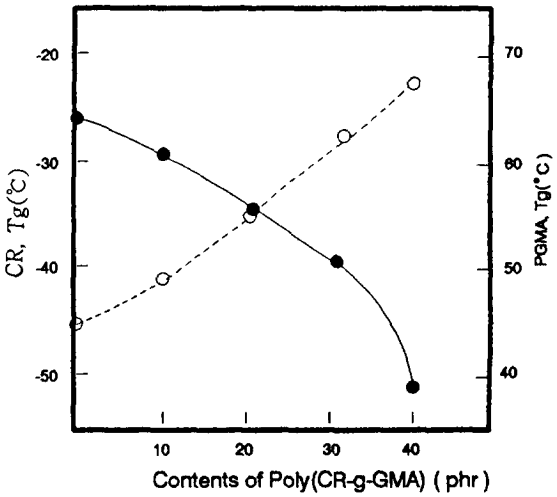


Fig. 6. Changes of the glass Transition temperatures of CR(○), and of PGMA(●) in the presence of poly (CR-g-GMA) in the 1/1 CR/PGMA blends.

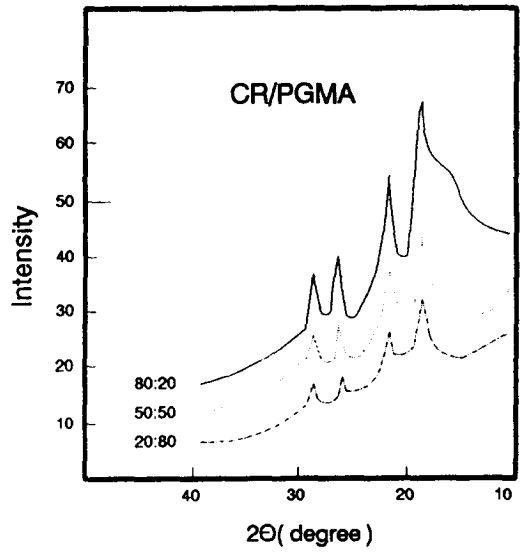


Fig. 7. X-ray diffractograms of CR/PGMA blends.

polymer and the graft copolymer. Comparison of Figs. 5 and 6 indicates that the copolymer shows better compatibilizing effect for the 50/50 CR/PGMA blends than the graft copolymer.

Fig. 7 shows the X-ray diffractograms of the CR and PGMA binary blends. Those diffractograms show superpositions of each characteristic peaks of CR/PGMA homopolymer with no additional peaks. The crystallinity of the blends can be determined from the ratio of the total integrated scattered intensity due to the crystals to the total real scattered intensity due to the samples as a whole but the degree of cryatallinity of blends was not estimated in this work. Note, however, that the relative degree of crystallinity of blends decreased with increasing PGMA contents, taking into consideration that the relative degree of crystallinity is proportional to the total integrated scattered intensity. The crystal structure of the CR is independent of blend content as can be seen from the constancy of the scattering angles.[19]

The effect of PGMA contents on the relative degree of crystallinity of CR/PGMA blends is shown in Fig. 8. The intensities of the X-ray diffractograms of the binary CR/PGMA were decreased with increasing the composition of PGMA. In this

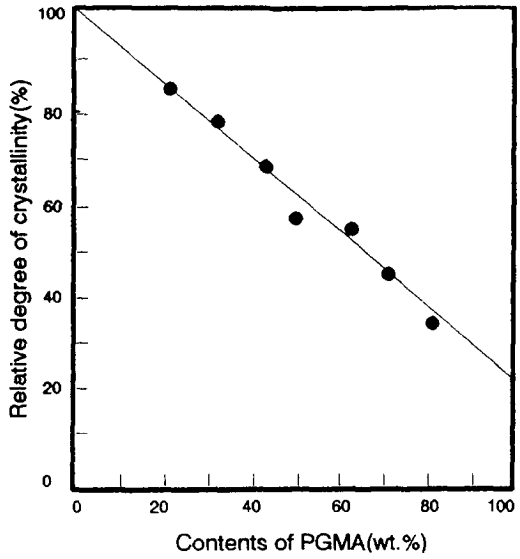


Fig. 8. Crystallinity with the PGMA content in the blends.

case, the degree of crystallinity of CR was set as 100%. The relative degree of crystallinity varies almost linearly with PGMA content in the blends. Crystallization in homopolymer/homopolymer blends has been studied extensively.[20~25]

Fig. 9 shows the relative degree of crystallinity of CR/PGMA/poly(CP-co-GMA) and CR/PGMA/

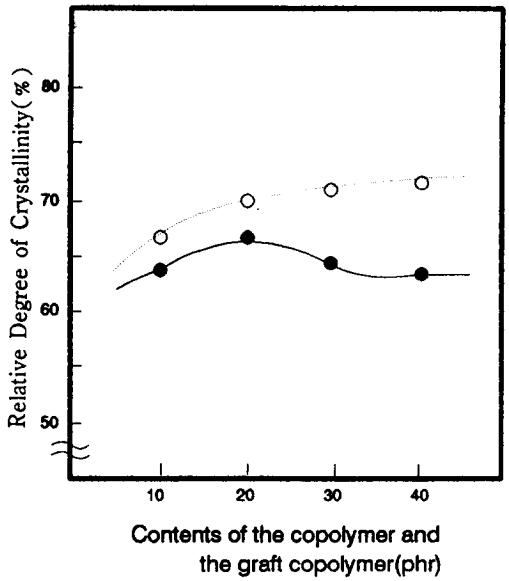


Fig. 9. Effects of the crystallinities in presence of poly (CP-co-GMA)(○) and poly(CR-g-GMA)(●) in the 1/1 CR/PGMA blends.

poly(CR-g-GMA) ternary blends. In this case, the composition of the CR/PGMA blend was fixed at 50/50 by weight and the content of copolymers ranged from 10 to 40 phr based on the CR/PGMA mixture. The degree of crystallinity slightly increased with increasing contents of the copolymer up to 20 phr and thereafter leveled off, when the copolymer was added. However, when the graft copolymer was added to the binary CR/PGMA blend, the degree of crystallinity of the blend showed a maxium at 20 phr of the graft copolymer contents.

This result means that the incorporation of poly (CP-co-GMA) and poly(CR-g-GMA) affected on the degree of crystallinity of the CR/PGMA blend with different mechanisms. It seems that the addition of the copolymer and the graft copolymer in CR/PGMA blends changes the overall surface morphology, i.e., the macroscopic phase continuity in fractured surface for SEM observations, even though the crystalline structure is not changed by their incorporations. That is, the fact that the incorporation of the amorphous copolymer increased the degree of crystallinity of the CR/PGMA blend

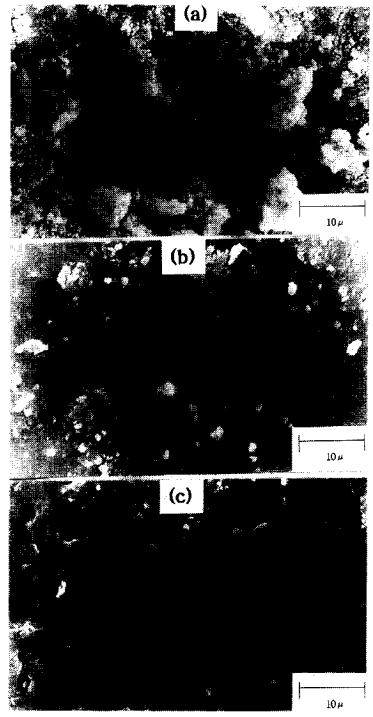


Fig. 10. SEM micrographs of samples : (a) 50/50 CR /PGMA ; (b) 50/50 CR/PGMA blends+30phr poly (CR-g-GMA) ; (c) 50/50 CR/PGMA blends+30phr poly(CP-co-GMA).

may be related to the change in overall surface morphology of the blend due to the interaction of the copolymer between CR and PGMA owing to the compatibilizing effect of the copolymer, whereas the effect is smaller in the case of the addition of the graft copolymer. The exact reason for the different results, however, is not clear at present.

The compatibilizing effect of the copolymer was also confirmed by the morphological studies. The morphologies of CR/PGMA, CR/PGMA/Poly(CP-co-GMA) and CR/PGMA/Poly(CR-g-GMA) blends were analyzed by scanning electron microscopy (SEM). Fig. 10(a) shows the SEM micrograph of the CR/PGMA blend of 50/50 composition by weight. It can be seen that the CR/PGMA blend is incompatible and the phase is grossly separated. When 30 phr of poly(CR-g-GMA) or poly(CP-co-GMA) was added to the binary blend, the morphology changes(see Figs. 10(b) and (c)).

The SEM micrograph of the ternary blend consisting of poly(CR-g-GMA)(Fig.10-b) shows finer domain structure than the binary blend without the graft copolymer. It is clearly seen that the ternary blend(c) consisting of poly(CP-co-GMA) shows much finer domain structure than the ternary blend(b) consisting of poly(CR-g-GMA) as well as the binary blend(a).

The result proves well our speculations that poly(CP-co-GMA) shows better compatibilizing effect for the CR/PGMA blend than poly(CR-g-GMA).

CONCLUSIONS

In this work, miscibility of CR and PGMA blends and the compatibilizing effect of poly(CP-co-GMA) in the 50/50 CR/PGMA blend were investigated. For comparison, poly(CR-g-GMA) was also prepared. Conclusions follow ;

1. The graft copolymer, poly(CR-g-GMA) has glass transition temperature of $-29.7℃$, and has some degree of crystallinity, whereas poly(CP-co-GMA) is amorphous.

2. CR and PGMA was incompatibile. The addition of poly(CR-g-GMA) as well as poly(CP-co-GMA), however, enhanced miscibility of CR and PGMA.

3. The addition of poly(CR-g-GMA) as well as poly(CP-co-GMA) significantly changed surface morphology of CR and PGMA blends, but did not change the crystalline structure of blends.

4. The addition of poly(CP-co-GMA) was more effective to enhance miscibility between CR and PGMA in the CR/PGMA blends than poly(CR-g-GMA).

5. The relative degree of crystallinity of the CR /PGMA blends varied almost linearly with PGMA contents.

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