Compatibilizing effects of copolymers of chloroprene and alkylmethacrylates with different alkyl groups in polychloroprene/poly(alkyl methacrylate) blends

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Miscibility of blends of polychloroprene (CR) and poly(alkyl methacrylate)s (PAMAs), such as poly(ethyl methacrylate) (PEMA), poly(isobutyl methacrylate) (PiBMA) and poly(glycidyl methacrylate) (PGMA) prepared by casting from tetrahydrofuran, were investigated by their glass transition temperature behaviours and morphologies. Since the blends of CR and PAMA were incompatible regardless of the different alkyl groups, copolymers of chloroprene and ethyl methacrylate (poly(CP-*co*-EMA)), isobutyl methacrylate (poly(CP-*co*-iBMA)) and glycidyl methacrylate (poly(CP-*co*-GMA)) were prepared as compatibilizers by radical solution copolymerization. Compatibilization effects of those copolymers were studied for the CR/PAMA blends of 50/50 wt% composition. For comparison, the graft copolymers of alkyl methacrylates onto CR were also prepared. The copolymers and graft copolymers showed compatibilizing effects in the blends consisting of each homopolymer, and the copolymers showed better compatibilizing effect than the graft copolymers. It was concluded that the compatibilizing effect of the copolymers in the CR/PAMA blends was more prominent in the order poly(CP-*co*-GMA) > poly(CP-*co*-iBMA) > poly(CP-*co*-EMA).

(Keywords: compatibilizing effect; blends; morphology)

Introduction

Polychloroprene (CR) is an important synthetic rubber, the chemical structures and physical properties of which have been investigated extensively[1–6]. CR has poor heat resistance and weatherability, in spite of its good mechanical strength and resistance to oil and solvents. Many attempts have therefore been made to improve its poor performance by preparing copolymers of chloroprene (CP) and a second monomer[7–10]. For example, the introduction of methyl methacrylate into the CP backbone has been widely investigated[11–13]. In earlier work, we synthesized and characterized copolymers of CP with ethyl methacrylate (EMA), isobutyl methacrylate (iBMA) and glycidyl methacrylate (GMA)[14,15].

In this work, the miscibility of CR with three homopolymers of different alkyl methacrylates (AMAs), i.e. EMA, iBMA and GMA, was investigated. Recently, compatibilizers or interfacial agents in polymer blends have attracted much interest from theoretical and practical standpoints[16–18]. Moreover, the use of a copolymer, especially a block or graft copolymer, as a compatibilizer in incompatible homopolymer/homopolymer blends has been one of the main research themes in the field of polymer blends.

Thus, the compatibilizing effect of the copolymers of CP with AMAs having different alkyl groups in the blends of CR and each homopolymer was investigated. For comparison, graft copolymers of AMAs onto CR were also prepared. The miscibility and compatibilizing effects are discussed in terms of their glass transition temperature (T_g) behaviours and morphologies using differential scanning calorimetry (d.s.c.) and scanning electron microscopy (SEM), respectively.

Experimental

Materials. EMA (Aldrich), iBMA (Aldrich), GMA (Aldrich), toluene (Junsei) and benzene (Junsei) were purified by standard methods. 2,2′-Azobisisobutyronitrile (AIBN) and benzoyl peroxide (BPO) were purified by recrystallization in dehydrated ethanol. 3,4-Dichloro-1-butene (DCB; Aldrich), tetrahydrofurfuryl alcohol (THFA; Aldrich) and sodium hydroxide (NaOH; Junsei) were used as received without further purification.

Synthesis of CP (2-chloroprene-1,3-butadiene). CP was prepared by reacting DCB in aqueous solution of NaOH in the presence of THFA at 60°C by the method described in our previous work[19]. CP was used as soon as possible after distillation because it polymerized slowly during storage, even at low temperature.

Syntheses of CR and poly(alkyl methacrylate)s (PAMAs). CR was obtained in a glass ampoule by polymerizing 0.2 mol of CP with 0.2 mol% of AIBN as an initiator at 50°C in 100 ml of benzene for 10 h. After reaction, the mixture was poured into a large amount of methanol. The product recovered from methanol was dried under vacuum at 30°C to remove all volatiles.

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PAMAs — poly(ethyl methacrylate) (PEMA), poly(isobutyl methacrylate) (PiBMA) and poly(glycidyl methacrylate) (PGMA) — were synthesized by the same method.

Syntheses of copolymers. The copolymers of CP with AMAs, i.e. EMA, iBMA and GMA, designated as poly(CP-*co*-EMA), poly(CP-*co*-iBMA) and poly(CP-*co*-GMA), respectively, were obtained by the same method as described for CR. Details of the preparation of CP–AMA copolymers are described elsewhere[14,15].

Syntheses of graft copolymers. The graft copolymer of EMA onto CR, designated as poly(CR-*g*-EMA), was obtained by dissolving 1 g of CR in 10 ml of benzene in a 100 ml glass tube. EMA (0.2 mol) was dissolved in 20 ml of benzene and then 0.2 mol% of BPO was added. The tube was sealed after charging with argon and the reactions were carried out at 70°C for 10 h. The other two graft copolymers, poly(CR-*g*-iBMA) and poly(CR-*g*-GMA), were synthesized by the same method. Purification of the polymers was accomplished by reprecipitation in methanol from the benzene solutions, followed by drying in a vacuum oven to constant weight.

Preparation of blends. Blends of CR with three different PAMAs were prepared by casting from THF. Most of the solvents were allowed to evaporate slowly in air at room temperature. The films obtained were completely dried in vacuum at 30°C to constant weight. In order to investigate the compatibilizing effects of the copolymers and graft copolymers in CR/PAMA blends, ternary blends containing 10, 20, 30 and 40 phr (parts per hundred resin) of the copolymers with 50/50 CR/PAMA by weight were also prepared by casting from THF. The amount of the copolymers is based on the total amount (100 g) of the mixture of CR and PAMA.

Measurement. The molecular weights of polymers, listed in *Table 1*, were measured by gel permeation chromatography (g.p.c.; Water 244) using polystyrene standards. THF was used as an eluent. The T_g was measured at a heating rate of 10°C min^{-1} using d.s.c. (Du Pont 2100). The T_g value, also listed in *Table 1*, was taken as the initial onset of the change of slope in the d.s.c. curve on the second run. SEM was performed using a Jeol JSM35-CF scanning electron microscope. Samples were cryogenically fractured in liquid nitrogen and metallized by gold coating prior to the installation in the SEM chamber.

Table 1 Average molecular weights and glass transition temperature of various samples

Sample	$\bar{M}_n$	$\bar{M}_w$	$\bar{M}_w/\bar{M}_n$	T_g (°C)
CR	81 000	194 000	2.40	−45.7
PEMA	80 000	143 000	1.79	57.5
poly(CR-*g*-EMA)	74 000	140 000	1.89	−42.3
poly(CP-*co*-EMA)	58 300	71 000	1.22	−34.5
PiBMA	74 000	134 000	1.81	46.4
poly(CR-*g*-iBMA)	67 000	126 000	1.88	−32.4
poly(CP-*co*-iBMA)	52 500	78 000	1.49	−29.7
PGMA	77 000	126 400	1.64	63.7
poly(CR-*g*-GMA)	63 000	128 000	2.03	−29.7
poly(CP-*co*-GMA)	45 600	74 200	1.63	−16.4

Table 2 Effects of the contents of CR–AMA graft copolymers and the CP–AMA copolymers on the glass transition temperatures of 50/50 CR/PAMA blends

Sample	Copolymer content (phr)	T_g, CR (°C)	T_g, AMA (°C)
poly(CR-*g*-EMA)	0	−45.7	56.0
	10	−45.0	56.0
	20	−44.8	55.8
	30	−42.8	55.0
	40	−39.8	45.0
poly(CP-*co*-EMA)	0	−45.7	56.0
	10	−43.5	53.0
	20	−42.6	47.0
	30	−41.0	29.8
	40	−32.7	26.2
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
poly(CR-*g*-GMA)	0	−45.7	63.7
	10	−41.1	61.1
	20	−35.7	55.1
	30	−27.8	51.1
	40	−22.4	39.6
poly(CP-*co*-GMA)	0	−45.7	63.7
	10	−36.4	55.7
	20	−30.1	45.1
	30	−22.8	40.3
	40	−12.2	34.3

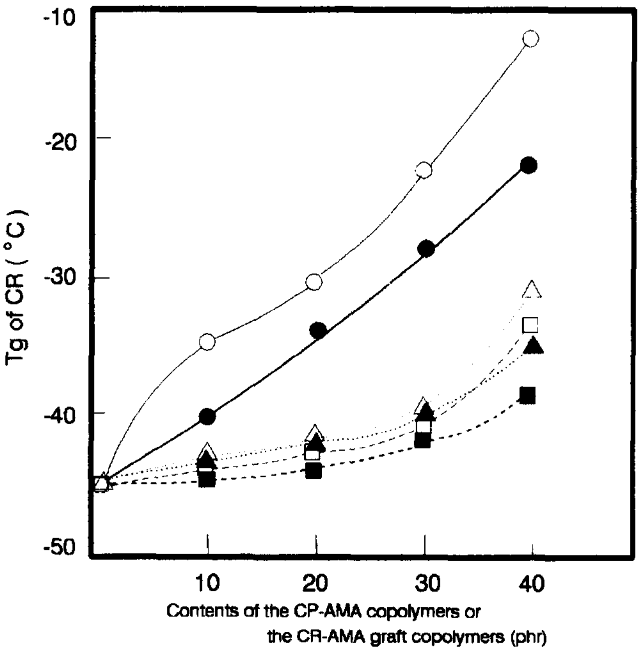

Figure 1 Effect of the addition of the CP–AMA copolymers and the CR–AMA graft copolymers on the glass transition temperatures of CR in the CR/PAMA blends of 50/50 composition by weight; □, poly(CP-*co*-EMA); △, poly(CP-*co*-iBMA); ○, poly(CP-*co*-GMA); ■, poly(CR-*g*-EMA); ▲, poly(CR-*g*-iBMA); ●, poly(CR-*g*-GMA)

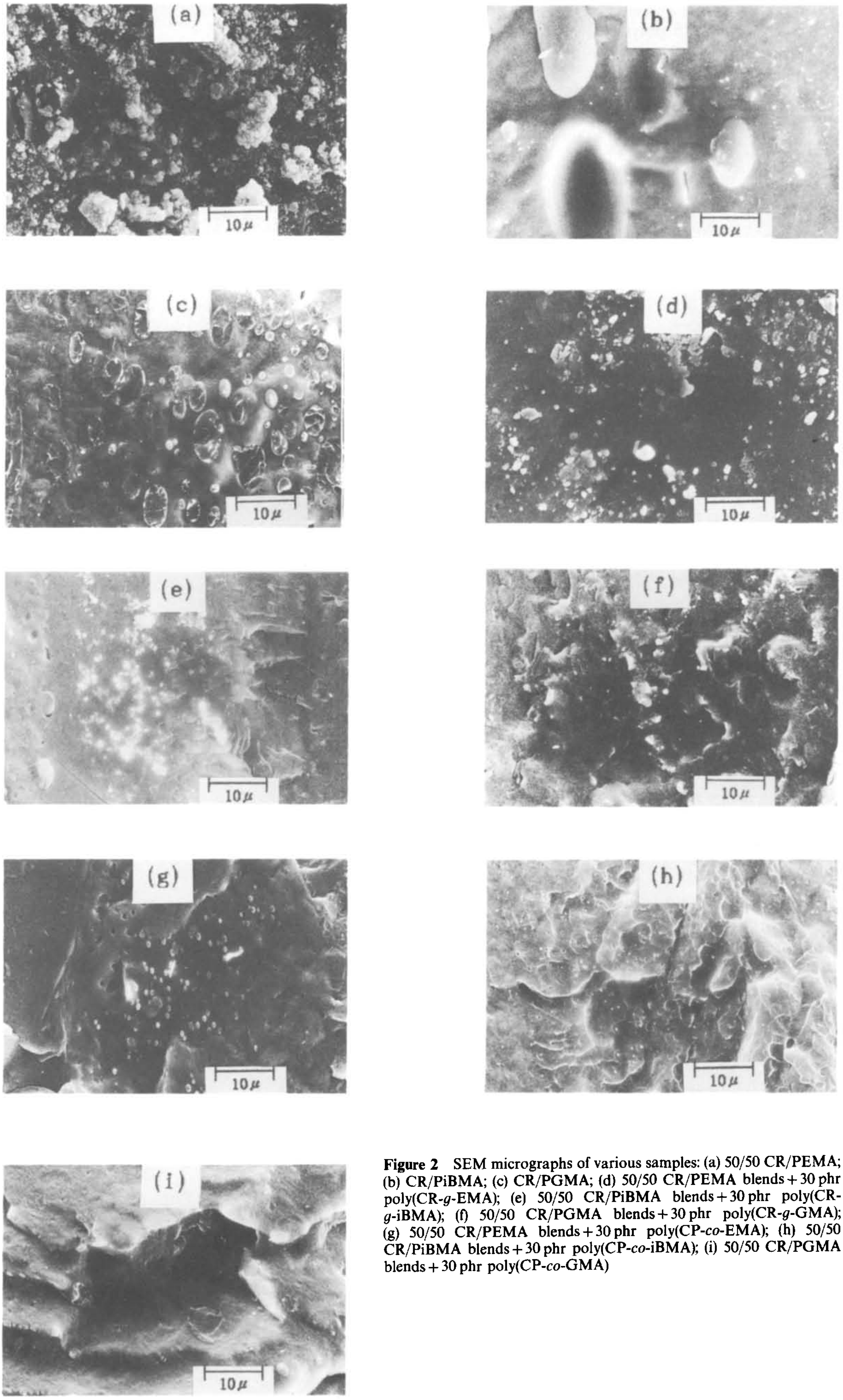

Figure 2 SEM micrographs of various samples: (a) 50/50 CR/PEMA; (b) CR/PiBMA; (c) CR/PGMA; (d) 50/50 CR/PEMA blends + 30 phr poly(CR-*g*-EMA); (e) 50/50 CR/PiBMA blends + 30 phr poly(CR-*g*-iBMA); (f) 50/50 CR/PGMA blends + 30 phr poly(CR-*g*-GMA); (g) 50/50 CR/PEMA blends + 30 phr poly(CP-*co*-EMA); (h) 50/50 CR/PiBMA blends + 30 phr poly(CP-*co*-iBMA); (i) 50/50 CR/PGMA blends + 30 phr poly(CP-*co*-GMA)

Results and discussion

All the binary blends of CR with PAMAs showed two separate T_gs, which were nearly identical to those of each homopolymer regardless of the different AMAs as well as blend concentrations. The result suggests that PEMA, PiBMA and PGMA are immiscible with CR. It has been reported that the homologous poly(methacrylate)s are usually miscible with other chlorine-containing polymers, such as poly(vinyl chloride) or chlorinated polyethylene, because of the molecular interaction between ether in the poly(methacrylate)s and the hydrogen on the chlorine-bearing methylene group in chlorine-containing polymers[19–21]. It has also been reported, however, that the miscibility becomes weaker as the chlorine content becomes smaller in the chlorine-containing polymers[19–22]. The CR used in this work has about 35 wt% of chlorine[11]. Thus, it is not surprising that the CR was not miscible with any PAMAs, in spite of their chlorines in the chain.

Table 2 shows the T_gs of CR/PAMA/copolymer and CR/PAMA/graft copolymer 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/PAMA mixtures.

When either the copolymers or the graft copolymers were added to the CR/PAMA binary blends, the T_g of each homopolymer changed considerably, even though the ternary blends consisting of each homopolymer and the copolymers showed two separate T_gs. These results imply that compatibilization was achieved in the CR/PAMA blends of 50/50 composition by weight in the presence of both the copolymers and the graft copolymers. It should be noted that the copolymers showed better compatibilizing effect for the 50/50 CR/homopolymer blends than the graft copolymers.

In *Figure 1*, the T_gs of CR in the ternary blends are plotted against the weight concentrations of the CP–AMA copolymers and CR–AMA graft copolymers. The T_gs of CR in the ternary blends increased with increasing copolymer or graft copolymer content. Poly(CP-*co*-GMA) and poly(CR-*g*-GMA) showed much clearer compatibilizing effect than poly(CP-*co*-iBMA) and poly(CR-*g*-iBMA), and poly(CP-*co*-EMA) and poly(CR-*g*-EMA). This may be due to the stronger polar properties of GMA than of EMA or iBMA. That is, the polarity due to the presence of the ether oxygen atom in the GMA appears to play an important role in the enhancement of miscibility of CR and PGMA[23]. Also note that the increase in T_g with increasing content of each copolymer was clearly seen in the order: CR/PGMA > CR/PiBMA > CR/PEMA blends. This indicates that the copolymer having longer AMA chain shows better compatibilizing effect in the blends containing their base component polymers.

The compatibilizing effects of the copolymers and the graft copolymers were also confirmed by morphological studies. The morphologies of the blends were analysed by SEM. *Figures 2a–c* show the SEM micrographs of the CR/PEMA, CR/PiBMA and CR/PGMA blends, respectively, of 50/50 composition by weight. It can be seen that the blends are incompatible and the phases are grossly separated. *Figures 2d–f* show the SEM micrographs of the CR/PEMA/poly(CR-*g*-EMA), CR/PiBMA/poly(CR-*g*-iBMA) and CR/PGMA/poly(CR-*g*-GMA) blends, respectively, consisting of 30 phr of the graft copolymers. The SEM micrographs of the ternary blends show finer domain structure than the binary blends without the graft copolymers. SEM micrographs of the CR/PEMA/poly(CP-*co*-EMA), CR/PiBMA/poly(CP-*co*-iBMA) and CR/PGMA/poly(CP-*co*-GMA) blends consisting of 30 phr of the copolymers are also shown in *Figures 2g–i*, respectively. It is clearly seen that the ternary blends consisting of the copolymers show much finer domain structure than the binary blends. Comparisons of the SEM micrographs in *Figures 2g–i* with those in *Figures 2d–f* indicate that the ternary blends consisting of the copolymers show relatively finer domain structure than the ternary blends consisting of the graft copolymers.

The result proves our speculation that the copolymers show better compatibilizing effects for the CR/PAMA than the graft copolymers, and also that poly(CR-*g*-GMA) and poly(CP-*co*-GMA), consisting of the more polar GMA group, show better compatibilizing effects than poly(CR-*g*-iBMA) and poly(CP-*co*-iBMA) as well as poly(CR-*g*-EMA) and poly(CP-*co*-EMA). It should be noted that when the polymer sample employed is not strictly monodisperse and the molecular weight differences are large, the miscibility is strongly dependent on the molecular weight characteristics of the polymers[24,25]. However, in this work, the molecular weight and the polydispersities of the copolymers used are comparable. Thus, in comparing the relative miscibility of various ternary blends containing copolymers, the conclusions drawn above should be unaffected by any minor errors due to differences in the molecular weight characteristics.

Conclusions

The T_g behaviours and morphologies of the CR/PAMA blends indicated that CR and homopolymers of AMAs, EMA, iBMA and GMA, were incompatible. The CR–AMA graft copolymers showed compatibilizing effects in the blends consisting of each homopolymer of 50/50 composition by weight. The CP–AMA copolymers, however, showed better compatibilizing effects for the CR/PAMA blends than the CR–AMA graft copolymers.

In conclusion, the copolymer of CP with AMAs having a longer and more polar alkyl group showed better compatibilizing effects in the blends of CP and AMA homopolymers.

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