Miscibility of poly(2-fluoroethyl methacrylate) and poly(1,1,1,3,3,3-hexafluoroisopropyl methacrylate) with various polymethacrylates

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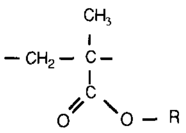
The miscibility behaviour of poly(2-fluoroethyl methacrylate) (P2FEMA) and poly(1,1,1,3,3,3-hexafluoroisopropyl methacrylate) (PHFPMA) with various polymethacrylates was studied by differential scanning calorimetry and for lower critical solution temperature (*LCST*) behaviour. Both P2FEMA and PHFPMA are miscible with poly(methyl methacrylate) (PMMA), poly(ethyl methacrylate) (PEMA) and poly(tetrahydrofurfuryl methacrylate) (PTHFMA), but are immiscible with poly(n-propyl methacrylate) (PnPMA), poly(isopropyl methacrylate) (PiPMA), poly(n-butyl methacrylate) (PnBMA) and poly(cyclohexyl methacrylate) (PCHMA). Phase separation could be induced by heating for blends of P2FEMA with PMMA and PEMA. For PHFPMA, only PHFPMA/PEMA blends showed *LCST* behaviour. The miscibility behaviour of P2FEMA and PHFPMA is similar to that of poly(2-chloroethyl methacrylate).

(Keywords: fluorine-containing polymers; polymethacrylates; miscibility)

INTRODUCTION

The miscibility behaviour of fluorine-containing polymers has been studied extensively. Poly(vinylidene fluoride) (PVDF) is miscible with a variety of polymers including polyacrylates[1], polymethacrylates[2,3], tertiary amide polymers[4-6] and poly(ε-caprolactone)[7]. PVDF is miscible with poly(methyl acrylate)[1], poly(vinyl acetate)[8] and poly(vinyl methyl ketone)[7], but immiscible with poly(vinyl methyl ether)[7], indicating the importance of carbonyl group in achieving miscibility. Fourier-transform infrared spectroscopy (*FT*i.r.) also shows the involvement of the carbonyl group of poly(methyl methacrylate) (PMMA) in intermolecular interaction with PVDF[9]. The miscibility behaviour of copolymers of fluorostyrene was extensively studied by Karasz and his co-workers[10-14]. Several recent papers reported the miscibility of fluorine-containing polyimides[15], polysulfones[16] and polycarbonates[17,18].

We have recently studied the miscibility of some halogen-containing polymethacrylates[19-24]. The ability of a halogen-containing polymethacrylate to be miscible with poly(alkyl methacrylate)s was found to decrease in the order poly(2-chloroethyl methacrylate) (P2CEMA) > poly(2-bromoethyl methacrylate) (P2BEMA) > poly(2-iodoethyl methacrylate) (P2IEMA). The differences in the miscibility behaviour of these halogen-containing polymethacrylates have been attributed to the different acidity of hydrogen atoms in the pendent $-CH_2X$ group. The higher electronegativity of chlorine makes the methylene protons more acidic, enabling P2CEMA to interact more intensely with poly(alkyl methacrylate)s. We have recently found that poly(1-chloroethyl methacrylate) (P1CEMA) shows a wide range of miscibility with poly(alkyl methacrylate)s as compared with P2CEMA, indicating that the acidity of α-hydrogen plays an important role in achieving miscibility[24]. We have extended our study to fluorine-containing polymethacrylates. In this communication, we report the miscibility of poly(2-fluoroethyl methacrylate) (P2FEMA) and poly(1,1,1,3,3,3-hexafluoroisopropyl methacrylate) (PHFPMA) with various poly(alkyl methacrylate)s.



$$-CH_2-C(CH_3)(COOR)-$$

R = $-CH_2CH_2F$ (P2FEMA)

$-CH(CF_3)_2$ (PHFPMA)

EXPERIMENTAL

Materials

2-Fluoroethyl methacrylate (2FEMA) and 1,1,1,3,3,3-hexafluoroisopropyl methacrylate) (HFPMA) were prepared by the reaction of corresponding alcohols with methacryloyl chloride in ether, in the presence of triethylamine and hydroquinone. To a mixture of 2-fluoroethanol or 1,1,1,3,3,3-hexafluoroisopropanol, triethylamine, hydroquinone and anhydrous ether, an etheral solution of methacryloyl chloride was added slowly over a period of 1.5 h under strirring, with temperature maintained below 5°C. The reaction mixture was then allowed to reflux for 2 h. Water was added to dissolve the amine salt. The product was extracted with

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ether and washed successively with 5% HCl, $NaHCO_3$ and water, and dried over anhydrous Na_2SO_4. After distillation, pure 2FEMA and HFPMA were obtained with the boiling points of 49–51°C at 15 mmHg and 49–50°C at 140 mmHg respectively (1 mmHg = 133.3 Pa).

For 2FEMA, i.r.: 1712 cm^{-1} (C=O), 1628 cm^{-1} (C=C); ^1H n.m.r., δ (ppm, in $CDCl_3$): 6.20 (1H, vinyl proton), 5.62 (1H, vinyl proton), 4.73–4.35 (4H, $-CH_2CH_2F$), 1.97 (3H, $-CH_3$); elemental analysis for F in $C_6H_9FO_2$: calculated 14.4%; found 14.3%.

For HFPMA, i.r.: 1748 cm^{-1} (C=O), 1632 cm^{-1} (C=C); ^1H n.m.r., δ (ppm, in $CDCl_3$): 6.34 (1H, vinyl proton), 5.84 (2H, methine and one vinyl proton), 2.02 (3H, $-CH_3$); elemental analysis for F in $C_7H_6F_6O_2$: calculated 48.3%; found 48.3%.

Polymerizations were carried out in 2-butanone at 70°C for about 24 h using 0.25 wt% of azobisisobutyronitrile as initiator. The polymer was obtained by precipitation of solution from excess n-hexane. The molecular weights of P2FEMA and PHFPMA were determined by g.p.c. using monodispersed polystyrenes as standards.

The main characteristics of various polymers used in this study are given in *Table 1*.

Polymer blends

Blends of P2FEMA and PHFPMA with various polymethacrylates were prepared by solution casting from tetrahydrofuran (THF). Solvent was allowed to evaporate slowly over a period of 1–2 days at room temperature. The cast films were then dried *in vacuo* at 90°C for at least a week.

T_g *measurements*

The glass transition temperature (T_gs) of various samples were measured with a Perkin–Elmer DSC-4 differential scanning calorimeter using a heating rate of 20°C min^{-1}. T_g was taken as the initial onset of the change of slope in the d.s.c. curve. The reported T_g values were average values of the second and subsequent runs.

Cloud-point measurement

All miscible blends were examined for the existence of lower critical solution temperature (*LCST*) behaviour using the method described previously[24]. The existence of *LCST* was indicated by the development of cloudiness of a transparent film upon heating. The temperature at which the film first showed cloudiness was taken as the cloud point.

RESULTS

P2FEMA/PMMA blends

All the P2FEMA/PMMA blends were transparent. Blends containing 25, 50, 75 and 90 wt% of P2FEMA turned cloudy upon heating, showing *LCST* behaviour. Phase separation could not be induced for a blend containing 10 wt% of P2FEMA upon heating to about 280°C where discoloration began to develop. The cloud-point curve is shown in *Figure 1*.

Owing to the closeness of the T_g values of P2FEMA and PMMA, it is difficult to ascertain the miscibility using normal d.s.c. measurement. It is well known that the enthalpy recovery of an annealed blend can be used to ascertain its miscibility[25,26]. Blends were first heated to 150°C and maintained at that temperature for 15 min and then annealed at 90°C for a week. D.s.c. measurements of these annealed blends showed that each blend had an enthalpy recovery peak which gradually moved to a lower temperature with increasing P2FEMA content in the blends, as shown in *Figure 2*. It is concluded that P2FEMA is miscible with PMMA.

P2FEMA/PEMA blends

All the P2FEMA/PEMA blends were transparent. Each blend showed a single composition-dependent T_g as shown in *Figure 3*. Blends containing 25, 50, 75 and 90 wt% of P2FEMA turned cloudy upon heating, showing *LCST* behaviour. The cloud-point curve is also

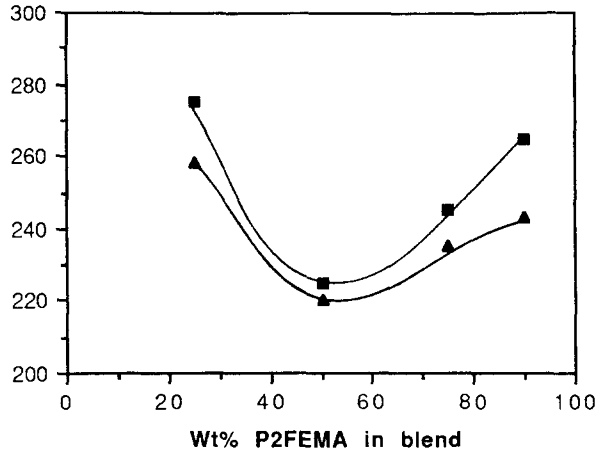

Figure 1 Cloud-point curves for: (■) P2FEMA/PMMA and (▲) P2FEMA/PEMA blends

Table 1 Characteristics of polymers

Polymer	Abbreviation	Source	Molecular weight (M_w) × 10^3	T_g (°C)
Poly(methyl methacrylate)	PMMA	Du Pont (Elvacite 2010)	120	100
Poly(ethyl methacrylate)	PEMA	Du Pont (Elvacite 2042)	310	65
Poly(n-propyl methacrylate)	PnPMA	Scientific Polymer Products	175	45
Poly(iso-propyl methacrylate)	PiPMA	Scientific Polymer Products	166	82
Poly(n-butyl methacrylate)	PnBMA	Du Pont (Elvacite 2044)	288	20
Poly(cyclohexyl methacrylate)	PCHMA	Scientific Polymer Products	66	95
Poly(tetrahydrofurfuryl methacrylate)	PTHFMA	Scientific Polymer Products	240	57
Poly(2-fluoroethyl methacrylate)	P2FEMA	This laboratory	484	96
Poly(1,1,1,3,3,3-hexafluoroisopropyl methacrylate)	PHFPMA	This laboratory	24	82

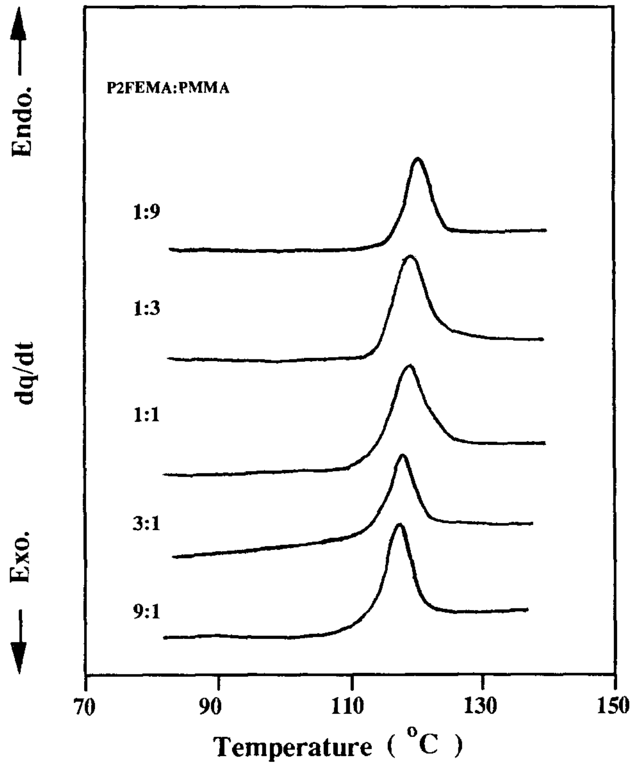

Figure 2 D.s.c. curves for annealed P2FEMA/PMMA blends

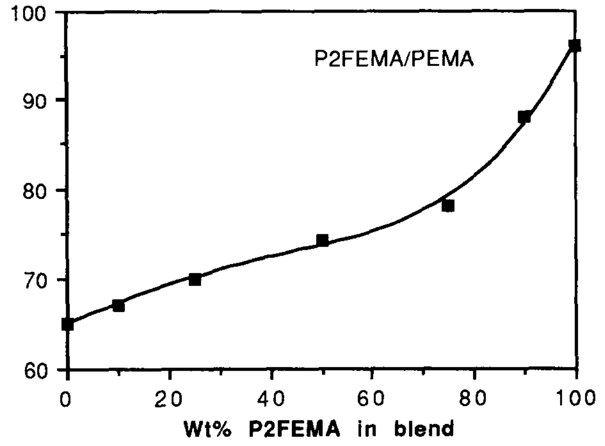

Figure 3 T_g–composition curve for P2FEMA/PEMA blends

shown in *Figure 1*. Therefore, P2FEMA is miscible with PEMA.

P2FEMA/PnPMA, P2FEMA/PiPMA and P2FEMA/PnBMA blends

All the blends were cloudy. D.s.c. measurements showed the existence of two T_gs for each blend. The T_g values correspond to those of the two component polymers. Therefore P2FEMA is immiscible with PnPMA, PiPMA and PnBMA.

P2FEMA/PTHFMA blends

All the blends were transparent and remained so upon heating to about 280°C. D.s.c. measurements show a single T_g for each blend. The T_g–composition curve is shown in *Figure 4*. It is inferred that P2FEMA is miscible with PTHFMA.

P2FEMA/PCHMA blends

All the P2FEMA/PCHMA blends were hazy. Although the T_g values of the two polymers are quite close to each other, two distinct T_gs can still be seen for each blend after annealing at 90°C for a week, indicating the immiscibility of P2FEMA with PCHMA.

PHFPMA/PMMA blends

All the PHFPMA/PMMA blends were transparent. Each blend had a single T_g, indicating that PHFPMA is miscible with PMMA. The T_g–composition curve for PHFPMA/PMMA blends is shown in *Figure 5*. No *LCST* behaviour was observed for PHFPMA/PMMA blends.

PHFPMA/PEMA blends

PHFPMA is miscible with PEMA as each of the PHFPMA/PEMA blends was transparent and had a single composition-dependent T_g as shown in *Figure 6*. All the PHFPMA/PEMA blends showed *LCST* behaviour and the cloud-point curve is shown in *Figure 7*.

PHFPMA/PCHMA blends

PHFPMA is miscible with PTHFMA as shown by the transparency and the existence of a single T_g for each blend. The T_g–composition curve is shown in *Figure 8*.

PHFPMA/PnPMA, PHFPMA/PnBMA and PHFPMA/PCHMA blends

All the blends were cloudy. D.s.c. measurements showed that each blend had two distinct T_gs which were close to those of the respective component polymers, indicating that PHFPMA is immiscible with PnPMA, PnBMA and PCHMA.

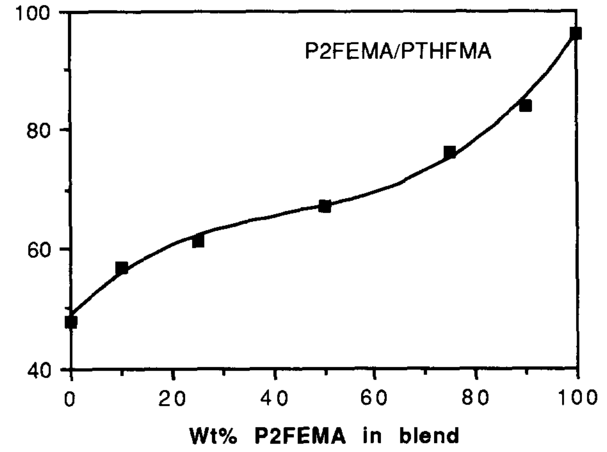

Figure 4 T_g–composition curve for P2FEMA/PTHFMA blends

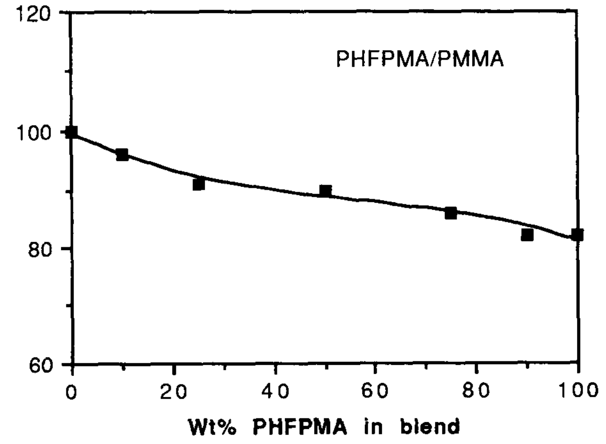

Figure 5 T_g–composition curve for PHFPMA/PMMA blends

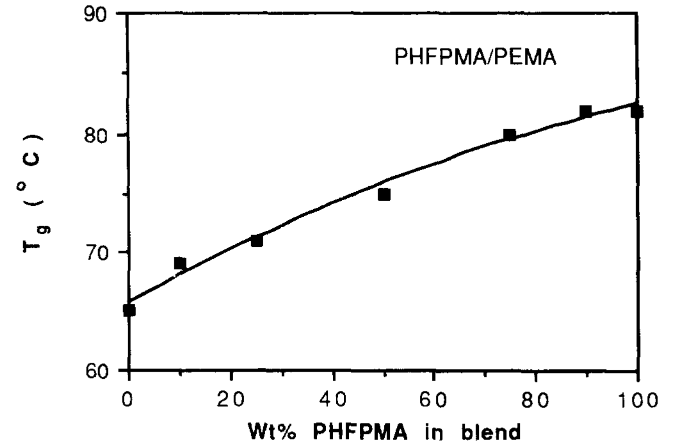

Figure 6 T_g-composition curve for PHFPMA/PEMA blends

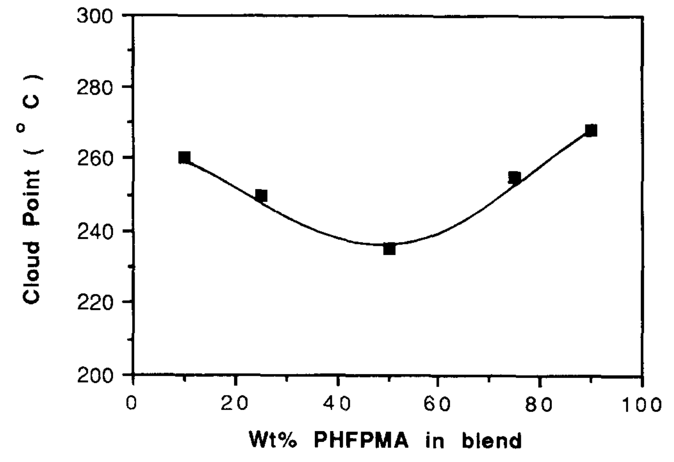

Figure 7 Cloud-point curve for PHFPMA/PEMA

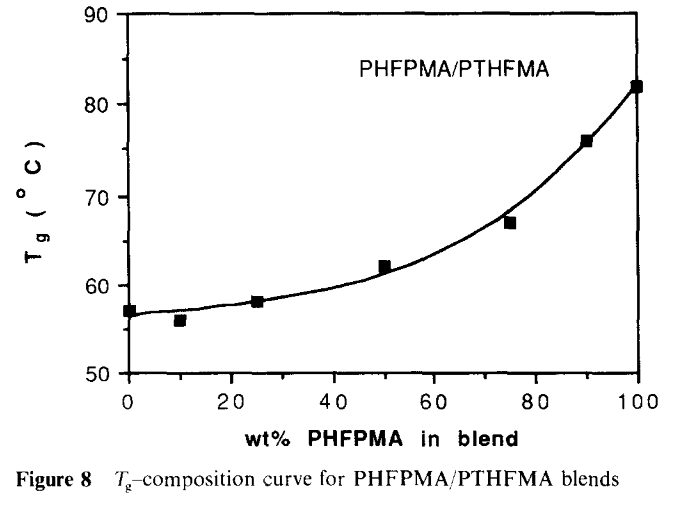

Figure 8 T_g-composition curve for PHFPMA/PTHFMA blends

PHFPMA/PiPMA blends

The blends were cloudy. Because of the closeness of T_g values of the two polymers, it is difficult to ascertain the miscibility using conventional d.s.c. measurement. However, an annealed physical mixture of PHFPMA with PiPMA did not show two enthalpy recovery peaks, showing that the miscibility of PHFPMA/PiPMA blends could not be ascertained by T_g measurement. Nevertheless, the cloudiness of the blends can be taken to indicate that PHFPMA is immiscible with PiPMA.

DISCUSSION

The present study shows that P2FEMA and PHFPMA exhibit similar miscibility behaviour toward polymethacrylates. Both of them are miscible with PMMA, PEMA and PTHFMA, but are immiscible with PnPMA, PiPMA, PnBMA and PCHMA. However, there are slight differences in the *LCST* behaviour of the two blend systems. P2FEMA/PMMA blends show *LCST* behaviour, but PHFPMA/PMMA blends degrade before phase separation could occur. The cloud-point curve for PHFPMA/PEMA blends lies at slightly higher temperatures than those for P2FEMA/PEMA blends. The temperature of phase separation has been used as a measurement of polymer–polymer interaction in a blend[2,27–29]. The present results then suggest that PHFPMA interacts marginally more strongly than P2FEMA with polymethacrylates.

Table 2 summarizes the miscibility behaviour of various halogen-containing polymethacrylates. The abilities of these halogen-containing polymethacrylates to form miscible blends with polymethacrylates decrease in the order P1CEMA > PCMMA > P2CEMA ~ PHFPMA > P2FEMA > P2BEMA > P2IEMA. We have earlier suggested that the acidity of methylene hydrogens in the $-CH_2X$ group and that of methine hydrogen in the $-CH(Cl)CH_3$ group play an important role in determining the miscibility. One would then expect P2FEMA and PHFPMA to be miscible with a wider range of polymethacrylates in view of the presence of strong electron-withdrawing fluorine in P2FEMA and trifluoromethyl group in PHFPMA.

The good miscibility of P2FEMA and PHFPMA is also expected from a non-hydrogen-bonded solubility parameter (δ_{nh}) approach proposed by Coleman *et al.*[30,31]. Miscibility is favoured when the δ_{nh} values of the two polymers are closely matched and intermolecular interactions are present. The δ_{nh} values of polymethacrylates decrease from 18.4 $J^{1/2}$ $cm^{-3/2}$ for PMMA to 17.8 $J^{1/2}$ $cm^{-3/2}$ for PnBMA; those of PCMMA, P1CEMA, P2CEMA, P2FEMA and PHFPMA are 20.7, 19.5, 20.0, 18.4 and 17.0 $J^{1/2}$ $cm^{-3/2}$, respectively. The δ_{nh} values are

Table 2 Miscibility behaviour of various blends

	P1CEMA (ref. 24)	PCMMA (ref. 19)	P2CEMA (ref. 20)	PHFPMA	P2FEMA	P2BEMA (ref. 21)	P2IEMA (ref. 23)
PMMA	Miscible	Miscible	Miscible	Miscible	Miscible[a]	Immiscible	Immiscible
PEMA	Miscible[a]	Miscible[a]	Miscible[a]	Miscible[a]	Miscible[a]	Immiscible	Immiscible
PnPMA	Miscible[a]	Miscible[a]	Immiscible	Immiscible	Immiscible	Immiscible	Immiscible
PiPMA	Miscible[a]	Miscible[a]	Immiscible	Immiscible	Immiscible	Immiscible	Immiscible
PnBMA	Miscible[a]	Immiscible	Immiscible	Immiscible	Immiscible	Immiscible	Immiscible
PCHMA	Immiscible	Immiscible	Immiscible	Immiscible	Immiscible	Immiscible	Immiscible
PTHFMA	Miscible	Miscible	Miscible	Miscible	Miscible	Miscible	Miscible[a]

[a] Showing *LCST* behaviour

calculated using the group molar attraction constants (F) and group molar volumes (V) given by Coleman *et al.*[30,31]. The F and V values for fluorine are not provided by Coleman *et al.* In this case, we use Small's F value of $249\ \mathrm{J}^{1/2}\,\mathrm{cm}^{3/2}\,\mathrm{mol}^{-1}$ and Fedor's V value of $18.0\ \mathrm{cm}^3\,\mathrm{mol}^{-1}$ for fluorine[32]. P2FEMA and PHFPMA are expected to be miscible with a wider range of polymethacrylates than the three chlorine-containing polymethacrylates, as their δ_{nh} values are more closely matched to various polymethacrylates.

However, the miscibility behaviour of the two fluorine-containing polymethacrylates is about the same as that of P2CEMA. The situation resembles that of the different miscibility behaviour of poly(vinyl chloride) (PVC) and poly(vinyl fluoride) (PVF). For example, Cousin and Prud'homme[33,34] found that PVC is miscible with a large number of polyesters, but PVF is immiscible with any of these polyesters. The miscibility of PVC/polyester blends is generally attributed to interactions involving the α-hydrogens in PVC with the polyester carbonyl groups[35,36]. The more acidic α-hydrogens in PVF are expected to interact with the carbonyl groups of polyesters. The immiscibility of PVF/polyester blends is explained by the high electronegativity of fluorine which leads to self-association between PVF instead of intermolecular interaction with polyesters as found with PVC[34].

Chen and Morawetz[37] studied the effects of various acid groups such as phenol, carboxyl, glycine and sulfonic acid in enhancing polymer miscibility and found that the acidity of the acid group is not the only factor controlling miscibility enhancement. Painter *et al.*[38] also pointed out that for blends involving strong specific interactions, it is important to consider the competition between self-assocation and inter-association, and the balance of this competition is not solely determined by the relative strengths of interactions. The poorer than expected miscibility of P2FEMA and PHFPMA may be due to their tendency to undergo self-association.

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REFERENCES

1 Wahrmund, D. C., Bernstein, R. E., Barlow, J. W. and Paul, D. R. *Polym. Eng. Sci.* 1978, **18**, 677

2 Paul, D. R., Barlow, J. W. and Wahrmund, D. C. *Polym. Eng. Sci.* 1978, **18**, 1225

3 Roerdink, E. and Challa, G. *Polymer* 1980, **21**, 1161

4 Galin, M. *Makromol. Chem., Rapid Commun.* 1987, **8**, 411

5 Galin, M. *Makromol. Chem.* 1987, **188**, 1391

6 Galin, M. *Makromol. Chem., Rapid Commun.* 1984, **5**, 119

7 Bernstein, R. E., Wahrmund, D. C., Barlow, J. W. and Paul, D. R. *Polym. Eng. Sci.* 1978, **18**, 1220

8 Bernstein, R. E., Paul, D. R. and Barlow, J. W. *Polym. Eng. Sci.* 1978, **18**, 683

9 Coleman, M. M. and Painter, P. C. *Appl. Spectrosc. Rev.* 1984, **20**, 255

10 Vukovic, R., Bogdanic, G., Kuresevic, V., Karasz, F. E. and MacKnight, W. J. *Eur. Polym. J.* 1988, **24**, 123

11 Solomons, W., ten Brinke, G. and Karasz, F. E. *Polym. Commun.* 1991, **24**, 529

12 Vukovic, R., Karasz, F. E. and MacKnight, W. J. *Polymer* 1983, **24**, 529

13 Vukovic, R., Kuresevic, V., Karasz, F. E. and MacKnight, W. J. *Thermochim. Acta* 1982, **54**, 349

14 Vukovic, R., Karasz, F. E. and MacKnight, W. J. *J. Appl. Polym. Sci.* 1983, **28**, 219

15 Chung, T. S., Vora, R. H. and Jaffe, M. J. *Polym. Sci., Polym. Chem. Edn* 1991, **29**, 1207

16 Jannarthanan, V., Karasz, F. E. and MacKnight, W. J. *Polymer* 1992, **33**, 3388

17 Kim, C. K. and Paul, D. R. *Polymer* 1992, **33**, 4929

18 Kim, C. K. and Paul, D. R. *Macromolecules* 1992, **25**, 3097

19 Goh, S. H., Lee, S. Y., Siow, K. S. and Neo, M. K. *Polymer* 1990, **31**, 1065

20 Neo, M. K., Lee, S. Y. and Goh, S. H. *J. Appl. Polym. Sci.* 1991, **43**, 1031

21 Neo, M. K. and Goh, S. H. *Macromolecules* 1991, **24**, 2564

22 Low, S. M., Lee, S. Y. and Goh, S. H. *Eur. Polym. J.* 1993, **29**, 909

23 Low, S. M., Lee, S. Y. and Goh, S. H. *Macromolecules* 1993, **26**, 2631

24 Peng, J., Goh, S. H., Lee, S. Y. and Siow, K. S. *Polymer* 1993, **34**, 4930

25 Bosma, M., ten Brinke, G. and Ellis, T. S. *Macromolecules* 1988, **21**, 1465

26 Jorda, R. and Wilkes, G. L. *Polym. Bull.* 1988, **20**, 479

27 Kwei, T. K., Pearce, E. M. and Min, B. Y. *Macromolecules* 1985, **18**, 2326

29 Ha, C. S., Cho, W. J., Ryou, J. H. and Roe, R. J. *Polymer* 1993, **34**, 505

30 Coleman, M. M., Serman, C. J., Bhagwager, D. E. and Painter, P. C. *Polymer* 1990, **31**, 1187

31 Coleman, M. M., Graf, J. F. and Painter, P. C. 'Specific Interactions and the Miscibility of Polymer Blends', Technomic, Lancaster, PA, 1991

32 Van Krevelen, D. W. 'Properties of Polymers', 3rd Edn, Elsevier, Amsterdam, 1990

33 Cousin, P. and Prud'homme, R. E. *Eur. Polym. J.* 1982, **18**, 957

34 Cousin, P. and Prud'homme, R. E. *Adv. Chem. Ser.* 1986, **211**, 87

35 Coleman, M. M. and Zarian, J. *J. Polym. Sci., Polym. Phys. Edn* 1979, **17**, 837

36 Varnell, D. F., Moskala, E. J., Painter, P. C. and Coleman, M. M. *Polym. Eng. Sci.* 1983, **23**, 658

37 Chen, C. T. and Morawetz, H. *Macromolecules* 1989, **22**, 159

38 Painter, P. C., Park, Y. and Coleman, M. M. *Macromolecules* 1988, **21**, 66