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Miscibility of poly(*p*-vinylphenol) with poly(dialkyl itaconate)s and poly(methoxycarbonylmethyl methacrylate)

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The miscibility of poly(*p*-vinylphenol) (PVPh) with several poly(dialkyl itaconate)s and poly(methoxycarbonylmethyl methacrylate) (PMOCMA) was studied by d.s.c. and Fourier transform infra-red (*FT*i.r.) spectroscopy. Poly(dimethyl itaconate) and a low molecular weight poly(diethyl itaconate) are miscible with four PVPh samples with molecular weights ranging from 1.7 to 30 kg mol^{-1}. A high molecular weight poly(diethyl itaconate) sample is completely miscible with only two PVPh samples with low molecular weights. Poly(di-*n*-propyl itaconate), poly(di-*n*-butyl itaconate) and PMOCMA are not completely miscible with PVPh as shown by the presence of two glass transitions in some blends. *FT*i.r. studies show the existence of hydrogen bonding interactions between PVPh and the carbonyls of $-CH_2COOR$ in poly(dialkyl itaconate)s and the carbonyl of $-COOCH_3$ in PMOCMA, but the interactions are weaker than the self-association of PVPh.

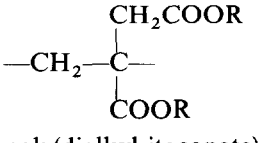
(Keywords: miscibility; poly(*p*-vinylphenol); poly(dialkyl itaconate)s)

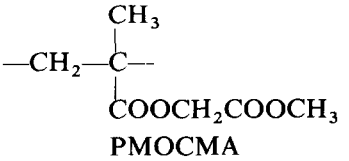
INTRODUCTION

The miscibility behaviour of poly(*p*-vinylphenol) (PVPh) with poly(alkyl methacrylate)s has been extensively studied[1–7]. PVPh is miscible with poly(methyl methacrylate) (PMMA), poly(ethyl methacrylate) (PEMA), poly(n-propyl methacrylate) (PnPMA), poly(isopropyl methacrylate) (PiPMA) and poly(tetrahydrofurfuryl methacrylate) as shown by the existence of a single glass transition temperature (T_g) in each blend[1]. Fourier transform infra-red (*FT*i.r.) spectroscopic studies show the existence of hydrogen bonding interactions between the hydroxyl groups of PVPh and the carbonyl groups of the poly(alkyl methacrylate)s[2–4]. However, the interpolymer hydrogen bonding is weaker than the self-association of PVPh. Solid-state n.m.r. spectroscopy has also been used to study PVPh/PMMA blends[6,7]. Zhang *et al.*[6] reported that apart from a 0.5 ppm downfield shift of the phenolic hydroxyl carbon of PVPh in a PVPh/PMMA (1/2) blend, no other significant change of the ^{13}C chemical shift was observed, suggesting weak or no hydrogen bonding between the two polymers. However, a recent study using two-dimensional heteronuclear correlation n.m.r. showed the presence of hydrogen bonding between PVPh and PMMA[7]. The miscibility behaviour of binary PVPh/poly(methyl methacrylate-*co*-ethyl methacrylate) and ternary PVPh/PMMA/PEMA blends was recently reported by Pomposo *et al.*[5,8,9].

As compared with poly(alkyl methacrylate)s, the miscibility behaviour of poly(dialkyl itaconate)s receives scant attention. It is of interest to study how the presence of an additional –COO– group in the poly(dialkyl itaconate) segment would affect the miscibility behaviour. Cowie and Elexpuru[10] found that while PMMA, PEMA, PnPMA and poly(*n*-butyl methacrylate) (PnBMA) are miscible with poly(α-methylstyrene-*co*-acrylonitrile) over certain copolymer composition ranges, the corresponding poly(dialkyl itaconate)s are immiscible with the copolymer. On the other hand, Cowie and Reilly[11] reported that PMMA, PEMA and poly(t-butyl methacrylate) as well as the corresponding poly(dialkyl itaconate)s are miscible with modified poly(α-methylstyrene) (PαMS) samples containing varying amounts of methyl carbinol or trifluoromethyl carbinol units. However, poly(di-n-propyl itaconate) (PDnPI) but not PnPMA is miscible with the modified PαMS samples. Landry *et al.*[12] recently reported that PVPh is miscible with three polyitaconate samples containing etheric side chains and the intermolecular interactions are dominated by the etheric side chains.

Here we report the miscibility of PVPh with several poly(dialkyl itaconate)s. Four PVPh samples with different molecular weights were used in the present study to examine a possible molecular weight effect on the miscibility of the blends. We also report the miscibility of PVPh with poly(methoxycarbonylmethyl methacrylate) (PMOCMA) which also possesses two –COO– groups in each polymer segment.


poly(dialkyl itaconate)


PMOCMA

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EXPERIMENTAL

Materials

Dimethyl itaconate was obtained from Fluka and was purified by fractional distillation (56°C, 0.6 mm Hg). Diethyl itaconate and di-n-butyl itaconate were obtained from Tokyo Kasei; the inhibitors in the monomers were removed by passing through a column packed with inhibitor remover. Di-n-propyl itaconate was prepared by esterification of itaconic acid and n-propanol in the presence of sulfuric acid.

Four PVPh samples with varying molecular weights were obtained from Polysciences, Inc.

Poly(dimethyl itaconate) (PDMI) and poly(diethyl itaconate) (PDEI-A) were prepared by solution polymerization in 2-butanone at reflux temperature for 22 h using 0.3 wt% azobisisobutyronitrile (AIBN) as initiator. PDMI and PDEI-A were recovered by precipitation in excess methanol and n-heptane, respectively.

Another PDEI sample, designated as PDEI-B, was prepared by bulk polymerization in a degassed sealed tube initiated by 0.4 wt% AIBN at 60°C for 30 h. Poly(di-n-propyl itaconate) (PDnPI) and poly(di-n-butyl itaconate) (PDnBI) were similarly prepared by bulk polymerization.

PMOCMA was prepared by solution polymerization as described earlier[13].

The weight-average molecular weights (M_ws) and glass transition temperatures (T_gs) of the polymers are given in *Table 1*.

Preparation of blends

All the blends were prepared by solution casting from 2-butanone and dried *in vacuo* at 90°C for 1 week.

T_g *measurements*

The T_gs of various blends were measured with a DuPont 910 or a Perkin–Elmer DSC-4 differential scanning calorimeter. A heating rate of 20°C min^{-1} was used and the T_g value was taken as the initial onset of the change of slope of the second and subsequent runs.

FT*i.r. study*

*FT*i.r. spectra were recorded on a Perkin–Elmer *FT*i.r. spectrophotometer (1725X) using 32 scans at a resolution of 2 cm^{-1}. Samples were prepared by casting the 2-butanone solutions onto KBr discs followed by drying *in vacuo* at 90°C for 24 h.

Table 1 Characteristics of polymers

Polymer	M_w (kg mol^{-1})	T_g (°C)
PDMI	15[a]	90
PDEI-A	9.4[a]	26
PDEI-B	61[a]	50
PDnPI	79[a]	34
PDnBI	75[a]	5
PMOCMA	62[a]	55
PVPh-A	1.5–7.0[b]	133
PVPh-B	9.0–11[b]	139
PVPh-C	22[b]	150
PVPh-D	30[b]	150

[a] Determined by g.p.c.
[b] Provided by supplier

RESULTS AND DISCUSSION

Glass transition behaviour

All the blends of PDMI with the four PVPh samples were transparent with a brownish tinge and remained so upon heating to 300°C. Each of the blends showed a single composition-dependent T_g, indicating that PDMI is miscible with PVPh. The T_g–composition curve for PDMI/PVPh-A blends is shown in *Figure 1a*. The concave curve is typical for many miscible polymer blends.

All the blends of PDEI-A with the four PVPh samples were also transparent. The single T_g nature of each blend also indicates that PDEI-A is miscible with PVPh. The T_g–composition curve for PDEI-A/PVPh-A blends is shown in *Figure 1b*. In this case, the T_g values of the blends are very close to the weight-average values. The T_g–composition curves for the other three PDEI-A/PVPh blends also show the same features.

The high molecular weight PDEI-B was found to be miscible with PVPh-A and PVPh-B at all compositions as shown by the transparency and the single T_g nature of each of the blends. PDEI-B/PVPh-C blends were also clear. D.s.c. measurements showed the existence of a

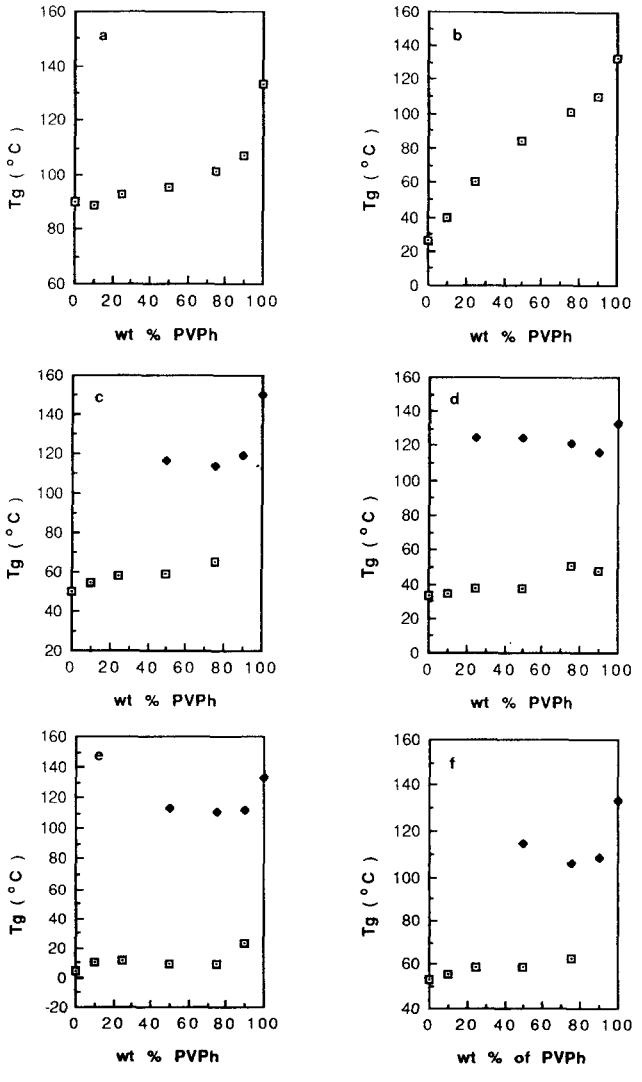

Figure 1 T_g–composition curves for the blends: (a) PDMI/PVPh-A; (b) PDEI-A/PVPh-A; (c) PDEI-B/PVPh-C; (d) PDnPI/PVPh-A; (e) PDnBI/PVPh-A; (f) PMOCMA/PVPh-A

single T_g for blends containing 10, 25 or 90 wt% PVPh-C. However, there were two T_gs for blends containing 50 or 75 wt% PVPh-C. The lower T_g values are slightly higher than that of PDEI-B, but the higher T_g values are substantially lower than that of PVPh-C. The T_g–composition curve for PDEI-B/PVPh-C blends is shown in *Figure 1c*. It is found that PDEI-B is, at best, partially miscible with PVPh-C. Similar behaviour was also found for PDEI-B/PVPh-D blends. The transparency of two T_g blends may arise from matching refractive indices of the two polymers or a small domain size. The present study shows that the miscibility of PDEI-B with PVPh is molecular weight dependent.

Figures 1d and *e* show the T_g–composition curves for PDnPI/PVPh-A and PDnBI/PVPh-A blends. Except at a low PVPh-A content, two T_gs were observed. The T_g values are different from those of the pure components. Similar behaviour was also found for blends of PDnPI and PDnBI with the high molecular weight PVPh-D. All the blends, including those with two T_gs, exhibited good optical clarity.

PMOCMA is isomeric to PDMI. However their miscibility behaviour with PVPh is different. For PMOCMA/PVPh-A blends, there is one T_g for blends containing 10, 25 or 90 wt% PVPh-A, and there are two T_gs for blends containing 50 or 75 wt% PVPh-A (*Figure 1f*). The higher T_g values are substantially lower than that of PVPh-A, indicating the presence of PMOCMA in the PVPh-rich phase. Similar behaviour was observed for blends of PMOCMA with the other three PVPh samples. Therefore, PMOCMA is, at best, partially miscible with PVPh. *Table 2* summarizes the miscibility of various blends.

FT*i.r. studies*

*FT*i.r. spectroscopy is a useful technique to study hydrogen bonding interactions in polymer blends. For the present systems, there is no question about the role of hydroxyl groups of PVPh in intermolecular interactions. However, it is difficult to ascertain whether one or both types of carbonyl groups in the di(alkyl itaconate)s and PMOCMA interact with PVPh. We have carried out *FT*i.r. studies on all the systems. Here we present the *FT*i.r. results for PDEI-B/PVPh-A, PDnBI/PVPh-A and PMOCMA/PVPh-A blend systems. The first represents a miscible system while the other two represent partially miscible systems.

Figure 2 shows the *FT*i.r. spectra, recorded at room temperature, of pure PVPh and PDEI-B/PVPh-A blends in the hydroxyl stretching region. Pure PVPh shows a broad band centred at 3372 cm^{-1} attributed to hydrogen-bonded hydroxyl groups (self-association), and a shoulder at 3525 cm^{-1} attributed to free hydroxyl groups. As the PDEI-B content in the blends is increased, the intensity of the free hydroxyl band decreases and the hydrogen-bonded band shifts to higher frequencies. The results indicate that the interaction between PVPh and PDEI-B is weaker than the self-association of PVPh. Coleman *et al.*[14–16] observed that for miscible PVPh/poly(vinyl acetate) (PVAc) and PVPh/poly(ε-caprolactone) (PCL) blends, the hydrogen-bonded hydroxyl band of PVPh shifted to higher frequencies. They asserted that although PVPh 'lost' through association with PVAc or PCL, the other polymers 'gained' through association with PVPh, and mixing was favoured on balance.

Table 2 Miscibility behaviour of various blends

	PVPh-A	PVPh-B	PVPh-C	PVPh-D
PDMI	M[a]	M	M	M
PDEI-A	M	M	M	M
PDEI-B	M	M	PM	PM
PDnPI	PM	ND	ND	PM
PDnBI	PM	ND	ND	PM
PMOCMA	PM	PM	PM	PM

[a] M, miscible; PM, partially miscible; ND, not determined

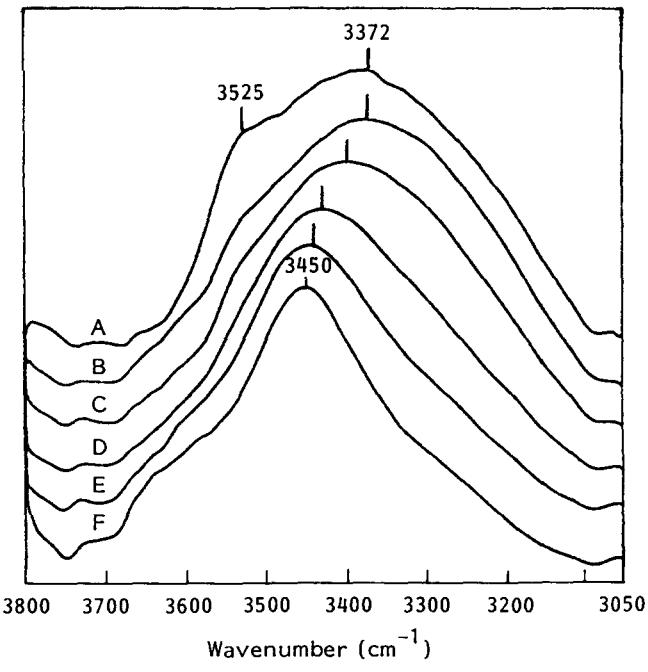

Figure 2 *FT*i.r. spectra in the hydroxyl stretching region of PDEI-B/PVPh-A blends: (A) 100; (B) 90; (C) 75; (D) 50; (E) 25; (F) 10 wt% PVPh-A

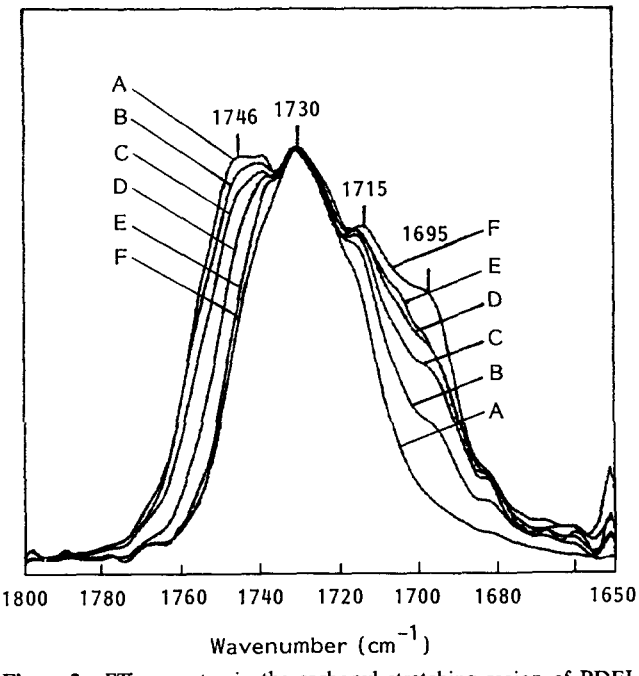

Figure 3 *FT*i.r. spectra in the carbonyl stretching region of PDEI-B/PVPh-A blends: (A) 0; (B) 10; (C) 25; (D) 50; (E) 75; (F) 90 wt% PVPh-A

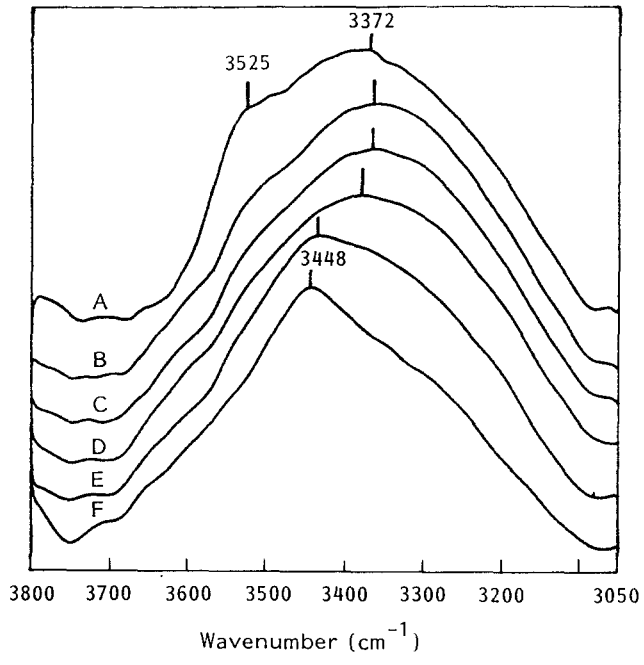

Figure 4 *FT*i.r. spectra in the hydroxyl stretching region of PDnBI/PVPh-A blends: (A) 100; (B) 90; (C) 75; (D) 50; (E) 25; (F) 10 wt% PVPh-A

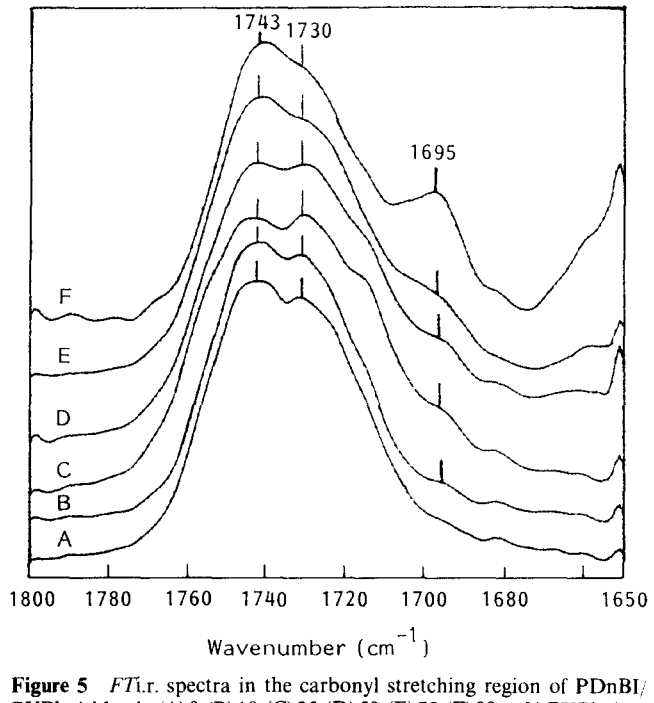

Figure 5 *FT*i.r. spectra in the carbonyl stretching region of PDnBI/PVPh-A blends: (A) 0; (B) 10; (C) 25; (D) 50; (E) 75; (F) 90 wt% PVPh-A

Figure 3 shows the *FT*i.r. spectra of the carbonyl bands of PDEI-B and various PDEI-B/PVPh-A blends. The two different carbonyl groups in PDEI-B are discernible. The band at 1746 cm^{-1} is assigned to the carbonyl group of $-CH_2COOC_2H_5$, and that at 1730 cm^{-1} is assigned to the other carbonyl group directly attached to the main polymer chain. The assignments are based on the steric effect shown by low molecular weight esters. In general, a carbonyl group attached to a bulky group absorbs at a lower frequency. For example, the carbonyl group of methyl proprionate absorbs at 1744 cm^{-1} and that of methyl pivalate absorbs at 1737 cm^{-1}. As the PVPh content is increased, the intensity of the $-CH_2COOC_2H_5$ carbonyl band decreases. At the same time new bands develop, most noticeably centred at 1715 and 1695 cm^{-1}, indicating the existence of intermolecular interactions with PVPh. The results show that the carbonyl group of $-CH_2COOC_2H_5$ is the preferred interacting site. The other carbonyl group, which is attached to the main chain, is less accessible for interaction with PVPh. For miscible PVPh/poly{bis[2-(2-methoxyethoxy)ethyl] itaconate} (PMEEI) (50/50) blends, Landry *et al.*[12] observed that the hydrogen-bonded hydroxyl band of PVPh shifts to a lower frequency, indicating a strong

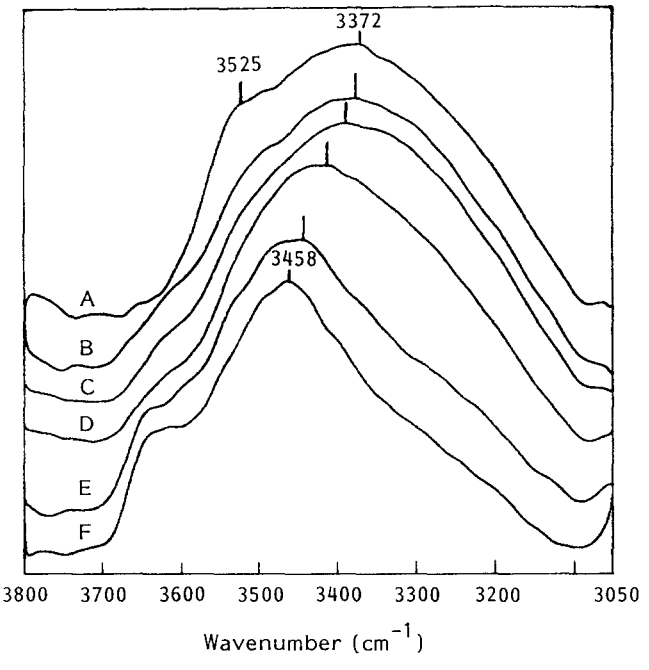

Figure 6 *FT*i.r. spectra in the hydroxyl stretching region of PMOCMA/PVPh-A blends: (A) 100; (B) 90; (C) 75; (D) 50; (E) 25; (F) 10 wt% PVPh-A

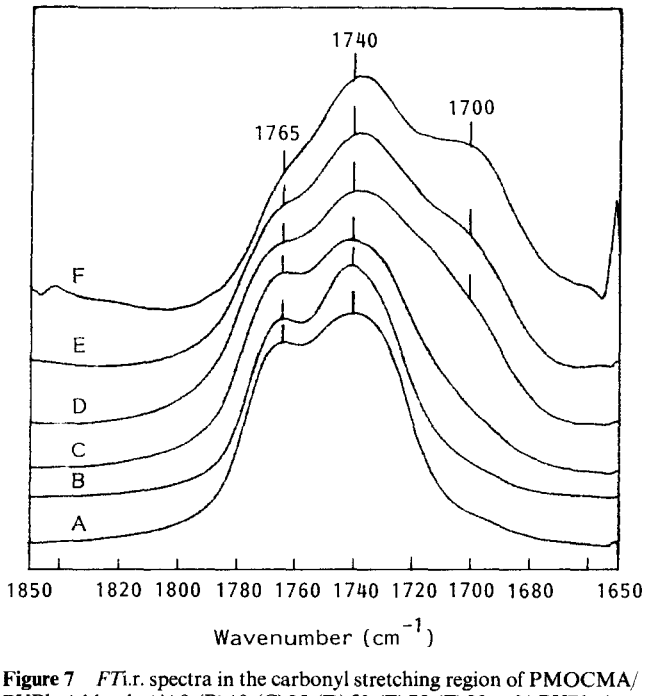

Figure 7 *FT*i.r. spectra in the carbonyl stretching region of PMOCMA/PVPh-A blends: (A) 0; (B) 10; (C) 25; (D) 50; (E) 75; (F) 90 wt% PVPh-A

interaction between the two polymers. They also observed two overlapping carbonyl bands at 1743 and 1728 cm^{-1} in PMEEI. The addition of PVPh leads to the development of a weak band at 1703 cm^{-1}, suggesting that very few carbonyl groups are hydrogen-bonded to PVPh and the interactions are dominated by the etheric side chains.

Figures 4 and *5* show *FT*i.r. spectra of PDnBI/PVPh-A blends. Even though the blends are not fully miscible as shown by d.s.c. studies, there are intermolecular interactions between the two polymers as shown by *FT*i.r. studies. The hydrogen-bonded hydroxyl band of PVPh shifts to higher frequencies upon blending with PDnBI. However, there appears to be little change in the intensity of the carbonyl band of $-CH_2COOR$, but the development of a band near 1695 cm^{-1} can be observed. Apparently, the intermolecular interactions between PDnBI and PVPh-A are not sufficiently strong to produce a completely miscible blend.

Figures 6 and *7* show the *FT*i.r. spectra of PMOCMA/PVPh-A blends. Similar to the poly(dialkyl itaconate)/PVPh systems, the hydrogen-bonded hydroxyl band of PVPh also shifts to higher frequencies, indicating a weaker PMOCMA–PVPh interaction as compared with the self-association of PVPh. The two different carbonyl groups of PMOCMA are also clearly discernible as shown in *Figure 7*. Similarly, the band at higher frequency (1765 cm^{-1}) is assigned to the carbonyl of the $-COOCH_3$ group and the other band at 1740 cm^{-1} is assigned to the carbonyl directly attached to the polymer chain. The addition of PVPh reduces the intensity of the band at 1765 cm^{-1} and leads to the development of a band centred at 1700 cm^{-1}. Once again, the results suggest that the carbonyl groups further away from the main chain interact with PVPh, but the interactions are still not sufficiently strong to achieve complete miscibility.

SUMMARY

The present study shows that as compared with poly(alkyl methacrylate)s, the presence of an additional carbonyl group in each poly(dialkyl itaconate) segment does not necessarily enhance its miscibility with PVPh. Only PDMI and a low molecular weight PDEI-A are miscible with PVPh of varying molecular weights. Higher members of the poly(dialkyl itaconate)s as well as PMOCMA are not completely miscible with PVPh. *FT*i.r. studies show the existence of hydrogen bonding interactions between the hydroxyl groups of PVPh and the carbonyl group of $-CH_2COOR$ in poly(dialkyl itaconate)s or the carbonyl group of $-COOCH_3$ in PMOCMA. However, the intermolecular hydrogen bonding interactions are weaker than the self-association of PVPh. It is not clear why poly(dialkyl itaconate)s show poorer miscibility with other polymers as compared with poly(alkyl methacrylate)s. Cowie and Elexpuru[10] suggested that the differences in free volume could be a possible factor but they did not have sufficient data to test this hypothesis.

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