The miscibility of polyacrylates and polymethacrylates with PVC: *In situ* polymerization and the miscibility of poly(methyl acrylate) and poly(ethyl acrylate) with PVC

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The *in situ* polymerization of vinyl chloride with various polyacrylates and polymethacrylates has been studied. The products were examined by dynamic mechanical analysis. Poly(methyl acrylate) and poly(ethyl acrylate) had previously produced two-phase blends with poly(vinyl chloride) (PVC) by solvent casting, but poly(ethyl acrylate) was shown to be miscible with PVC when blends were produced by *in situ* polymerization. Poly(methyl acrylate) and poly(octyl acrylate) were found to be immiscible with PVC whereas other polyacrylates and polymethacrylates with intermediate ester group concentrations were found to be miscible, confirming previous studies. The glass transition temperatures of the blends were measured and the deviations from the expected mean of the two base polymers were calculated as an indication of the strength of interaction between the polymers. The polymers having intermediate ester group concentrations showed the strongest interactions and the results correlated well with previously measured interaction parameters.

Keywords Miscibility; compatability; polymerization; vinyl chloride; poly(vinyl chloride); polyacrylate; polymethacrylate

INTRODUCTION

In a recent paper[1] we showed poly(vinyl chloride) (PVC) to be miscible with a wide range of acrylates and methacrylates with ester side chains up to 4 and 6 carbon atoms in length respectively. With longer side chains the blends were immiscible. The blends were prepared by solvent casting from butan-2-one and produced clear films which showed a single glass transition. Two exceptions were poly(methyl acrylate) and poly(ethyl acrylate) which gave heterogeneous blends.

Blends were also prepared by *in situ* polymerization by polymerizing vinyl chloride in the presence of the polyacrylates and polymethacrylates. Crosslinking occurred during polymerization and the products were insoluble in common solvents. The materials showed identical results to the solvent-cast blends concerning the miscibility of the polymers, except in the case of poly(methyl acrylate) and poly(ethyl acrylate) which produced homogeneous blends when prepared by this technique. The question remained: are the two polymers miscible with PVC but rendered immiscible by the presence of the solvent during solvent casting, or are they immiscible and made miscible as a result of crosslinking and grafting occurring during the *in situ* polymerization?

Solvents are known to cause heterogeneity in miscible polymer systems. For example, in the compatible system polystyrene–poly(methyl vinyl ether), blends cast from some chlorinated solvents formed two-phase structures[2]. Furthermore, in the miscible blends of PVC with polyacrylates, one-phase systems were formed when the polymers were cast from butanone but two phases were produced from THF[1]. It is also quite possible that a very high degree of grafting between two immiscible polymers would result in the appearance of miscibility.

In a more recent paper[3] we showed that it was possible to prepare blends of PVC and poly(butyl acrylate) by *in situ* polymerization, without serious problems of grafting or crosslinking, by using a different intiator, a peroxydicarbonate, and a lower polymerization temperature. It was found that if around 50% or less vinyl chloride was present in the mixture at the start of the polymerization, then homogeneous blends were formed. If more than 50% vinyl chloride was present the polymerization route passed through a two-phase region in the vinyl chloride/PVC/poly(butyl acrylate) three-component phase diagram (shown in *Figure 1*) and inhomogeneous blends were formed. Homogeneous blends with higher PVC content could be prepared by a two or more step polymerization procedure avoiding the two-phase region.

The reason for the miscibility of polyacrylates with PVC has been investigated by inverse gas chromatography[4]. It was found that the polymers had interaction parameters favourable for mixing. It was, of course, impossible to use this method to investigate blends which phase separate during solvent casting as this would produce heterogeneous films on the chromatographic support. This is known to give results which are a weighted mean of those of the two separate polymers[5].

In this paper we describe the results of *in situ* polymer-

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ization of vinyl chloride in poly(methyl acrylate) and poly(ethyl acrylate) which suggest that the former is immiscible with PVC and the latter miscible. We also describe the results of *in situ* polymerizations with other polyacrylates and polymethacrylates and compare them with the above and with the results of solvent casting.

EXPERIMENTAL

Materials

Poly(methyl acrylate), poly(ethyl acrylate), poly(butyl acrylate), poly(octyl acrylate) and poly(hexyl methacrylate) were supplied as solutions in toluene (Polysciences). Most of the toluene was removed on a rotary evaporator. The remainder was removed on a vacuum line until constant weight was achieved (2 weeks at 10^{-3} mm Hg). Poly(methyl methacrylate) (I.C.I.) and poly(ethyl methacrylate) and poly(butyl methacrylate) (Polysciences) were supplied in bead form and used as supplied. The polymers were characterized by gel permeation chromatography with THF as a solvent and the molecular weights were determined relative to polystyrene standards. The results are shown in *Table 1*.

Vinyl chloride was obtained in gas cylinders (Cambrian Gas) and was used as supplied.

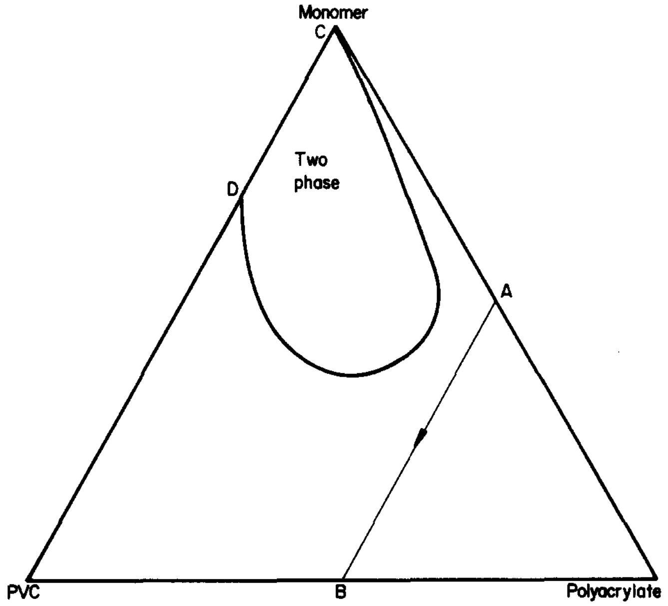

Figure 1 The vinyl chloride/PVC/polyacrylate phase diagram showing a polymerization pathway A→B. The limit of miscibility shown is for poly(butyl acrylate)[3] but it must have the same form for all miscible polymer pairs as the points C and D are fixed. Only the size of the two-phase regions can vary

Table 1 Molecular weights of polymers

Polymer	$\bar{M}_n$	$\bar{M}_w$
Poly(methyl acrylate)	9900	26 000
Poly(ethyl acrylate)	51 000	227 000
Poly(butyl acrylate)	33 000	119 000
Poly(octyl acrylate)	9500	23 000
Poly(methyl methacrylate)	44 000	106 000
Poly(ethyl methacrylate)	71 000	235 000
Poly(butyl methacrylate)	54 000	175 000
Poly(hexyl methacrylate)	52 000	288 000

t-Butyl cyclohexyl peroxydicarbonate (Laporte) was recrystallized from methanol and stored at below 0°C until required.

Preparations

Samples of blends were prepared by *in situ* polymerizations of vinyl chloride with the various polymers using t-butyl cyclohexyl peroxydicarbonate as an initiator, at 0.1% based on vinyl chloride, in sealed ampoules.

The initiator was introduced as a solution in methanol (A.R.) and the solvent removed by evaporation on a vacuum line. The polymer was then introduced into the ampoules. The vinyl chloride was then distilled into the ampoules on a vacuum line (in a fume cupboard; n.b. carcinogen). The vacuum line had been previously calibrated by introducing a known weight of dichloromethane and measuring the pressure it achieved using a manometer connected to the vacuum line. We thus knew the volume of the line. Vinyl chloride gas was admitted into the vacuum line from the cylinder until the pressure, read on the manometer, showed that the required weight of monomer was in the line. The cylinder was then isolated from the line and the monomer condensed into the ampoule using liquid nitrogen. The ampoule was then sealed off and the contents left to equilibrate for at least 12 h, turning occasionally to aid mixing. The ampoules were heated for 10 h in a water bath at 40°C while in a metal gauze container in case of explosion. The product was then removed from the ampoule, and, after allowing residual monomer to evaporate overnight, the sample was weighed in order to check the extent of conversion. By using a slight excess of vinyl chloride, samples within ±2% of 1:1 composition could be prepared. Samples for dynamic mechanical analysis were sectioned from the product using a hand microtome.

Previous results on the poly(butyl acrylate) blend had shown that the molecular weight averages of the blend (as determined by g.p.c. relative to polystyrene standards) were not higher than the base polymer which suggested that little grafting took place[3]. Samples of this blend have since also been extracted with cyclohexane (a solvent for the acrylate but not PVC) until no further weight loss was observed (108 h). It was found that 15% of the poly(butyl acrylate) was not extracted, which suggests that a small amount of grafting may in fact take place, but this is not thought to be sufficient to affect the results significantly.

Dynamic mechanical analysis

Dynamic mechanical measurements were used to confirm the phase structure of the blends. These were performed using a Rheovibron (Model DDV-II, Toyo Measuring Instrument Co. Ltd). A strip of the sample was subjected to an imposed oscillatory frequency of 11 Hz. A temperature range −180° to 120°C was scanned at 1°C min^{-1} heating rate and a plot of tan δ against temperature obtained. A maximum in tan δ was taken as a measure of T_g. A single peak suggests a homogeneous blend whereas two separate peaks suggest a two-phase structure.

RESULTS AND DISCUSSION

The dynamic mechanical results for a 50:50 PVC:poly(ethyl acrylate) blend are shown in *Figure 2*. They show one glass transition intermediate between those of the

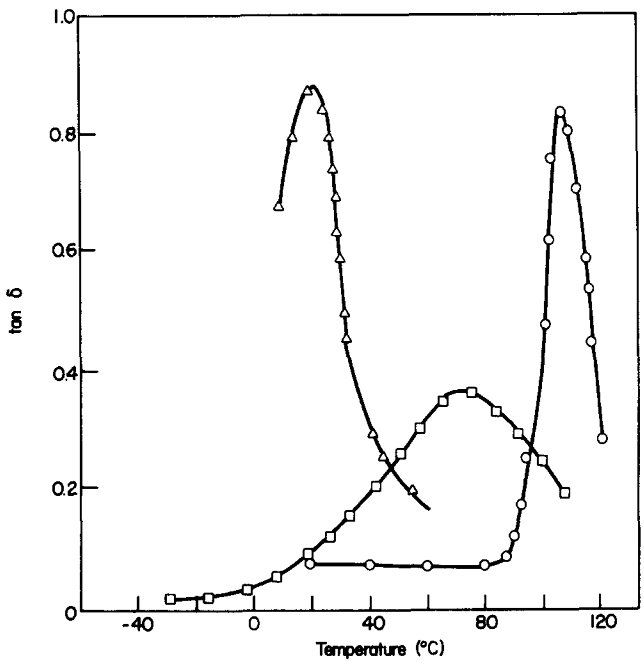

Figure 2 Plots of tan δ (not normalized) against temperature for PVC (○), poly(ethyl acrylate) (△), and a 50:50 *in situ* polymerized blend (□), showing a single intermediate glass transition indicative of a one-phase, miscible blend

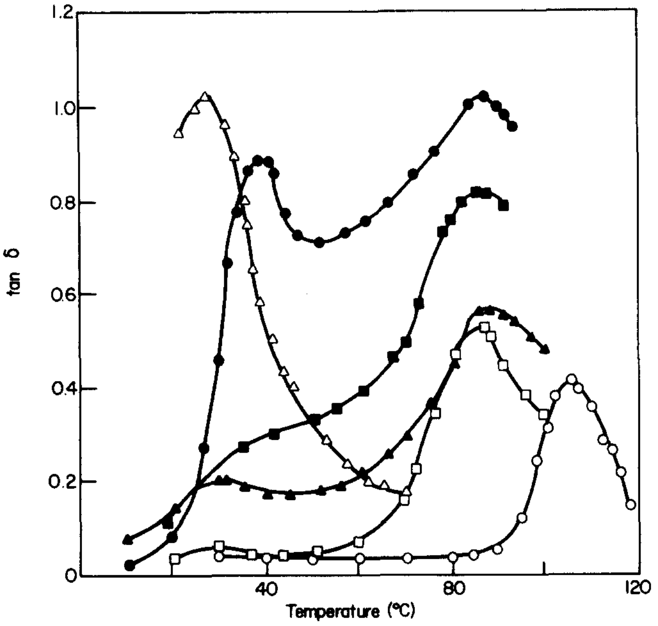

Figure 3 Plots of tan δ (not normalized) against temperature for PVC (○) and poly(methyl acrylate) (△) and PMA/PVC blends at compositions 80:20 (●), 60:40 (■), 50:50 (▲) and 20:80 (□). The blends show the presence of two glass transitions indicative of a two-phase, immiscible blend

Table 2 Glass transition temperatures of polymers and blends

Polymer	T_g (°C)	T_g (50:50 PVC blend)	T_g* (Fox)	ΔT_g (exp. – Fox)	Gordon–Taylor parameter, K
Poly(methyl acrylate)		(two T_g's)			
Poly(ethyl acrylate)	15	71	53	18	1.75
Poly(butyl acrylate)	–25	54†	26	28	1.61
Poly(octyl acrylate)		(two T_g's)			
Poly(methyl methacrylate)	128	118	115	3	1.5
Poly(ethyl methacrylate)	85	105	94	11	–10
Poly(butyl methacrylate)	40	82.5	68.5	14	2.07
Poly(hexyl methacrylate)	15	45	53	–8	0.48

* Calculated using a value of 103°C for the T_g of PVC

† This is a lower value than quoted previously[3]. The exact value has been found to vary with molecular weight and this value is chosen as a mean

components. The blend was transparent and flexible. This suggests that these two polymers are miscible.

The results for blends of PVC with poly(methyl acrylate) at various compositions are shown in *Figure 3*. It can be seen that two peaks are present. The blends were both turbid and brittle, with white particles appearing on the broken edges of fractured specimens. A wide range of compositions was tried in case a two-phase region existed in the three-component phase diagram similar to that shown in *Figure 1*. The two polymers may have been miscible, but the 50:50 polymerization route A→B (as shown in *Figure 1*) may have produced a two-phase mixture depending on the size of the two-phase region. This was shown not to be the case. The loss peaks of the blends have, however, shifted inwards from those of their pure components, which suggests that partial mixing has taken place.

Of the other blends prepared, all at 50:50 composition, those of poly(methyl methacrylate), poly(ethyl methacrylate), poly(butyl methacrylate), poly(hexyl methacrylate) and poly(butyl acrylate) were all miscible with PVC, showing a single glass transition at the temperature shown in *Table 2*. The poly(octyl acrylate) produced a cloudy blend which showed two glass transitions. The results for these blends[5] confirmed those found for solvent-cast blends described previously[1]. It is worth noting that the glass transition temperatures reported here are consistently higher than those quoted previously for solvent-cast blends. We believe that this is due to problems of residual solvent in the latter. Any residual vinyl chloride in the *in situ* blends will diffuse out of the samples very much faster than butan-2-one in solvent-cast blends.

Empirical or semi-theoretical relations connecting T_g and the composition, developed for copolymers, have been extended to polymer blends. The Fox equation[6]

$$\frac{1}{T_g}=\frac{w_1}{T_{g1}}+\frac{w_2}{T_{g2}}$$

gives the weighted average of the blend components, where T_g is the glass transition of the blend and w_i and T_{gi} are the weight fractions and glass transitions of the component polymers. Any positive deviation from this weighted average can be considered as evidence for interactions between the two polymers in the blend. *Table 2* also shows the predicted value for T_g and the difference from the experimental value.

Another expression for the T_g of a blend is the Gordon–Taylor equation[7]

$$T_g = \frac{w_1 T_{g1} + K w_2 T_{g2}}{w_1 + K w_2}$$

where K is a constant that gives an indication of the strength of the interaction between the two polymers. When $K=1$ we get the weighted average. When $K<1$, the T_g is lower than expected. When $K>1$, T_g is higher than expected, which suggests strong interactions. When the T_g equals that of the higher component, $K=\infty$. The K values tend to be larger when the T_g values of the components are similar for a given temperature deviation from the Fox equation. The values of K for the blends are shown in *Table 2*.

The poly(ethyl methacrylate) blend has a T_g above that of PVC so the K parameter gives a value of -10. This implies a very strong interaction. The poly(hexyl methacrylate) blend shows very unfavourable interactions and this blend is known to phase separate on heating giving an *LCST* below 120°C[1]. The other polymer for which the PVC blend is known to phase separate on heating, poly(butyl acrylate)[1,3], also has a fairly low K value. These values therefore give a reasonable indication of the strength of the interactions in the systems. One can also note that the poly(ethyl acrylate) blend has an appreciable K value despite the fact that the results of solvent-casting experiments had suggested that it was not miscible.

One can also compare the K values found with values of the polymer–polymer interaction parameters (χ_{23}) obtained by inverse gas chromatography[4]. These are for blends of PVC with poly(butyl acrylate) (0.98), with poly(butyl methacrylate) (-0.96) and with poly(ethyl methacrylate) (-3.03), all normalized with respect to one mole of PVC and measured at 120°C. It can be seen that the blend with the most favourable (negative) interaction parameter (PVC/PEMA) also has the strongest interaction inferred from the K value.

CONCLUSION

It has been shown that *in situ* polymerization can be successfully used to prepare a wide range of one-phase blends of polyacrylates and polymethacrylates with PVC.

It has been demonstrated that poly(ethyl acrylate) is miscible with PVC. Solvent casting had previously been shown to produce two-phase blends but one-phase blends can be prepared by *in situ* polymerization. Poly(methyl acrylate), however, still produces two-phase mixtures with PVC over a range of compositions when prepared by *in situ* polymerization. This suggests that it may be immiscible with PVC.

The glass transition temperatures of *in situ* polymerized blends have been measured and found to be consistently higher than those of solvent-cast blends. This is attributed to the effect of residual solvent.

The deviations of the T_g from the values expected from the Fox equation, and the Gordon–Taylor parameter, were calculated for each of the blends. The Gordon–Taylor parameter appears to give a good indication of the strength of interactions in the systems.

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