Miscibility studies in blends of poly(*N*-vinyl pyrrolidone) and poly(methyl methacrylate) with epoxy resin: a comparison

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(Received 8 February 1991; revised 21 August 1991; accepted 12 October 1991)

The results of *FT*i.r. studies of blends of poly(*N*-vinyl pyrrolidone) (PVPr) and poly(methyl methacrylate) (PMMA) with poly(diglycidal ether of bisphenol-A) (epoxy) are discussed. The changes observed in the OH and carbonyl stretching frequency region of the blend compositions studied are discussed in terms of hydrogen bonding interaction between the OH groups of epoxy resin and carbonyl groups of PVPr and PMMA. Qualitative as well as quantitative data have been obtained about these interactions and are compared. The *FT*i.r. results indicate a high degree of mixing at the molecular level for both blend systems at all compositions studied. It is observed that in the PVPr/epoxy blend system the strength of the hydrogen bonding interaction between the OH groups of epoxy and C═O groups of PVPr is much stronger than the interaction between the self-associated OH groups in pure epoxy resin. A more uniform hydrogen bonding between the OH groups of epoxy and C═O groups of PMMA was observed and is also discussed.

(Keywords: *FT*i.r.; epoxy; miscibility; hydrogen bonding; polymer blends)

INTRODUCTION

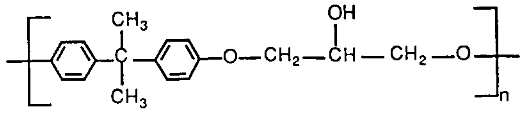
In a recent publication[1] we presented results of an *FT*i.r. study of a poly(*N*-vinyl pyrrolidone) (PVPr) and poly(vinyl alcohol) (PVA) blend system. The results indicated the miscibility of this system in the amorphous phase and we described the presence and nature of interactions between the two polymers. Evidence for hydrogen bonding between the C═O groups of PVPr and the hydroxyl groups of PVA was observed. We further reported that hydrogen bonding was maximal for 70 wt% PVA in the blends and that crystallinity of PVA was destroyed in the presence of PVPr for compositions with less than 60 wt% PVA.

The above results prompted us to blend the PVPr with another hydroxyl-containing polymer, poly(diglycidal ether of bisphenol-A) (epoxy resin), and compare the results with another C═O containing polymer, poly(methyl methacrylate) (PMMA), blended with epoxy resin. Goh and Siow[2] recently reported that blends of PVPr with poly(hydroxy ethyl methacrylate) and poly(hydroxy propyl methacrylate) are miscible, whereas they are immiscible with poly(ethyl methacrylate), indicating the importance of hydroxyl groups in achieving miscibility.

EXPERIMENTAL

Materials

Epoxy resin was synthesized[3] from bisphenol A and epichlorohydrin taken in a ratio of 1:3. The reaction was carried out at 60°C in the presence of an alkali, and the degree of polymerization was 2.75. The repeat unit, with epoxide rings as end groups, is shown below.



The weight per epoxide equivalent was 693, and it has a glass transition temperature (T_g) of 120°C.

PMMA (Aldrich) had an average molecular weight of 20 000 and a T_g of 105°C. PVPr (Fluka) had a number average molecular weight of 24 000 and a T_g of 150°C.

Method

Blends of various compositions were prepared from 2% (w/v) solution of chloroform. Thin films of both blend systems were cast on KBr windows for *FT*i.r. studies and allowed to evaporate slowly at room temperature. After most of the solvent had evaporated, the films were dried at 70°C in a vacuum oven for 24 h to remove any residual solvent. For thermal analysis, the films were cast on mercury and the same drying protocol was used.

Infra-red spectra were taken on a Nicolet 170SX *FT*i.r. spectrometer with a resolution of 2 cm^{-1}. Sixty-four scans were signal averaged and stored on magnetic discs. The frequency scale was internally calibrated with a reference He-Ne laser to an accuracy of 0.2 cm^{-1}. All the films used in this study were sufficiently thin to be within an absorbance range where the Beer–Lambert law is obeyed.

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0032-3861/92/173593-05

Differential scanning calorimetry (d.s.c.) studies were carried out on a Dupont 9900 thermal analyser in a nitrogen atmosphere with a heating rate of 10°C min^{-1}. The weight of samples used for thermal analysis ranged between 10 and 15 mg.

RESULTS AND DISCUSSION

The present study mainly concerns the carbonyl and hydroxyl frequency region of the i.r. spectrum. The i.r. spectrum of PVPr is detailed in ref. 1. The main features of the i.r. spectrum of epoxy resin are discussed elsewhere[4], and it has been shown that the i.r. region most sensitive to hydrogen bonding interaction is the OH stretching frequency region of 3000–3600 cm^{-1}. The OH stretching frequency region of epoxy resin is characterized by two bands, a relatively weak band centred at 3553 cm^{-1} assigned to unassociated OH groups, and a broad peak centred at 3405 cm^{-1} attributed to self-associated OH groups. Also, the fact that the i.r. spectrum of epoxy resin shows a window in the region 2000–1650 cm^{-1} allows interpretation of the C=O peaks of PVPr even for blend compositions rich in epoxy resin.

OH stretching frequency region

Figure 1 shows the *FT*i.r. spectra of pure epoxy resin and a few compositions of epoxy/PVPr blends in the region 3800–3100 cm^{-1}. The self-associated OH band at 3405 cm^{-1} and the unassociated OH band at 3553 cm^{-1} in pure epoxy are shown in *Figure 1A*. Upon blending with PVPr the following changes occur: the self-associated OH stretching frequency band at 3405 cm^{-1} is shifted to the low frequency side, to 3380 cm^{-1} for 50 wt% epoxy, and to 3330 cm^{-1} for 20 wt% epoxy resin in the blends. The unassociated OH stretching frequency band at 3553 cm^{-1} apparently remains constant for all compositions in the blend.

These results can be explained in terms of hydrogen bonding. The low frequency band at 3380 cm^{-1} for 50 wt% epoxy resin is assigned to the stretching vibration of the groups responsible for the hydrogen bonding interaction between the OH groups of epoxy resin and the C=O groups of PVPr. As the concentration of epoxy resin is reduced in the blends, this band further shifts to 3330 cm^{-1}, indicating hydrogen bonding. It should be noted that PVPr is hydrophilic, that it dissolves in water, and that the blend samples absorb moisture. Although every attempt was made to exclude moisture, we cannot definitely state that there is no contribution from moisture in this region.

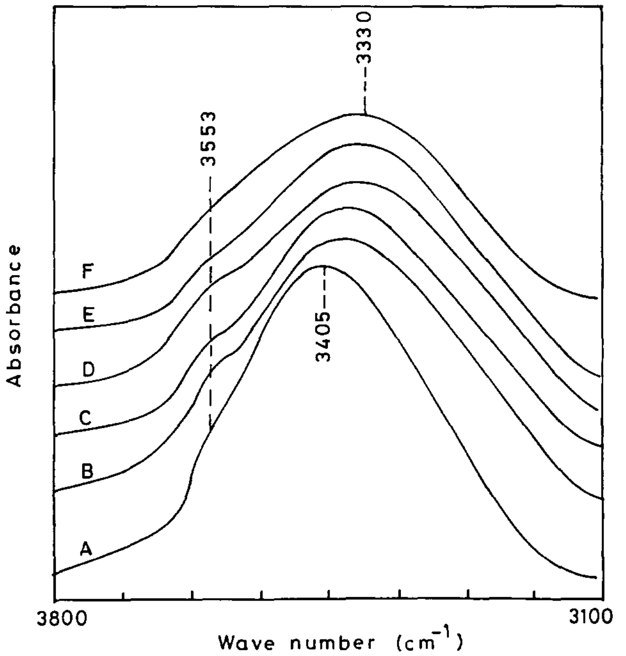

Figure 1 *FT*i.r. spectra in the region 3800–3100 cm^{-1} of PVPr/epoxy blends containing: A, 100; B, 80; C, 70; D, 60; E, 50; F, 40 wt% epoxy

The frequency difference between the free OH stretching vibration and the vibrations of the hydrogen-bonded species is a measure of the average strength of intermolecular interaction[5]. If the position of free hydroxyl stretching vibration at 3553 cm^{-1} is used as a reference, then the frequency difference ($\Delta\nu$) for hydroxyl–hydroxyl interaction (self-association) in pure epoxy resin is about 143 cm^{-1} while that of epoxy hydroxyl–PVPr carbonyl interaction is 223 cm^{-1}. This would imply that the intermolecular interaction in the epoxy–PVPr blend system is considerably stronger than the self-association of hydroxyl groups in pure epoxy resin.

Conversely, the results from epoxy/PMMA blends in the hydroxyl stretching frequency region is quite different, as shown in *Figure 2*. In the lowest concentration of

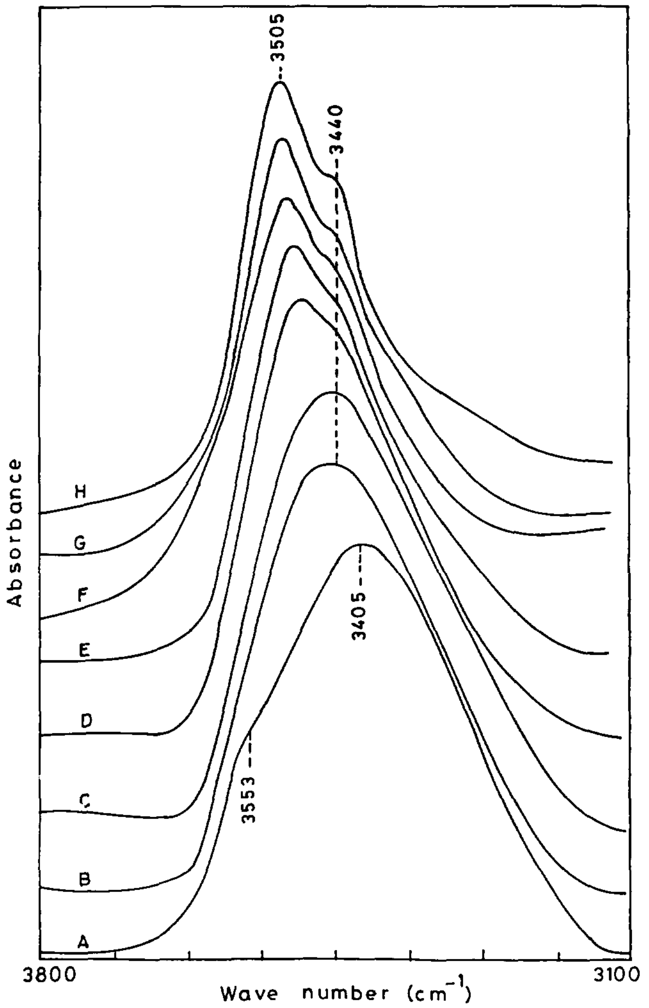

Figure 2 *FT*i.r. spectra recorded in the region 3800–3100 cm^{-1} for PMMA/epoxy blends containing: A, 100; B, 80; C, 70; D, 60; E, 50; F, 40; G, 30; H, 20 wt% epoxy

epoxy resin (20 wt%) two bands are observed, one at 3505 cm^{-1} and the other at 3440 cm^{-1}. As the concentration of epoxy is increased in the blends, the band at 3505 cm^{-1} gradually shifts to the low frequency side and merges with the band at 3440 cm^{-1} for 80 wt% epoxy resin. The high frequency band may be attributed to hydrogen bonding between the hydroxyl groups of epoxy resin and the C=O groups of PMMA. As the concentration of epoxy resin is increased, the band at 3505 cm^{-1} shifts to 3440 cm^{-1}, indicating the composition dependence of hydrogen bonding. On the other hand, the band at 3440 cm^{-1} remains constant for all compositions. This may be attributed to the self-associated OH groups of epoxy resin, which, instead of occurring at 3405 cm^{-1} as in pure epoxy, are shifted by 35 cm^{-1} to the high frequency side. This shows that the presence of PMMA molecules weakens the self-association of non-hydrogen-bonded hydroxyl groups in epoxy resin. It is also interesting to note that the unassociated OH stretching frequency band at 3553 cm^{-1} is absent in all blend compositions. The strength of the intermolecular interaction between the hydroxyl groups and carbonyl groups is weaker ($\Delta\nu = 113$ cm^{-1}) than the interaction of the self-associated OH groups, contrary to the results of the epoxy/PVPr blend system.

The most striking feature of *Figure 2* is the overall decrease in relative broadness of the hydrogen-bonded hydroxyl band with increasing PMMA content. This band was isolated from that of the non-interacting hydroxyl groups by spectral subtraction using pure epoxy hydroxyl band as reference, as shown by Musto *et al.*[6]. A plot of epoxy resin composition *versus* width at half height is shown in *Figure 3*. The width at half height is reduced from 300 cm^{-1} in pure epoxy resin to 190 cm^{-1} in 20 wt% epoxy resin in the blends. This can be explained as follows. In pure epoxy the distribution of hydrogen bonds would be expected to be random due to steric constraint. The uniformity of hydrogen bond distances and geometries would be prevented by the bulky benzene rings in pure epoxy. But in the miscible epoxy/PMMA blends the OH groups of epoxy would be able to form a more uniform distribution of hydrogen bond distances and geometries with PMMA molecules, leading to the narrowing of the hydrogen-bonded band. This kind of narrowing was observed in miscible blends of phenoxy resins and novalac resins[7,8].

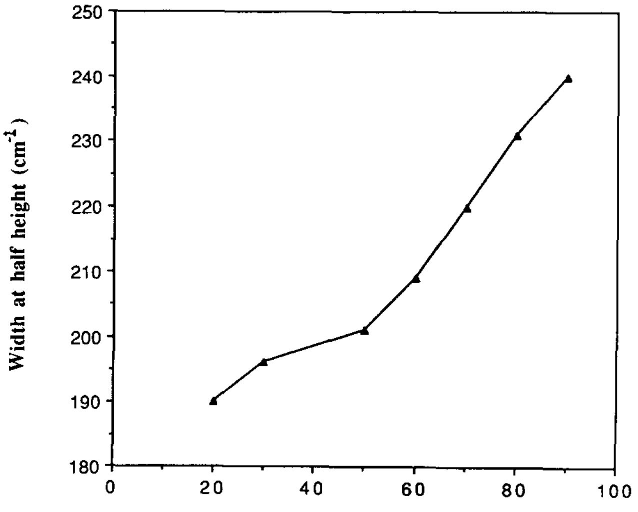

Figure 3 Plot of width at half height of hydroxyl stretching frequency band *versus* wt% epoxy resin

C=O stretching frequency region

The results observed in the hydroxyl stretching frequency region were expected to be reflected in the carbonyl stretching frequency of the i.r. spectrum. *Figure 4* shows the C=O stretching frequency region of pure PVPr and various compositions of PVPr/epoxy blends. The C=O stretching vibration of pure PVPr occurs at 1675 cm^{-1}. This band is a mixed mode containing contributions from C=O stretching and N–C stretching vibrations, which explains the relatively low frequency of this mode. Upon blending PVPr with epoxy resin, a second band is developed at 1658 cm^{-1}, which can be assigned with little difficulty to the hydrogen-bonded carbonyl groups. The intensity of this band is increased at the expense of non-hydrogen-bonded C=O group band for high concentrations of epoxy resin.

To obtain quantitative information about the number of interacting carbonyl groups of PVPr with hydroxyl groups of epoxy resin, spectral subtraction[9] was performed in this spectral region. The area of the hydrogen-bonded carbonyl group band gives a direct measure of the number of interacting C=O groups[10]. This hydrogen-bonded band, centred at 1658 cm^{-1}, is isolated by eliminating the non-interacting carbonyl groups band with pure PVPr as a reference using spectral subtraction. The subtraction results are remarkably clean, with a single symmetric band centred at 1658 cm^{-1}. Quantitative determination of the fraction of hydrogen-bonded carbonyl groups for all the blend compositions at room temperature were obtained and are listed in *Table 1*. The fraction of hydrogen-bonded

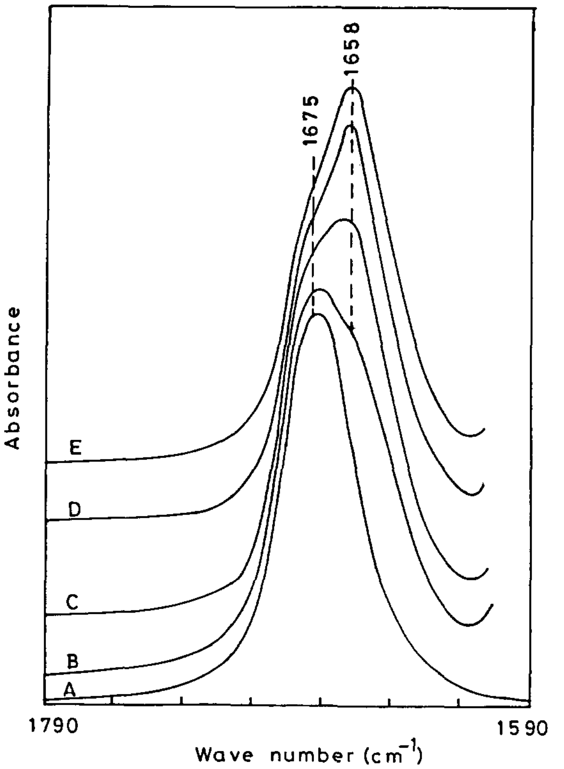

Figure 4 *FT*i.r. spectra recorded in the region 1790–1590 cm^{-1} for PVPr/epoxy blends containing: A, 100; B, 70; C, 40; D, 30; E, 20 wt% PVPr

Table 1 Results of spectral subtraction

PVPr (wt%)	Fraction C=O H-bonded
70	0.223
50	0.295
40	0.356
30	0.484
20	0.595

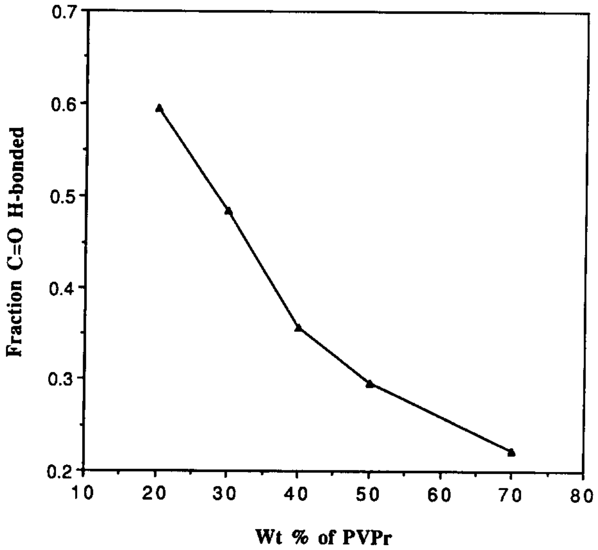

Figure 5 Plot of fraction hydrogen-bonded carbonyl group *versus* wt% PVPr

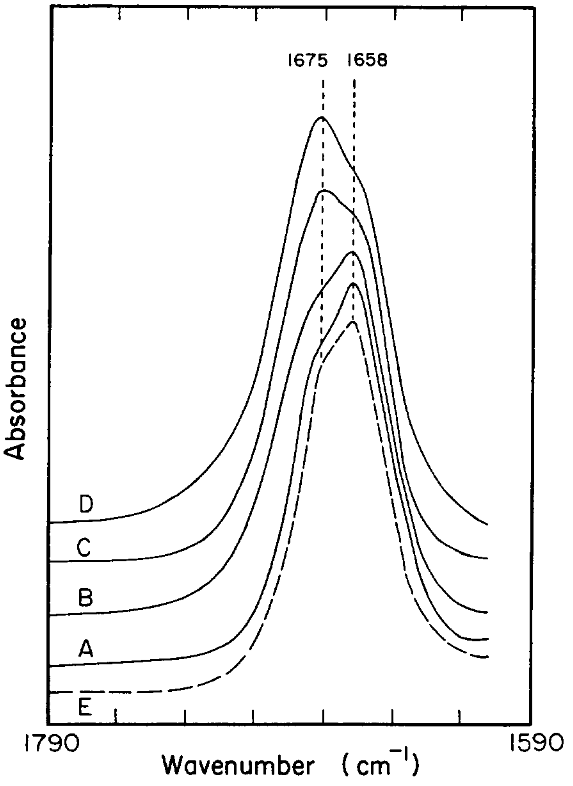

Figure 6 *FT*i.r. spectra recorded in the region 1790–1590 cm^{-1} for 70/30 composition of epoxy/PVPr blend at: A, room temperature; B, 100°C; C, 150°C; D, 175°C; E, after cooling to room temperature

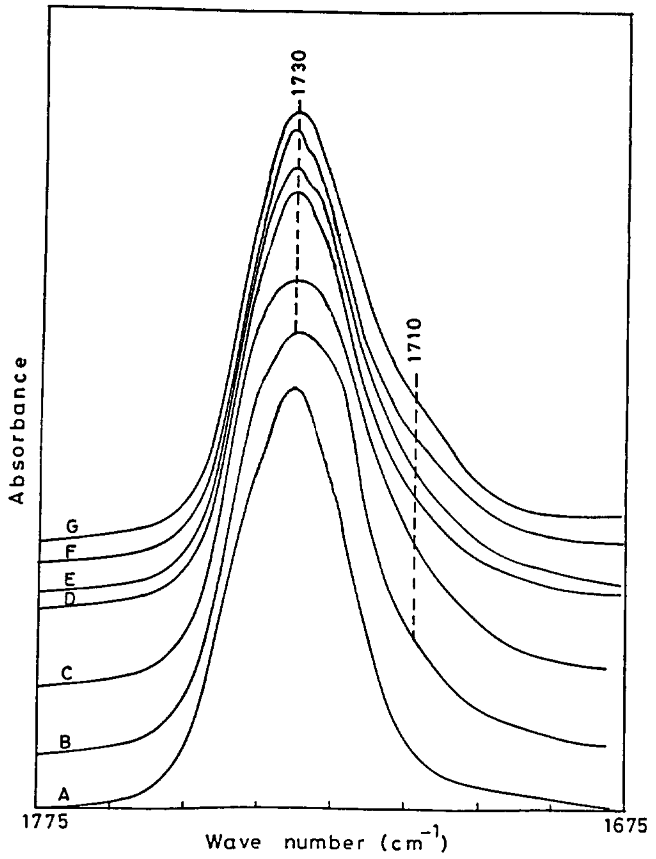

Figure 7 *FT*i.r. spectra recorded in the range 1775–1675 cm^{-1} for PMMA/epoxy blends containing: A, 100; B, 70; C, 60; D, 50; E, 40; F, 30; G, 20 wt% PMMA

carbonyl is plotted against wt% PVPr, as shown in *Figure 5*. From the plot it is apparent that the number of interacting C=O groups with OH groups of epoxy resin increased with decreasing concentration of PVPr; for the lowest concentration, almost 60% of C=O groups are hydrogen-bonded with epoxy OH groups. At equilibrium the ability to recover the initial fraction of hydrogen-bonded carbonyls upon heating and cooling is a necessary requirement and implies the existence of a single phase system in the temperature range studied. For a single phase system the observed decrease in the bonded fraction at high temperature simply reflects the effect of temperature on the equilibrium state of the system. *FT*i.r. spectra in the carbonyl region of 70/30 composition of epoxy/PVPr blend recorded as a function of increasing temperature are shown in *Figure 6*. As the temperature is increased to 175°C the intensity of the free carbonyl band increases at the expense of the hydrogen-bonded band. Upon cooling to room temperature the carbonyl region of the spectrum is almost identical to that of the initial spectrum before heating. As explained before, this kind of behaviour indicates a single phase system, which was confirmed by d.s.c. measurements.

Similar results were observed for the epoxy/PMMA blend system, whose C=O stretching frequency region is shown in *Figure 7*. The C=O stretching vibration of pure PMMA occurs at 1730 cm^{-1}. Upon blending PMMA with epoxy resin, the width at half height of the 1730 cm^{-1} band increased asymmetrically on the lower frequency side. This kind of asymmetrical broadening is due to the development of a new band, whose position

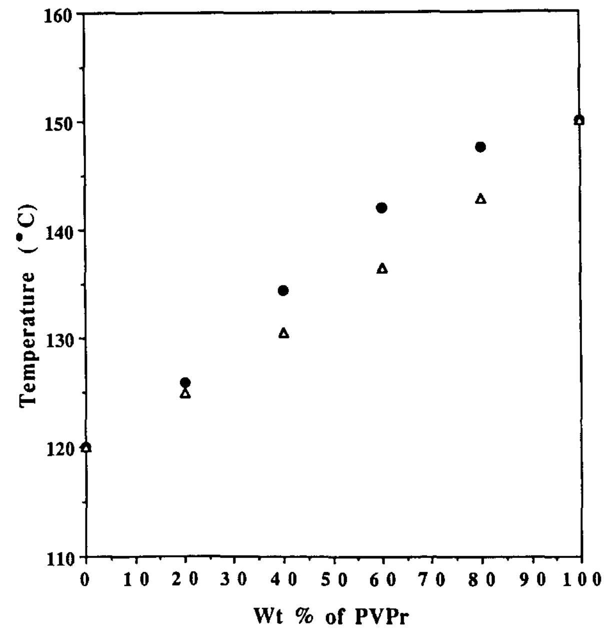

Figure 8 Plot of glass transition temperature *versus* wt% PVPr in PVPr/epoxy blends: ●, experimental; △, calculated using Fox equation

was determined using second derivative analysis[11,12]; this showed two negative lobes at 1730 cm^{-1} and at 1710 cm^{-1}. This new low frequency band can be easily assigned to hydrogen-bonded carbonyls in PMMA. Unlike the PVPr/epoxy blend system, the intensity of this band is very small, even for the lowest concentration of PMMA. Attempts to isolate this band using the spectral subtraction method failed and resulted in a derivative type of curve. Nevertheless, evidence for hydrogen bonding between C=O groups of PMMA and OH groups of epoxy is observed in this system.

The above results are substantiated by measuring the T_g of the blend system. A plot of T_g *versus* blend composition is shown in *Figure 8* for the PVPr/epoxy system, and the theoretical value of T_g (calculated using the Fox equation[13]) is shown for comparison. (As the T_gs of PMMA and epoxy are very close, we could not measure the blend T_g by d.s.c. Nevertheless evidence for miscibility is observed from *FT*i.r. studies.) In the PVPr/epoxy blend system a single composition-dependent T_g is observed, indicating the miscibility of this blend system. An interesting observation in the PVPr/epoxy blend system is that the experimental T_g is higher than the calculated T_g. This kind of positive deviation in T_g is expected if there is very strong hydrogen bonding between the two polymers[14], which the *FT*i.r. results clearly corroborate.

The above results indicate that both blend systems are miscible at the molecular level. *FT*i.r. spectroscopy results provide evidence for hydrogen bonding interaction between C=O groups of PVPr and PMMA with OH groups of epoxy resin. The strength of hydrogen bonding in the PVPr/epoxy blend system is much stronger than self-associated hydrogen bonding in pure epoxy resin, and there exists evidence for more uniform hydrogen bonding in the PMMA/epoxy blend system.

ACKNOWLEDGEMENT

The authors thank Dr P. Nagarajan for providing the epoxy resin used in this study.

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