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Miscibility in blends of poly(vinyl acetate-co-vinyl alcohol) with poly(N,N-dimethylacrylamide)

Luis G. Parada, Luis C. Cesteros, Emilio Meaurio and Issa Katime*
Grupo de Nuevos Materiales, Departamento de Química Física, Facultad de Ciencias, Universidad del País Vasco, Campus de Leioa, Apartado 644, Bilbao, España

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Miscibility of poly(N,N-dimethylacrylamide) (PDMA) with poly(vinyl acetate) (PVAC), poly(vinyl alcohol) (PVAL) and poly(vinyl acetate-co-vinyl alcohol) (ACAL copolymers) has been investigated over a wide composition range. Differential scanning calorimetry (DSC) results indicate that PDMA is immiscible with PVAC, but is miscible with PVAL and ACAL copolymers in certain range of compositions. The ACAL/PDMA phase diagram for different copolymer compositions has been determined. The variation of the glass transition temperature with blend composition for miscible systems was found to follow the Kwei equation. Infrared spectroscopy studies of blends reveal the existence of specific interactions via hydrogen bonding between hydroxyl groups in vinyl alcohol units and the carbonyl group in the tertiary amide, which appear to be decisive for miscibility. © 1997 Published by Elsevier Science Ltd. All rights reserved.

(Keywords: hydrogen bonding; specific interactions; polymer miscibility)

INTRODUCTION

The entropy of mixing for long molecules is usually small, and so the predominant term in the free Gibbs energy of mixing in those systems is the enthalpic one. Therefore, many reported miscible blends involve polymers with dissimilar chemical structures capable to establish specific interactions between chains, giving place to a negative enthalpy of mixing[1–10].

Polymers containing proton donating groups, such as carboxylic, phenolic or alcoholic hydroxyl groups, can form miscible blends with polymers containing proton-accepting groups through hydrogen bonding. For example, the proton acceptor polymer poly(4-vinyl pyridine) forms miscible blends with polymers containing hydroxyl groups such as poly(vinyl phenol)[1], poly(hydroxy ether) of bisphenol A (phenoxy)[2], or poly(vinyl acetate-co-vinyl alcohol) (ACAL copolymers)[3], and also forms strong polymer–polymer complexes (interpolymers) with polyacids[4–6].

Other proton acceptor polymer is poly(N,N-dimethylacrylamide) (PDMA), a polymer with tertiary amide groups, whose miscibility has been reported with poly(2-hydroxypropyl methacrylate)[7], poly(monomethyl itaconate)[8], poly (vinyl phenol)[9] and poly(styrene-co-allyl alcohol)[10].

Here we report on a miscibility study in blends of poly(N,Ndimethylacrylamide) with poly(vinyl acetate), poly(vinyl alcohol) and poly(vinyl acetate-co-vinyl alcohol) (ACAL copolymers). The vinyl alcohol units are proton donor and can interact by hydrogen bonding with the amide carbonyl groups of the tertiary polyamide. The possibility of hydrogen bond formation between hydroxyls and neighbouring carbonyls in the copolymer imply a short-scale competition of specific interactions. The objective has been to find new combinations of miscible polymers, analysing the influence over the miscibility behaviour of factors such as the degree of hydrolysis of the copolymers and the temperature. Additionally, the type of specific interactions existing in pure components and blends has been analysed.

EXPERIMENTAL

Materials

Poly(N,N-dimethylacrylamide) (PDMA) was obtained by solution polymerization in 2-propanol at 50°C for 2 h using AIBN as the initiator under nitrogen atmosphere. The monomer was supplied by Aldrich Chemical Co. and was used without further purification. The polymer was purified by dissolution in methanol and precipitation in ether. Molar mass was measured in an Ubbelohde type viscometer in methanol, at 25°C, using the following equation[11]: $[\eta] = 1.75 \times 10^{-4} M^{0.6}$, which leads to the value M_v = 53.000 g/mol.

Poly(vinyl acetate) (PVAC) (Erquipol S. A. sample B-17) was purified by dissolution in methanol and precipitation in water. Molar masses were measured at room temperature by size exclusion chromatography (SEC) of polymer solutions in tetrahydrofuran (THF) using for calibration the viscometric equation for PVAC in this solvent[12]: $[\eta] = 3.5 \times 10^{-2} M^{0.63}$. The results were 39.000 g mol^{-1} and 2.9 for molar mass and polydispersity, respectively.

Poly(vinyl alcohol) (PVAL) was obtained by total saponification of a alcoholic solution of PVAC with a NAOH aqueous solution (40% wt/v) at 50°C. The precipitate PVAL was purified by Soxhlet extraction with methanol.

Poly(vinyl acetate-co-vinyl alcohol) (copolymers ACAL) were synthesized by hydrolysis–methanolysis of PVAC at 50°C in an acid medium. The degree of hydrolysis was

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* To whom correspondence should be addressed at: Avda. Basagoiti, 8-1°C, 48990 Algorta, Guecho, Vizcaya, España.

Table 1 Degree of hydrolysis, glass transition temperature and heat capacity increase for PVAC, PVAL and ACAL copolymers used in this work

Polymer	Degree of hydrolysis (mol% VAL)	T_g (°C)	ΔC_p ($J\ g^{-1} {}^\circ C^{-1}$)
PVAC	0	44.3	0.40
ACAL08	7.8	46.2	0.46
ACAL15	15.3	48.2	0.46
ACA121	20.8	50.4	0.40
ACAL39	39.2	52.5	0.37
ACAL52	51.7	54.3	0.50
ACAL84	84.4	76.1	0.31
PVAL	99.5	82.0	0.14

Table 2 Glass transition temperature and melting point for blends of PVAC and PVAL with PDMA

Polymer	PDMA (wt%)	T_g (°C)	T_m (°C)
PVAC	0	44.3	—
	20	45.4, 122.3	—
	40	45.4, 119.4	—
	60	46.3, 120.3	—
	80	45.5, 118.5	—
	100	122.4	—
PVAL	0	82.0	231.2
	20	88.8	229.0
	40	94.1	228.9
	60	106.1	228.4
	80	108.9	227.9

Table 3 Glass transition temperature for blends of poly(vinyl acetate-co-vinyl alcohol) with PDMA

Copolymer	PDMA (wt%)	T_g (°C)
ACAL08	0	46.2
	20	52.7
	40	49.5, 115.4
	60	49.6, 119.5
	80	49.6, 118.5
ACAL15	0	48.2
	20	54.0
	40	58.0
	60	79.5
	80	100.8
ACA121	0	50.4
	20	55.5
	40	66.2
	60	78.1
	80	100.9
ACAL39	0	52.5
	20	58.1
	40	68.7
	60	83.5
	80	100.9
ACAL52	0	54.3
	20	62.2
	40	71.5
	60	84.9
	80	102.2
ACAL84	0	76.3
	20	83.5
	40	84.8
	60	101.2
	80	112.5

controlled by varying the time of reaction, and was determined by titration of residual acetate groups[13,14]. Reaction products with low degrees of hydrolysis (less than 60%) were precipitated in water followed by dissolution in methanol and reprecipitation in water. Reaction products with higher degrees of hydrolysis were precipitated in methanol and purified by Soxhlet extraction for at least 4 h.

For the synthesis method used, a random distribution of hydroxyl groups in the copolymer chain is expected[13,15]. Glass transition temperatures and ΔC_p at T_g of the copolymers are compiled in *Table 1*.

Preparation of blends

Polymer blends were prepared by solvent casting from methanol or water solutions (depending upon the solubility of the components) with a total polymer concentration of 40 mg ml^{-1}. Solutions were poured into petri dishes, and the solvent was evaporated under an air stream. When water was the solvent, the temperature of evaporation was kept at 120°C, whereas for methanol solutions the temperature was 80°C.

Thermal analysis

Thermal analysis was performed in a Mettler TA4000 differential scanning calorimeter, previously calibrated with indium. A thermal pretreatment was applied to polymer blends. As PDMA is highly hygroscopic, all the samples were preheated to 125°C and held at that temperature for 10 min to ensure complete removal of any moisture or residual solvent. After this the samples were cooled rapidly to −40°C and scanned between −40 and 180°C at 20°C min^{-1}. The blends containing PVAL where scanned until 250°C. Reported results correspond to the values obtained in the second scan. Samples used for calorimetric measurements weighed between 10 and 12 mg. The glass transition temperature (T_g) was taken as the inflection point of the jump in heat capacity. Reported melting points correspond to the minimum of the melting peak.

Spectroscopic analysis

Infrared spectra for polymers and polymer blends were recorded on a Nicolet-520 Fourier transform infrared spectrophotometer (FTIR). Spectra were taken with a resolution of 2 cm^{-1} and were averaged from 100 scans. Films for FTIR analysis were cast from solutions (20 mg ml^{-1}) in the same way as calorimetric samples. Samples dissolved in methanol were cast directly on KBr pellets, and AgCl pellets were used for samples dissolved in water. All films were vacuum dried.

RESULTS AND DISCUSSION

Miscibility analysis

Calorimetric results clearly show that the PVAC/PDMA blends are immiscible. For all the compositions tested, films were turbid and two distinct values of glass transition temperature were observed, each close to the T_g of the correspondent homopolymer (see *Table 2*). Since the solvent used to obtain the blend may have affected the miscibility, blends were prepared in methanol and acetone, but again immiscibility was found. Even blends prepared by coprecipitation in ether in order to minimize the solvent effect were immiscible.

Blends of PVAL/PDMA, prepared by solvent casting from water solutions, are miscible over the whole composition range, films are transparent and thermograms show a single T_g located between the T_gs of the pure components.

For blends of ACAL copolymers with PDMA, miscibility depends on the degree of hydrolysis and blend composition. For hydrolysis degrees of 8% the system is miscible if the PDMA content in the blend is lower than 20%. Films obtained are transparent and thermograms show a single T_g (see *Table 3*). For PDMA compositions higher than 20% (wt/wt), films are opaque and thermograms show two T_gs close to the ones of the pure components. For ACAL

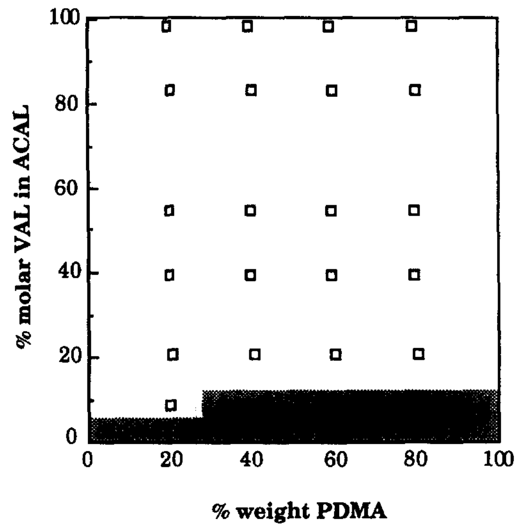

Figure 1 Phase diagram of PDMA/ACAL copolymer blends, at room temperature: (■) immiscible and (□) miscible blends

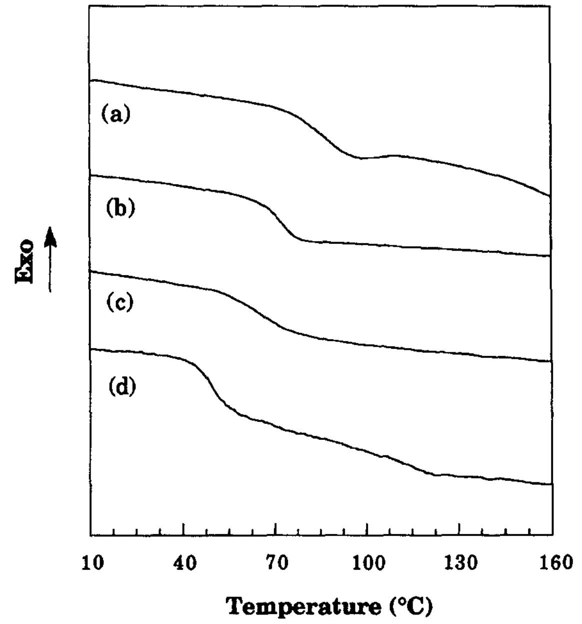

Figure 2 Thermograms for polymer blends 60/40 (wt/wt): (a) ACAL84/PDMA; (b) ACAL52/PDMA; (c) ACAL21/PDMA; (d) ACAL08/PDMA

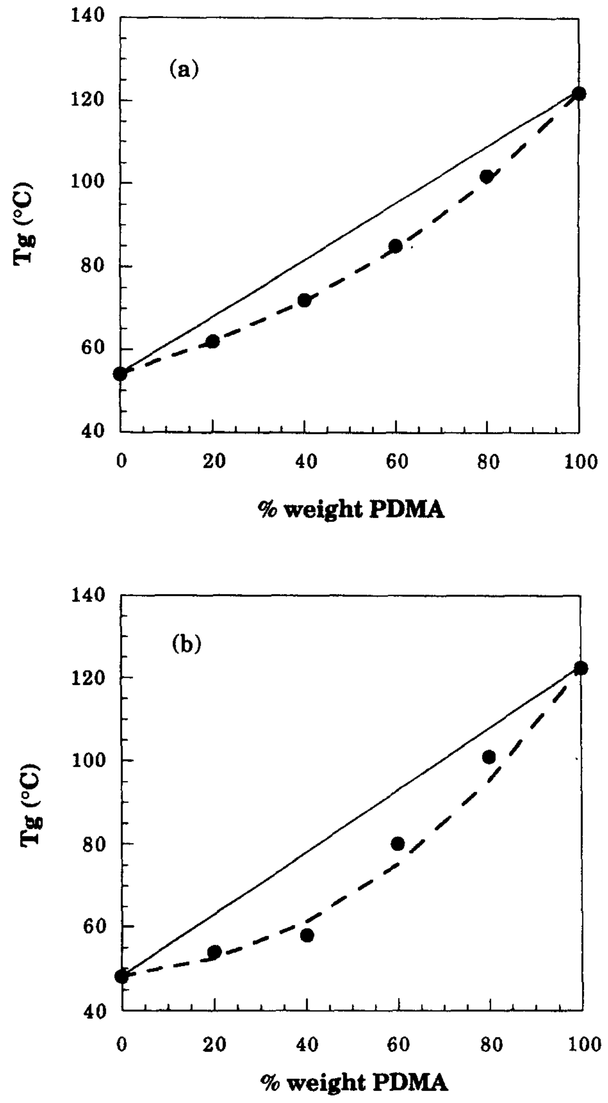

Figure 3 Plot of T_g *versus* PDMA content for two miscible blends: (a) ACAL52/PDMA, and (b) ACAL15/PDMA. Dotted lines indicate the Kwei fit

copolymers with degrees of hydrolysis ranging from 15% the systems are miscible for all compositions.

Figure 1 presents the phase diagram of the studied systems obtained from calorimetric results as a function of copolymers and blends composition. It appears that miscibility is favoured by an increase in the degree of hydrolysis and that there is a low miscibility limit. This behaviour is clear from *Figure 2*, which shows the calorimetric curves for different blends with the same PDMA content.

The phase diagram presented displays the behaviour of the blends at temperatures close to the degradation of the pure component with lower thermal stability. No phase separation is observed for temperatures up to 250°C, where the polymer degrades.

Polymers blends are commonly characterized by the dependence of T_g on the composition of miscible systems[16,17]. In *Figure 3*, the variation of T_g with composition for two ACAL/PDMA blends is shown. In all cases the T_g of the blend is lower than the average T_g of the pure components. The dependence of T_g on blend composition can be represented by the Kwei equation[18]:

$$T_g = \frac{(w_A T_{gA} + k w_B T_{gB})}{(w_A + k w_B)} + q w_A w_B$$

where w_A and w_B are the weight fractions of the components, T_{gA} and T_{gB} are the corresponding glass transition temperatures; $k = \Delta C_{pB}/\Delta C_{pA}$ and q is a constant. ΔC_{pA} used is the heat capacity increase of PDMA (0.28 J g^{-1}°C^{-1}). ΔC_{pB} values, corresponding to ACAL copolymers, are listed in *Table 1*. *Figure 3* shows the fitting of experimental data to the Kwei equation. The values of q, that have been taken as an adjustable parameter, are -35.0, -26.0, -2.5 and -8.0 for ACAL15, ACAL39, ACAL52 and ACAL84, respectively. The q parameter should not be considered as simply reflecting the strength of interactions in blends. According to Painter *et al.*[19] the q parameter can have negative values and depends upon the balance between the processes of self-association and interassociation in the blend and of the temperature dependence of the specific heats of the components.

As can be seen in *Figure 3*, the negative deviation from additivity of the glass transition temperatures increases with decreasing hydroxyl group content in the copolymer. This behaviour can be attributed to deviations from linearity of the free volume in the blends. Free volume changes are related with the interactions between chains, that give place to orientation effects: free volume becomes lower when orientation effects increases. Therefore the free volume increment and the negative deviation respect to linearity are greater when the specific interactions between blend components are smaller. In other words, the mobility of the chains diminishes due to the presence of hydrogen bonds that act as effective cross-links.

Specific interactions analysis

Infrared spectroscopy can be used to detect the existence of specific interactions in polymer blends, especially hydrogen bonding which is suspected to occur between the hydroxyl groups of PVAL and ACAL copolymers and the amide carbonyl groups of PDMA.

Several regions of the infrared spectra of ACAL copolymers are influenced by self-association through hydrogen bonding. *Figure 4* show the FTIR spectra in the 2900–3700 cm^{-1} range for PVAL and different ACAL copolymers. It is obvious that hydrogen bonding affects the hydroxyl stretching band. This broad band can be considered to be composed of narrow contributions corresponding to hydroxyl groups surrounded by different environments. When the spectra of ACAL copolymers are compared, a shift of the peak maximum toward higher wavenumbers is observed as the acetate content in the copolymer increases; at the same time the band becomes narrower. These results suggest that there are different types of hydroxyl groups in ACAL copolymer (in descending order with respect to wavenumber)[20]: free, hydrogen bonded to carbonyl groups and self-associated hydroxyl groups in the form of dimers, trimers, etc.

In the case of ACAL84/PDMA blends (*Figure 5*), infrared spectra show a clear shift of the hydroxyl band toward higher wavenumbers, compared with the position of this band in pure ACAL copolymer. As the PDMA content in the blend increases, the band gradually shift to higher

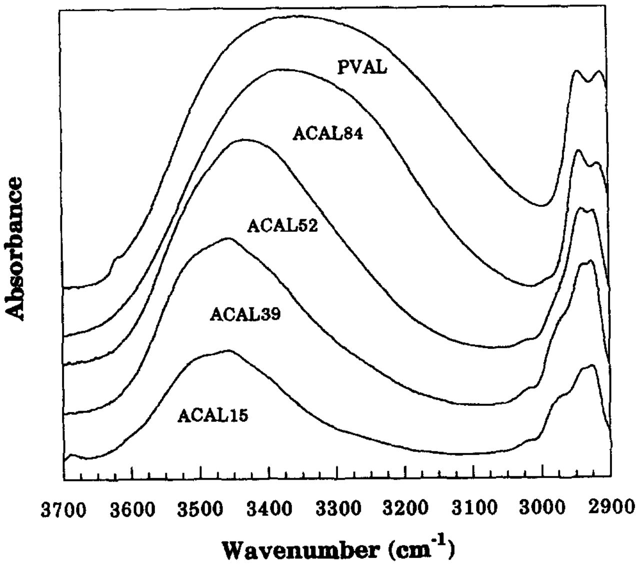

Figure 4 Infrared spectra of the stretching hydroxyl region of PVAL and some ACAL copolymers

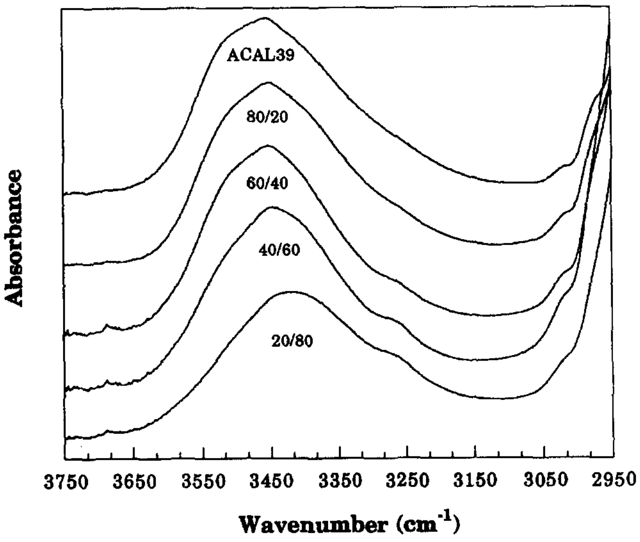

Figure 6 Infrared spectra of the hydroxyl stretching region of pure ACAL39 and ACAL39/PDMA blends with different compositions (wt/wt)

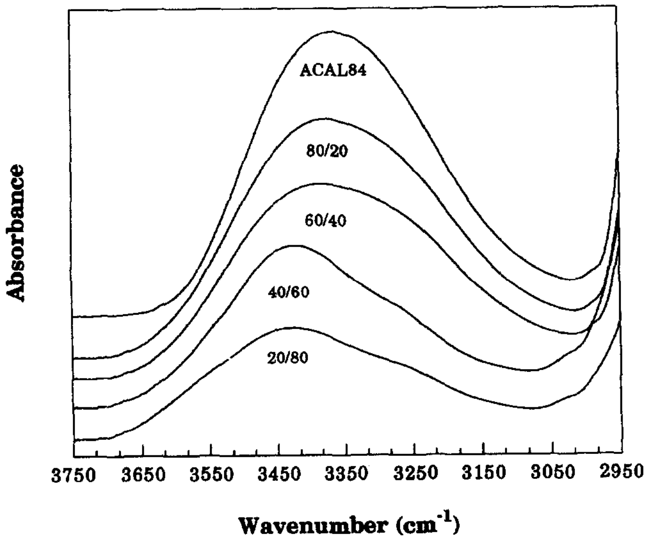

Figure 5 Infrared spectra of the hydroxyl stretching region of pure ACAL84 and ACAL84/PDMA blends with different compositions (wt/wt)

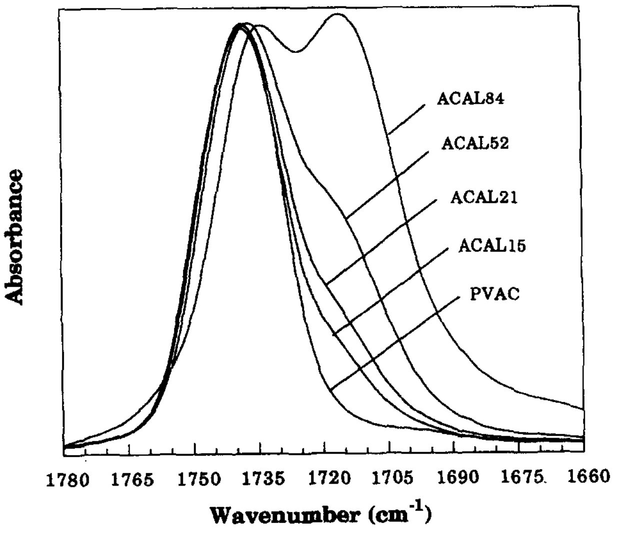

Figure 7 Infrared spectra of the stretching carbonyl region of PVAC and some ACAL copolymers

frequencies, which can be considered as evidence for existence of specific interactions (hydroxyl–amide carbonyl). The displacement direction indicates that the intensity of this interaction is lower than the self-association in the pure copolymer (mainly hydroxyl–hydroxyl). The blends PVAL/PDMA present similar results in this spectral region.

For ACAL39/PDMA blends, infrared spectra show a clear displacement of the hydroxyl stretching band toward lower wavenumbers, compared with the position in pure ACAL39 (see *Figure 6*). This copolymer has a degree of hydrolysis smaller than ACAL84, and therefore a great number of hydroxyl–acetate carbonyl interactions. The modifications of the band in this case show that the intensity of the hydroxyl–amide carbonyl interactions in blends is higher than the hydroxyl–acetate carbonyl interactions in ACAL39. In *Figure 6* a small shoulder is observed at 3265 cm^{-1}, this band is an overtone of the amide carbonyl stretching mode.

To sum up, infrared data clearly prove the involvement of ACAL hydroxyl groups in the specific intermolecular interactions responsible for the miscibility of the blends.

The carbonyl stretching band for PVAC is located at 1738 cm^{-1}. When PVAC is partially hydrolysed, a new band occurs at lower wavenumbers, whose relative intensity increases with the hydrolysis degree (see *Figure 7*). The new contributions in ACAL copolymers spectra corresponds to hydrogen bonded carbonyl groups.

The introduction of amide carbonyl groups in the blend leads to a competition with acetate carbonyl groups for hydrogen bonding with hydroxyl groups. As can be seen in *Figure 8*, this competition is evident in the evolution of carbonyl stretching bands of ACAL copolymers in blends. Thus, for a particular ACAL copolymer a decrease in the contribution corresponding to hydrogen-bonded carbonyl groups (progressive disappearance of the shoulder at low wavenumber) is observed as the content of PDMA in the blend increases. In other words, hydroxyl–amide carbonyl interactions prevails over hydroxyl–acetic carbonyl self-association.

The band corresponding to amide carbonyl stretching in PDMA has a strong absorption centred at 1642 cm^{-1}. This band also shows a different profile when amide carbonyls are hydrogen bonded. Fortunately, ACAL copolymers do not show a significant absorbance in this region and, in this way, we can observe without interferences the evolution of amide carbonyl modes in the blends.

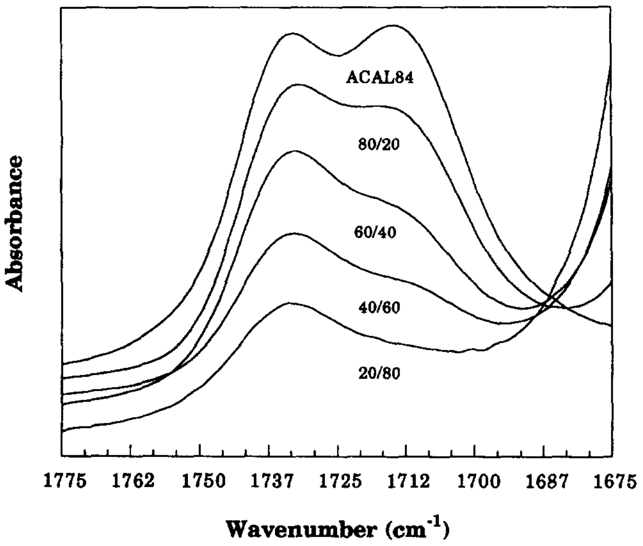

Figure 8 Infrared spectra of the stretching carbonyl region of ACAL84 and blends ACAL84/PDMA

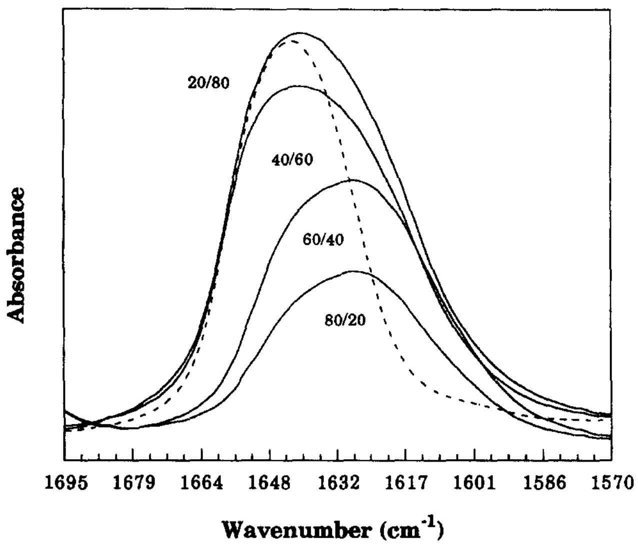

Figure 9 Infrared spectra of the stretching carbonyl region of PDMA (- - -) and blends ACAL84/PDMA

All the miscible blends show the same trend for 1642 cm^{-1} band: as the ACAL content increases in the blend, the band shifts toward low wavenumbers (see *Figure 9*). In addition, this band is broader in the blends than in pure PDMA. In other words, we have two classes of amide carbonyl bands: those hydrogen bonded to hydroxyl groups (with a corresponding effect over the hydroxyl stretching) and those non-hydrogen bonded. The addition of their spectral contributions results in a broadening and shifting of the band. From a qualitative point of view this is a logical behaviour because, as the content of ACAL copolymer increases in the blend, a larger number of hydroxyl groups are available to hydrogen bond with the amide carbonyl groups.

CONCLUSIONS

Miscibility was found between PVAL and PDMA, but not in blends of PDMA with PVAC. The miscibility behaviour of this systems is not a surprising result taking into account the chemical structures of the blend components. Hydrogen bond formation between amide carbonyl and hydroxyl groups has been observed by means of infrared spectroscopy.

For ACAL/PDMA blends, miscibility was found to depend upon blend composition and degree of hydrolysis of the copolymer. The phase diagram has a low miscibility limit. Infrared analysis of the blends allows us to conclude that specific interactions through hydrogen bonding are responsible of the miscibility behaviour of these systems. In ACAL copolymers with lower hydroxyl content, the density of possible hydrogen bonds is insufficient to provide miscibility.

Glass transition temperatures of the blends are lower than the average T_g of the pure components. The deviation increases with decreasing the hydroxyl group content in the copolymer. This deviation from additivity can be attributed to deviations with respect to free volume linearity in the blends. Free volume changes are related with the interactions between chains, that give place to orientation effects. Therefore, the free volume increment and the negative deviation respect to linearity are greater when the specific interactions between blend components are smaller.

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