

Poly(*N,N*-dimethylacrylamide)/copolymers of vinyl alcohol blends: effect of the comonomer

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Abstract

The miscibility behaviour of poly(*N,N*-dimethylacrylamide) (PDMA), with poly(ethylene-co-vinyl alcohol) (EVAL) of different compositions has been investigated and compared to that of the blends with poly(vinyl acetate-co-vinyl alcohol) (ACAL). Differential Scanning Calorimetry (DSC) results indicate that PDMA is miscible with EVAL78, EVAL68 and EVAL56 but immiscible with EVAL25, which has lower degree of hydrolysis. The limit of miscibility is lower in this case, indicating the influence of the vinyl alcohol content in miscibility. Fourier transformed infrared spectroscopy (FTIR) studies of miscible blends reveal the existence of specific interactions by hydrogen bonding between hydroxyl groups in vinyl alcohol units of the copolymers and the amide-carbonyl group in the PDMA, which appear to be decisive for miscibility. © 1999 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Polymer miscibility in most cases is the result of specific interactions between chains that provide an enthalpy of mixing negative enough that the Gibbs free energy is also negative [1,2]. Homopolymer blends mainly require “complementary dissimilarity” between both polymers in order to establish favourable specific interactions. Nevertheless, when copolymers are present, the “copolymer effect” may be responsible for a miscibility window due to an advantageous combination of interactions and repulsions [3,4].

Recently, we have reported several polymer blends with components having complementary chemical structures favourable for specific interactions by hydrogen bonding, but with a miscibility behaviour also controlled by other factors [5,6]. These systems are blends of random poly(vinyl acetate-co-vinyl alcohol) (ACAL copolymers) with different degree of hydrolysis with a tertiary amide polymer, poly(*N,N*-dimethylacrylamide) (PDMA); the former act as proton donors and the latter as proton acceptors (see chemical structures in Fig. 1). We found that PDMA is miscible with ACAL copolymers in a wide range of copolymer compositions, where the low limit of

miscibility corresponds to the copolymer with only 8% molar of vinyl alcohol units.

According to previous results [7,8], there are spectral evidences of hydrogen bonding in ACAL/PDMA blends. Hydrogen bonding takes place not only between amide and vinyl alcohol units but also between vinyl alcohol and vinyl acetate units. We conclude that specific interactions are responsible for the miscibility window, and the copolymer composition is decisive in the miscibility behaviour of the blends.

This work is an extension of our previous studies, the systems polyamide tertiary/poly(ethylene-co-vinyl alcohol) are less complicated than polyamide tertiary/poly(vinyl acetate-co-vinyl alcohol) from the point of view of specific interactions; their miscibility behaviour will be compared. These new systems offer the possibility of analysing the influence of the comonomer of vinyl alcohol on the miscibility behaviour.

2. Experimental part

2.1. Materials

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

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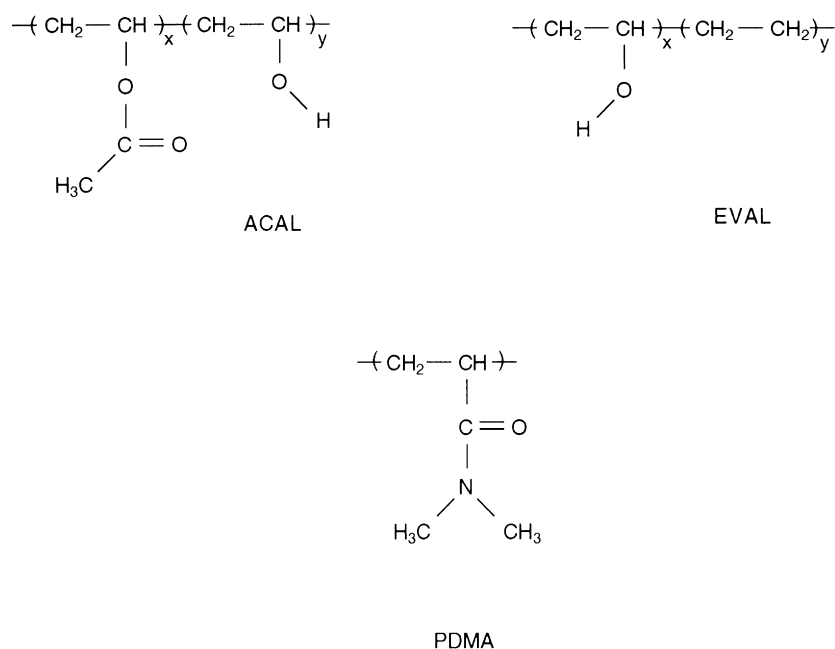


Fig. 1. Chemical structures of the repetitive units correspondent to ACAL copolymers, EVAL copolymers and PDMA.

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, at 25°C, in an Ubbelohde type viscometer in methanol using the viscometric equation [9]: $[\eta] = 1.75 \times 10^{-4} M^{0.68}$, which leads to the value $M_v = 50\,000$ g/mol.

Poly(ethylene-co-vinyl alcohol) (copolymers EVAL) were supplied by Polysciences Inc. Their copolymer compositions were 25, 56 and 68 mol% of vinyl alcohol units with $M_w = 30\,000$ g/mol, as indicated by the manufacturer. The EVAL78 copolymer was synthesised in our laboratory and its degree of hydrolysis was determined by ^{13}C RMN. All the samples were purified by dissolution in *N,N*-dimethylformamide and precipitation in ethyl ether. The glass transition temperatures, melting points and melting enthalpies of the copolymers are compiled in Table 1.

2.2. Preparation of blends

Polymer blends were prepared by solvent casting from *N,N*-dimethylformamide with a total polymer concentration of 40 mg/ml. The solutions were poured into petridishes, and the solvent was evaporated under an air stream. The temperature of evaporation was kept at 130°C for 1 h. The

Table 1
Glass transition temperature, melting point and melting enthalpy of the EVAL copolymers

Copolymer	T_g (°C)	T_m (°C)	ΔH_m (J/g)
EVAL78	60	191	54.9
EVAL68	58	183	59.7
EVAL56	53	165	58.3
EVAL25	24	109	49.4

Table 2
Glass transition temperature, melting point and melting enthalpy for blends of EVAL copolymers with PDMA

Copolymer	PDMA (wt.%)	T_g (°C)	T_m (°C)	ΔH_m (J/g)
EVAL78	0	60	191	54.9
	20	65	189	38.8
	30	72	190	32.4
	40	74	184	25.6
	60	71	171	3.1
	80	88	–	–
EVAL68	0	58	183	59.7
	20	70	182	46.6
	30	71	180	35.9
	40	73	179	31.8
	60	77	164	10.7
	70	90	–	–
	80	98	–	–
EVAL56	0	53	165	58.3
	20	66	166	38.9
	30	72	163	35.6
	40	61	156	23.1
	60	75	–	–
	70	90	–	–
	80	98	–	–
EVAL25	0	24	109	49.4
	20	25	^a	^a
	40	21	^a	^a
	60	20	^a	^a
	70	17	117	^a
	80	21	117	^a
	100	122	–	–

^a See the text.

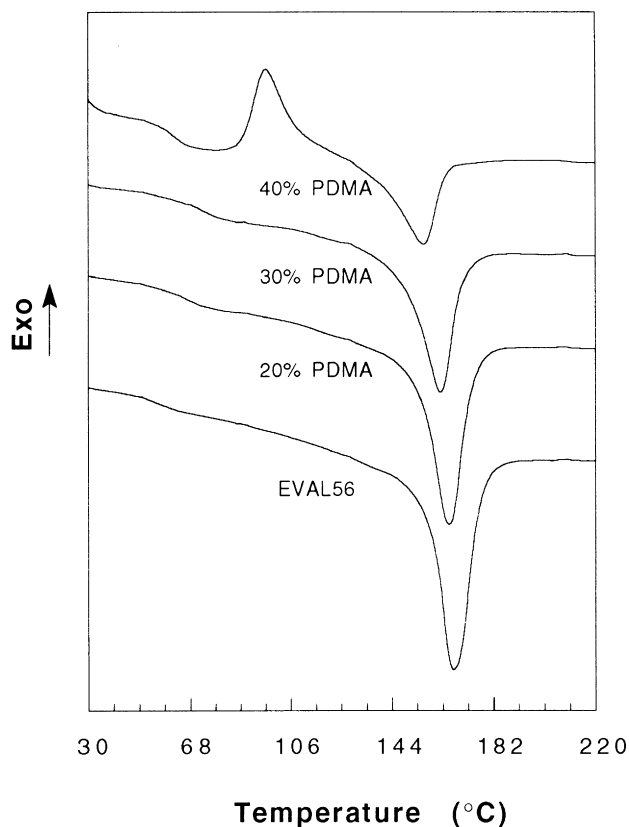


Fig. 2. Thermograms of pure EVAL56 and blends EVAL56/PDMA as a function of PDMA wt.%.

total removal of the solvent was checked by infrared spectroscopy, using one of the vibration modes of DMF at 698 cm^{-1} , as this band does not overlap with any of the bands of the polymers used in this work.

2.3. Thermal analysis

Thermal analysis was performed in a Mettler TA4000 differential scanning calorimeter 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 moisture and residual solvent. Next, the samples were cooled rapidly to -40°C and scanned between -40 and 250°C at $20^\circ\text{C}/\text{min}$. 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.

2.4. 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

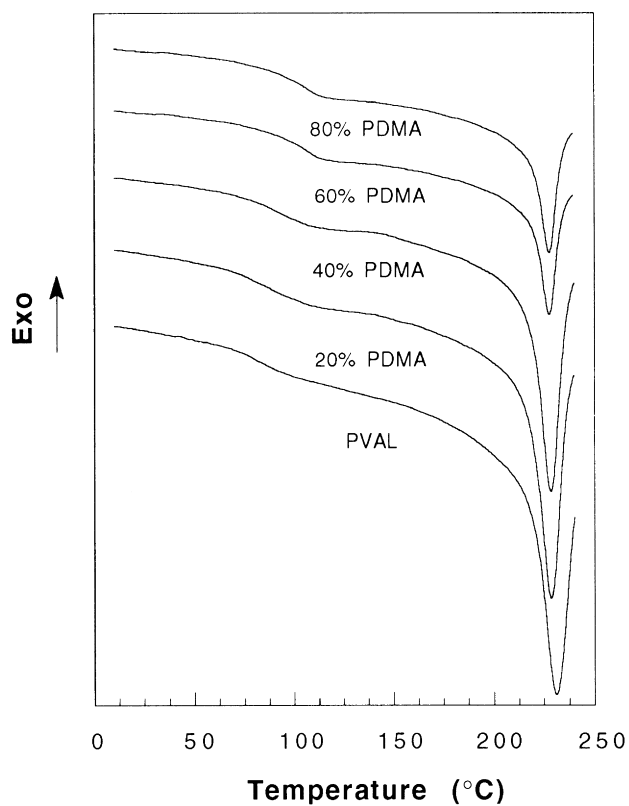


Fig. 3. Thermograms of pure PVAL and blends PVAL/PDMA as a function of PDMA wt.%.

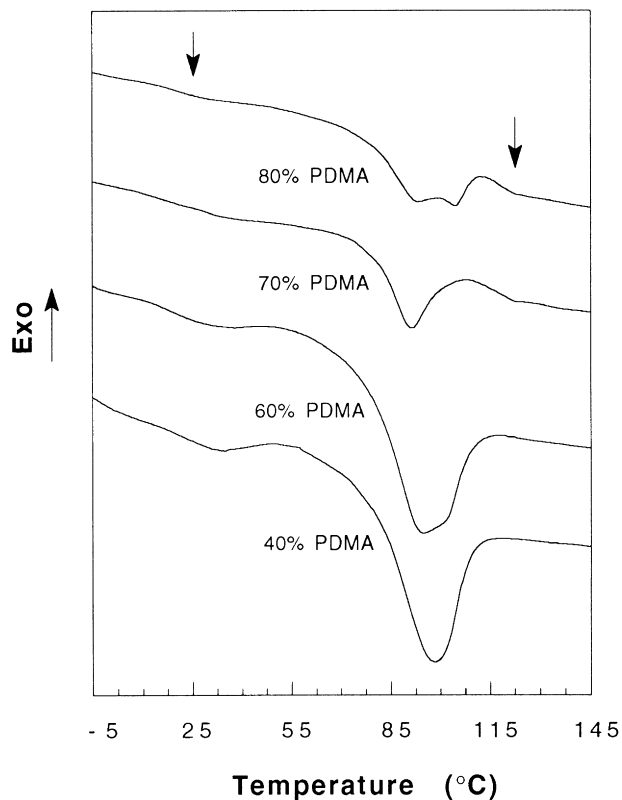


Fig. 4. Thermograms of blends EVAL25/PDMA as a function of PDMA wt.%.

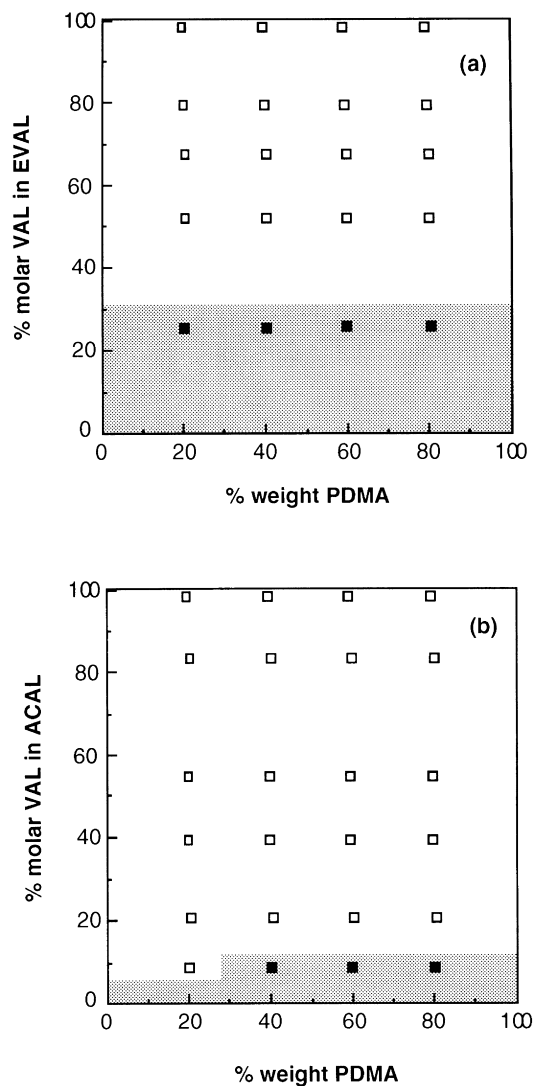


Fig. 5. Phase diagram of (a) EVAL/PDMA and (b) ACAL/PDMA blends. (■) immiscible and (□) miscible blends.

of 2 cm^{-1} and were averaged from 120 scans. Films for FTIR analysis were cast from *N,N*-dimethylformamide solutions (20 mg/ml) directly on AgCl pellets. The samples were vacuum dried and annealed at 120°C to eliminate residual solvent and assure thermal equilibrium.

3. Results and discussion

3.1. Miscibility analysis

The existence of a single glass transition temperature is used as a criterion for miscibility in the EVAL/PDMA systems. These blends, prepared by solvent casting from *N,N*-dimethylformamide solutions, are miscible over the whole composition range; their films are transparent and thermograms show a single T_g located between the T_g s of the pure components (see Table 2). A depression of the

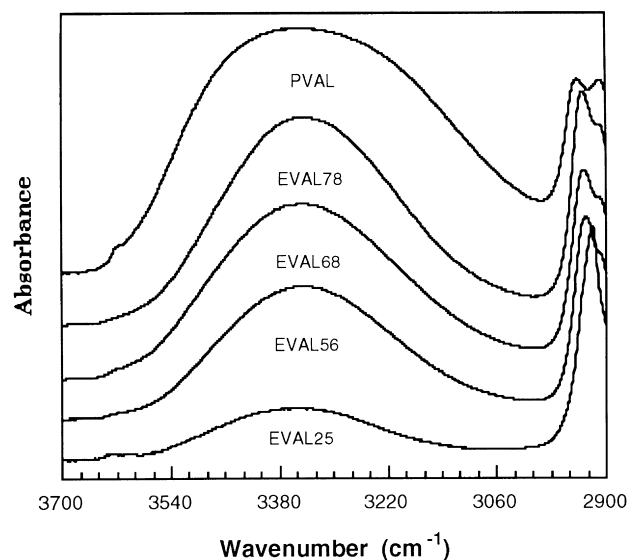


Fig. 6. Infrared spectra of the stretching hydroxyl region of PVAL and EVAL copolymers.

melting points of the copolymers in the blends is also observed.

Although a number of theoretical expressions have been developed to analyse the glass transition temperature-composition dependence in polymer blends, special care must be taken in these systems. As the amount of crystalline phases in the blends is not negligible, the overall copolymer composition in the blend does not match that of the amorphous phase. Besides the presence of PDMA interferes with the crystallisation process (see Fig. 2). This figure presents the second scan as obtained after melting during the first scan followed by a fast quenching. For blends of intermediate composition recrystallisation processes are detected during the second scan, a behaviour observed earlier in others blends of EVAL copolymers [10].

PDMA is also miscible with PVAL [5,6]. In fact, the thermograms of these systems show a single glass transition temperature located between the glass transition of the pure components (see Fig. 3). As PDMA is immiscible with poly(ethylene), there should be a low limit of miscibility for copolymers with small degrees of hydrolysis (i.e. low content of vinyl alcohol units). The EVAL25/PDMA system shows a special behaviour because, in some blends, the fusion peak of the copolymer (at 109°C) overlaps with the glass transition of the polyamide (122°C). As it can be seen in Fig. 4, the thermograms of the blends with compositions rich in PDMA (70 and 80 wt.%) present two glass transition temperatures which are identical to the glass transitions of the pure components. However, the thermogram of the EVAL25/PDMA blend with 60 wt.% of PDMA (Fig. 4), only one T_g is observed, which corresponds to the T_g of the copolymer. However, it is obvious that the endothermic peak that appears at ca. 100°C is asymmetric and is the result of the overlapping of two processes: the fusion of

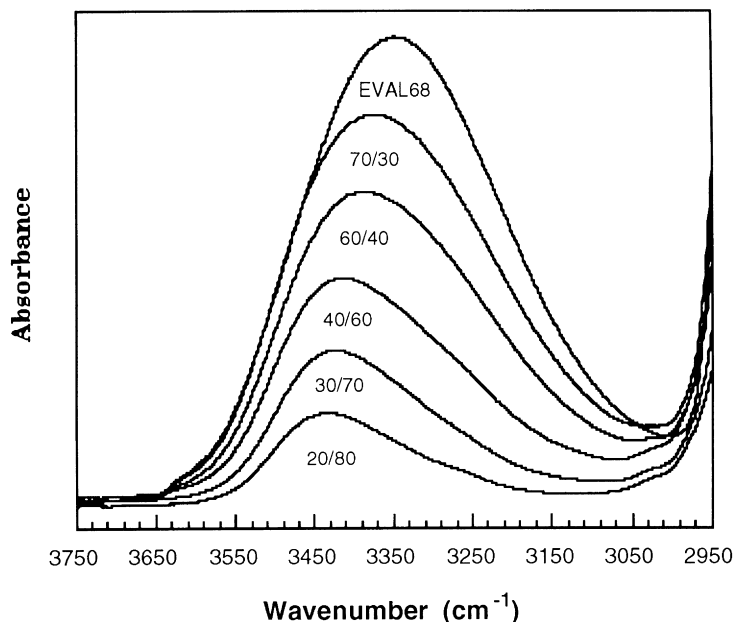


Fig. 7. Infrared spectra of the hydroxyl stretching region of EVAL68 and EVAL68/PDMA blends.

the crystalline part of the copolymer and the glass transition of the polyamide. For blends which have a lower PDMA content, i.e. 40 wt.%, the contribution of the glass transition of the polyamide in the fusion peak is least evident (Fig. 4). Nevertheless, the derivate of the calorimetric curve shows that the peak is the product of two contributions and, therefore, we conclude that the blends of EVAL25 and PDMA are immiscible.

Fig. 5 shows the phase diagram of EVAL/PDMA and ACAL/PDMA [5,6] blends deduced from DSC. As it can

be seen, the miscibility window is considerably reduced in the case of EVAL copolymers. This result provides clear evidence of the influence of the number of vinyl alcohol units in the phase behaviour of these blends. To explain this result, it is necessary to take into account the unfavourable dispersive contributions, characterised by the difference in the solubility parameters of the components, to the mixing free energy of the system. The repetitive structural unit of the tertiary polyamide has a solubility parameter of $\delta = 9.0 \text{ (cal/cm}^3)^{1/2}$; the presence of the

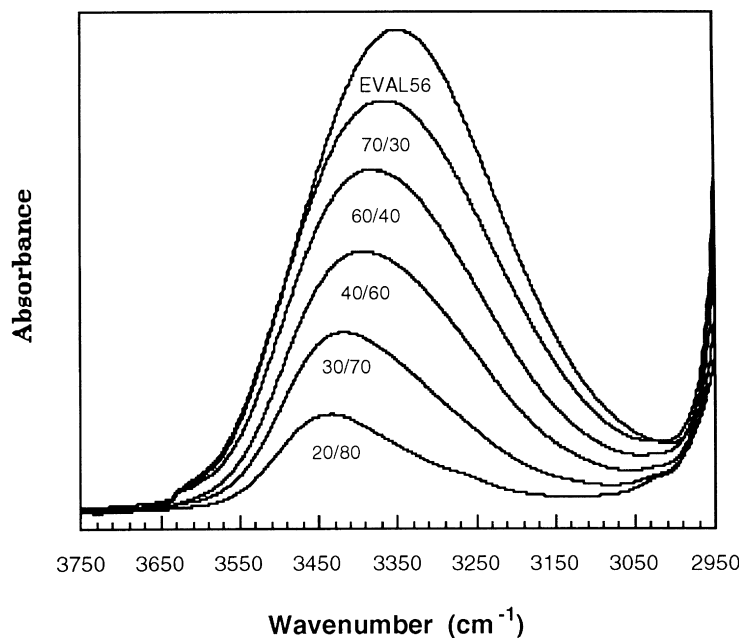


Fig. 8. Infrared spectra of the hydroxyl stretching region of EVAL56 and EVAL56/PDMA blends.

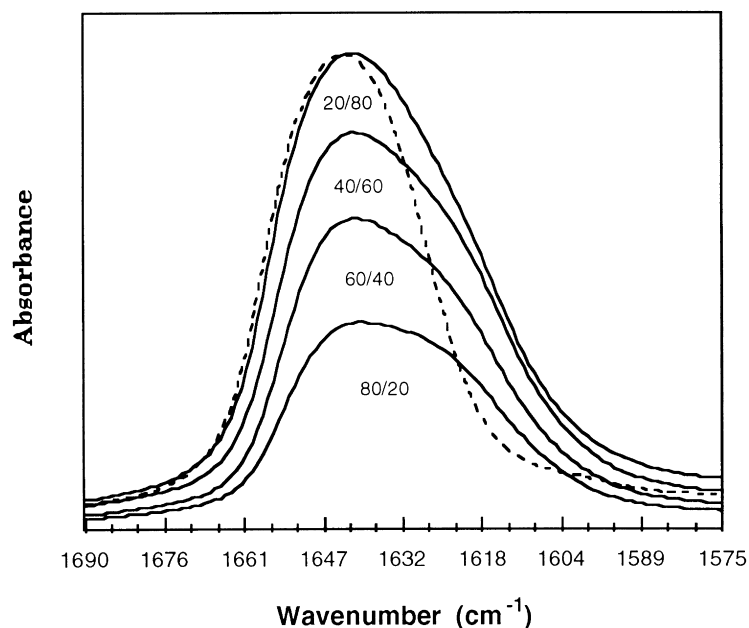


Fig. 9. Infrared spectra of the carbonyl stretching region of PDMA (---) and EVAL68/PDMA blends.

ethylene units ($\delta = 8.0 \text{ (cal/cm}^3)^{1/2}$) in the copolymer is less favourable than the presence of the vinyl acetate units ($\delta = 9.4 \text{ (cal/cm}^3)^{1/2}$) for obtaining miscible blends.

To verify the existence of a lower critical solution temperature (LCST) behaviour in EVAL/PDMA blends, thermal stabilities of the pure components were studied by thermogravimetry. Analysis of the pure components indicate that the EVAL copolymers undergo thermal degradation with appreciable mass loss at temperatures above 300°C. On the contrary, PDMA is thermally more stable. Accordingly, the thermal stability analysis of EVAL/PDMA mixtures were performed at different temperatures below 300°C by annealing for up to an hour. The posterior calorimetric scans showed no indication of phase separation phenomena.

3.2. Specific interactions analysis

Specific interactions in polymer blends are commonly studied by IR spectroscopy [11–13]. According to the chemical structures of the polymers involved in these blends, hydrogen bonding among the hydroxyl groups of EVAL and the amide-carbonyl group of PDMA can be expected. Then, hydrogen bonding must influence the IR spectral modes related with these chemical groups.

The hydroxyl stretching region of the infrared spectra of EVAL copolymers are influenced by self-association through hydrogen bonding. Fig. 6 shows the FTIR spectra in the 2900–3700 cm^{-1} region for PVAL and EVAL copolymers. It is obvious that hydrogen bonding affects the hydroxyl-stretching band. This broad band is considered to be composed of narrow contributions of hydroxyl groups surrounded by different environments: hydroxyl groups

hydrogen-bonded with other hydroxyl groups in the same or neighbouring chains, forming dimers, trimers, etc. and non-hydrogen-bonded hydroxyl groups. When the spectra of EVAL copolymers are compared, the maximum of the band is observed at $\approx 3350 \text{ cm}^{-1}$ independent of the degree of hydrolysis. This result suggests that the type of interactions in the copolymers is not modified as the number of ethylene units increases.

The spectra of the EVAL/PDMA blends (Figs. 7 and 8) show significant changes in the 2900–3700 cm^{-1} region, suggesting a redistribution in the arrangement of the hydroxyl group associations. The comparison of the spectra corresponding to the same system as a function of the PDMA composition reveals a progressive shift of this band toward high wavenumbers as the tertiary polyamide content increases. This behaviour suggests that a significant part of the hydroxyl groups involved in the association processes previously described for pure EVAL copolymers, are now hydrogen bonded to the amide-carbonyl groups in PDMA. The shift toward lower wavenumbers indicates that the intensity of this interassociation is lower than the self-association in the pure copolymer.

To demonstrate the presence of hydrogen bonding involving amine groups is useful to examine the stretching band of this group located at 1642 cm^{-1} in PDMA. There are two possible accepting sites in the amide group: the carbonyl group and the nitrogen atom. Studies performed in model compounds have shown that hydrogen bonding takes place mainly with the carbonyl group [14,15].

In spectra of EVAL/PDEM blends, this band shifts toward low wavenumbers and broadens. As with other blends, this shift is more pronounced as the copolymer content in the blend increases (see Figs. 9 and 10). The

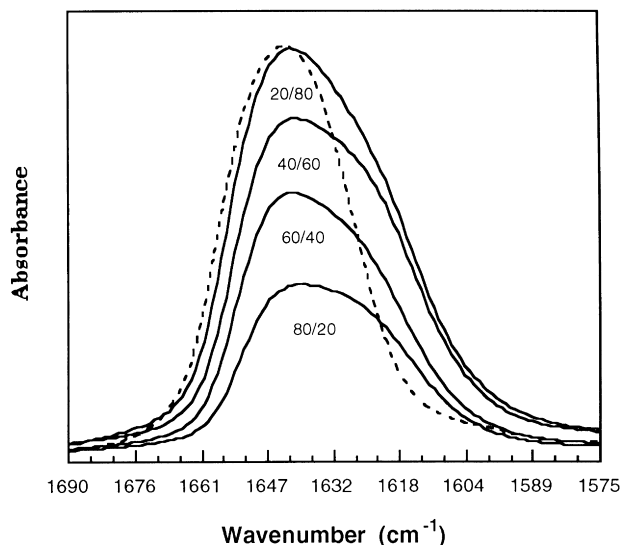


Fig. 10. Infrared spectra of the carbonyl stretching region of PDMA (---) and EVAL56/PDMA blends.

modification can be attributed to the addition of a new spectral contribution, the hydrogen-bonded amide carbonyl band. As this mode is too close to the free amide carbonyls band, neither a new discernible maximum nor a clear shoulder is observed. Nevertheless, derivative procedures show undoubtedly the presence of both contributions.

4. Conclusions

Miscibility was found between the poly(ethylene-co-vinyl alcohol) (EVAL) of higher degrees of hydrolysis (78, 68 and 56%) and poly(*N,N*-dimethylacrylamide) (PDMA). The blends of the EVAL25 copolymer with PDMA are immiscible at all proportions examined. The IR spectra of the miscible blends reveal hydrogen bonding between the hydroxyl groups of the EVAL copolymers and the carbonyl groups of PDMA. These specific interactions promote miscibility in the studied systems.

The influence of vinyl alcohol content in the comonomer on the miscibility has been demonstrated: the phase diagram of the EVAL/PDMA blends has a low limit miscibility, which is higher than that of the ACAL/PDMA systems. This means that the presence of the ethylene units is less favourable for miscibility than the presence of the vinyl acetate units. Miscibility depends primarily upon a balance

between the unfavourable “physical” non-specific contributions to the free energy of mixing, embodied in the Flory χ parameter, and the favourable “chemical” contributions to the free energy of mixing due to specific interactions [16]. The Flory parameter, which is estimated from solubility parameters, is greater in EVAL/PDMA systems than in ACAL/PDMA systems and, therefore, the unfavourable “dispersive” contributions to the free energy of mixing are more important.

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