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Intermolecular interactions in blends of poly(vinyl alcohol) with poly(acrylic acid): 2. Correlation between the states of sorbed water and the interactions in homopolymers and their blends

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Water–polymer interactions have been studied by d.s.c. and *FT*i.r. in water vapour-saturated poly(vinyl alcohol), poly(acrylic acid) and their blends before and after thermal treatment (0.5 h at 180°C). The 3600–3000 $\mathrm{cm^{-1}}$ (OH stretching), 1800–1700 $\mathrm{cm^{-1}}$ (C=O stretching) and 1700–1600 $\mathrm{cm^{-1}}$ (HOH bending) regions have been used. Water–polymer and polymer–polymer interactions which are respectively formed and destroyed in the presence of water have been identified. For this purpose, subtraction of the spectrum of dry samples from the spectrum of water-saturated films has been performed. Changes in crystallinity of poly(vinyl alcohol) were also measured by *FT*i.r. D.s.c. has been used to confirm the strength of water–polymer interactions and to demonstrate changes in the miscibility of polymer components. Copyright © 1996 Elsevier Science Ltd.

(Keywords: poly(vinyl alcohol); poly(acrylic acid); polymer blend)

INTRODUCTION

The use of polymer films in membrane processes or controlled drug delivery systems gave rise to numerous studies concerning the nature of interactions between polymers and the transport liquid. Hydrophilic, water-swellable polymers and water-polymer interactions have been examined by various experimental techniques: i.r.[1–4], d.s.c.[5–7], n.m.r.[8,9] and others[7,10,11]. As a conclusion of the results obtained by the numerous investigators in this field, two concepts have been proposed to classify the physical state of water absorbed in polymers[5,8]:

- *Free water*, involved only in water–water interactions. This water has the same crystallization and melting temperatures as bulk water. Various other names are used in the literature: unbound water, 'freezable' water, 'freezing' water. It must be emphasized that the term 'free' is correct with respect to the polymer, but water molecules termed as free are engaged in H bonding with neighbouring water molecules.

- *Bound water*, in which two subdivisions exist:
  —Intermediate water which undergoes both water–water and water–polymer interactions, the last one being very weak. It is also named 'freezing bound water', and crystallizes at a lower temperature than bulk water.
  —Polymer-bound water which is only involved in water–polymer interactions. This type of water has no solid–liquid transitions, and is also termed 'associated' or 'non-freezing' water.

In a water-swollen polymer the different types of water can coexist. An important point is that at low water contents, all this water is non-freezing bound water. To each polar polymer is associated a maximum quantity of water that it can incorporate as polymer-bound water. In the case of poly(vinyl alcohol) (PVA1), the quantity found by different authors is about 0.4 g of H_2O/1 g of PVA1 or 1 mol of H_2O/1 mol of repeating unit of PVA1[5,9,10,12].

We have shown in a previous work[13] that on blending PVA1 with poly(acrylic acid) (PAA), H-bonding self-association in pure PVA1 and PAA is partly replaced by interpolymer interactions in the miscible blends. In the pure self-associated PVA1, the broad OH absorption (stretching) at 3340 $\mathrm{cm^{-1}}$ results from the superposition of multiple polymeric H bonds with $\nu_{\max}$ at 3260 $\mathrm{cm^{-1}}$ associated with the crystalline phase and of dimeric H bonds associated with the amorphous phase with $\nu_{\max}$ at 3500 $\mathrm{cm^{-1}}$. The OH stretching of PAA with $\nu_{\max} =$ 3126 $\mathrm{cm^{-1}}$ results from cyclic dimers but also from a small fraction of non-cyclic dimers and monomers. These bands at 3340 and 3126 $\mathrm{cm^{-1}}$ are replaced in the blends by a band with a maximum which is not the superposition of the absorption of both components and depends on

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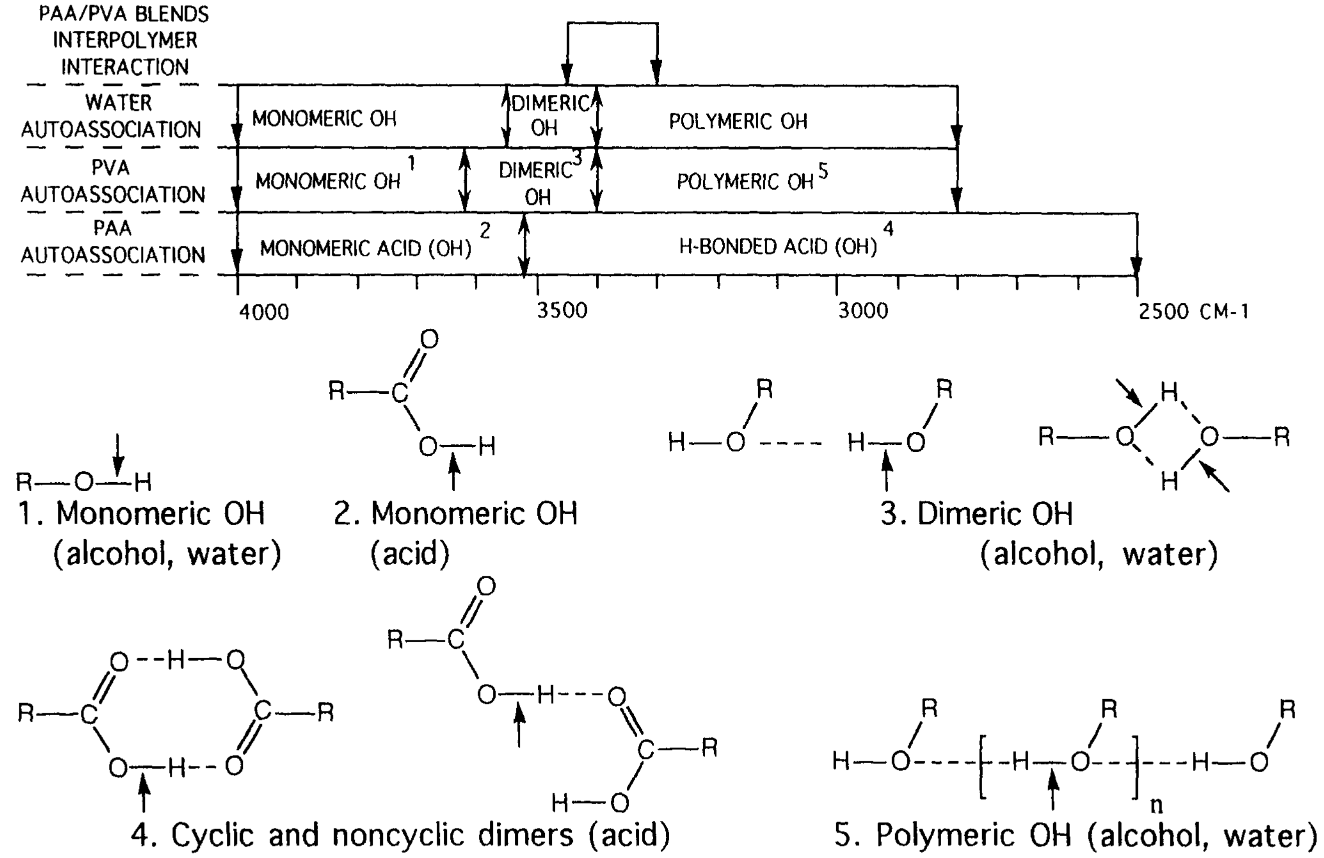


Scheme 1 Autoassociation in water, PVA and PAA. Interactions in PAA/PVA blends

composition. For an equimolar blend, ν_{max} is situated at 3248 cm^{-1}; crystallinity is completely suppressed as a result of interactions between PAA and PVAl. The results obtained for polymer–polymer interactions using data on simple molecular compounds give in refs 14–16 are summarized in *Scheme 1*.

The presence of water could modify self-association of PVAl and PAA and also interactions between components in the blend. This could give information about the miscibility of PAA and PVAl. These two polymers are heat-sensitive; after thermal treatment their absorption capacity for water is modified.

Bulk water shows two broad absorptions in the medium i.r. They are respectively centred at 3400 cm^{-1} (ν_{OH} stretching) and at 1645 cm^{-1} (δ_{HOH} bending)[17,18]. As in the case of alcohols, an increase in the strength of interactions (free OH< dimeric OH< polymeric OH) shifts the stretching frequency to lower values. Two absorptions have been reported for dilute solutions of water in CCl_4 at 3700 cm^{-1}(antisymmetrical) and 3600 cm^{-1} (symmetrical)[19]. The free OH groups of alcohols absorb in the same regions[14,16]. In a study[20] of bulk water absorption, the frequency range higher than 3450 cm^{-1} (ν_{max} at 3540 and 3620 cm^{-1}) was assigned to non-H-bonded monomeric water; the frequency range lower than 3450 cm^{-1} (ν_{max} at 3247 and 3435 cm^{-1}) was assigned to H-bonded lattice water[20]. In another study of liquid water[18], absorptions at 3530 cm^{-1} and at 3200 cm^{-1} were respectively attributed to ν_{OH} (stretching) and to $2\delta_{HOH}$(bending). In liquid water, δ_{HO} was observed at 1645 cm^{-1} [18]. Vaporization of water shifts OH stretching to 3660 cm^{-1} and OH bending to 1595 cm^{-1} [3]. This opposite shift of ν_{OH} and δ_{OH} on decreasing the degree of H bonding of water molecules was confirmed by Van Thiel *et al.*[21].

The crystallinity and melting range of dry PVAl have been previously determined by d.s.c., which involves programmed heating of the sample up to about 250°C[13]. For an unannealed sample, the crystallinity is better evaluated by i.r. spectroscopy. Indeed, amorphous and crystalline phases show partly resolved absorptions in the 1150–1000 cm^{-1} region[4]. Nuclear magnetic resonance[22] (^{13}C CP/MAS) has shown that PVAl possesses an 'intermediate' region in addition to the usual crystalline and amorphous phases. It is situated at the surface of the lamellae and constitutes a transition between the completely ordered crystalline phase and the completely disordered amorphous phase. Such an intermediate phase has been identified in other polymers, and will be shown to play a significant role in the hydration of PVAl.

The purpose of the present work is to investigate water–polymer interaction in PAA, PVAl and their blends either thermally treated (0.5 h at 180°C) or not. Special attention has been paid to the effect of absorbed water and of thermal treatment on the crystallinity of PVAl and its blends.

EXPERIMENTAL

PAA ($MW = 250\,000$) was purchased from the Aldrich Chemical Co., and PVAl ($MW = 48\,000$, degree of hydrolysis = 98 mol%) was received from Hoechst. Films were obtained by evaporation of aqueous solutions. Materials used in this study, sample preparation, apparatus and techniques are described in the first

Table 1 Water content of water vapour-saturated samples in (a) H_2O/ polymer (g/g) and (b) H_2O/ repeating units (mol/mol)

	PVA		0.25/1 molar PAA/PVA1		1/1molar PAA/PVA1		PAA	
Samples	(a)	(b)[a]	(a)	(b)[a]	(a)	(b)[a]	(a)	(b)[a]
Unannealed	0.27	0.66	0.22	0.62	0.31	1.06	0.47	1.88
Annealed	0.15	0.37	0.18	0.51	0.23	0.80	0.48	1.92

[a] PVA1—only amorphous region considered

Table 2 Effect of water vapour saturation on ν_{max} for the OH stretching band of polymers

Polymer	Dry sample, ν_{max} (cm^{-1})	Vapour water-saturated sample, ν_{max} (cm^{-1})	Shift of ν_{max} from the dry to water-saturated sample (cm^{-1})
Unannealed			
PVA	3340	3336	−4
PAA	3126	3114	−12
Equimolar	3248	3369	+121
Annealed			
PVA	3350	3344	−6
PAA	3153	3107	−46
Equimolar	3360[a]	3399	+39
	3198	3239[a]	+41

[a] Shoulder

Table 3 Effect of thermal treatment on ν_{max} for the OH stretching band of water absorbed in polymers

Water absorbed in polymers	Unannealed sample, ν_{max} (cm^{-1})	Annealed sample, ν_{max}(cm^{-1})	ν_{max} shift, annealed–unannealed (cm^{-1})
Weak H bonds			
In PVA	3500[a]	3489[a]	−11
In PAA	3522	3503	−19
Equimolar	3573[a]	3477[a]	−96
Strong H bonds			
In PVA	3186	3280	+94
In PAA	3014[a]	3028[a]	+14
Equimolar	3390	3477	+87

[a] Shoulder

paper[13]. Additional operations were undertaken for water vapour saturation and thermal treatment (annealing) of samples. Thermal treatment of samples (annealing) was performed by heating the samples at 180°C for 0.5 h in air. Annealed and non-annealed samples were saturated with water vapour by keeping them in a water vapour-saturated atmosphere at room temperature until sorption equilibrium was reached (constant weight).

I.r. spectra were recorded with a Bruker IFS45 spectrometer. The difference spectra were obtained using the same samples before and after water vapour saturation or thermal treatment.

D.s.c. measurements were performed on samples of approximately 10 mg with a Perkin-Elmer DSC-7 instrument, in an N_2 atmosphere with heating rate of 20°C min^{-1}. The heating scan was carried out from 0 to 250°C.

RESULTS AND DISCUSSION

In the present work, water–polymer interactions in water vapour-saturated films are identified by *FT*i.r. using the 3600–3000 cm^{-1} region for ν_{OH}(stretching), the 1700–1800 cm^{-1} region for $\nu_{C=O}$ stretching and the 1600–1700 cm^{-1} region for water δ_{HOH}(bending). These spectra will be considered and discussed in the following sections. Subtraction of the spectrum of the dry film from that of the water-saturated films gives a difference spectrum that we shall call the spectrum of the absorbed water. In fact, this spectrum includes also the transformations in the H-bonding distribution induced by the presence of water in the polymer. Positive contributions result from water interacting with the polymers. Any negative contribution is indicative of polymer–polymer interactions which are destroyed in the presence of water. The same subtraction realized in the 1700–1800 cm^{-1} regions, where water does not absorb, indicates the presence of interactions involving C=O groups which are formed in the presence of water and the absence of those which are destroyed in the presence of water. To characterize interactions involving

Table 4 Melting point and crystallinity ratio of PVA1 and the 0.25/1 blend with PAA

	PVA			0.25/1 molar PAA/PVA		
	Melting point (°C):	Crystallinity ratio (%)		Melting point (°C):	Crystallinity ratio (%)[a]	
Sample	D.s.c.	*FT*i.r.[d]	D.s.c.	D.s.c.	*FT*i.r.[d]	D.s.c.
Unannealed						
Dry	221.8	18.0	[b]	192.1	2.5	[b]
Water vapour saturated	[c]	24.0	[b]	[c]	15.0	[b]
Dry after Saturation	222.5	22.0	[b]	197.2	13.0	[b]
Annealed						
Dry	220.2	49.4	49.4	201.3	22.1	22.1
Water vapour saturated	[c]	48.0	[b]	[c]	22.0	[b]
Dry after saturation	221.2	47.0	47.2	198.0	21.9	22.2

[a] Corresponding to the PVA1 fraction
[b] Heating of unannealed or water vapour-saturated samples during the measurement in the d.s.c. apparatus changes their crystallinity
[c] Meaningless measurement owing to the presence of water
[d] Crystallinity peak at 1140 cm^{-1}

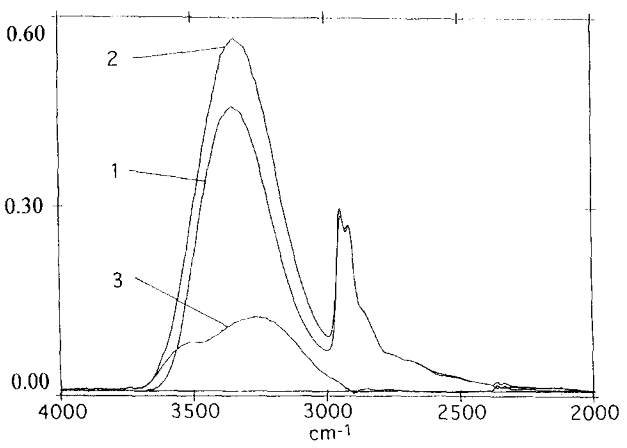


Figure 1 *FT*i.r. spectra of PVA1: dry (1), saturated with water vapour (2) and the difference spectrum (curve 2 – curve 1) (3) (2000–4000 cm^{-1})

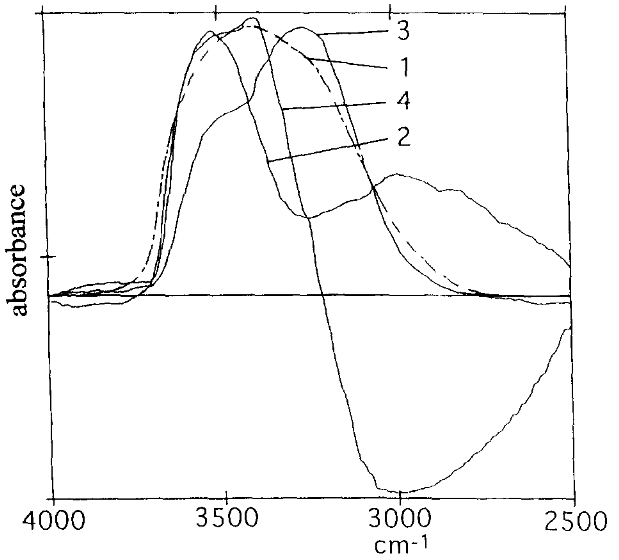


Figure 2 Spectrum of bulk water (1) and difference spectra at 2000–4000 cm^{-1} (dry polymer subtracted from water vapour saturated polymer): PAA (2), PVA1 (3) and PAA/PVA1 1/1 blend (4)

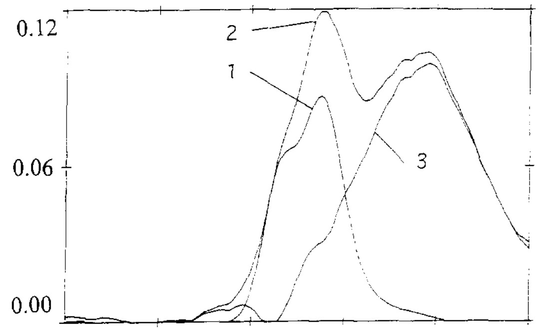


Figure 3 *FT*i.r. spectra of PVA1: dry (1), saturated with water vapour (2) and the difference spectrum (curve 2 – curve 1) (3) (1600–1850 cm^{-1})

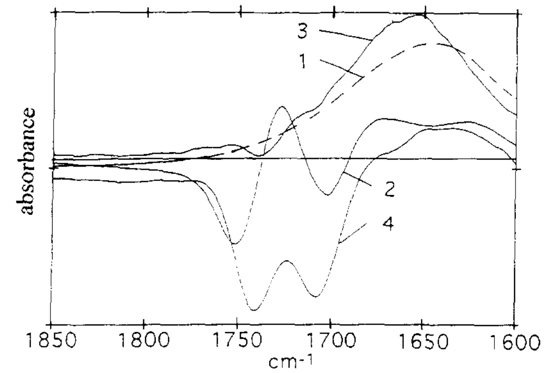


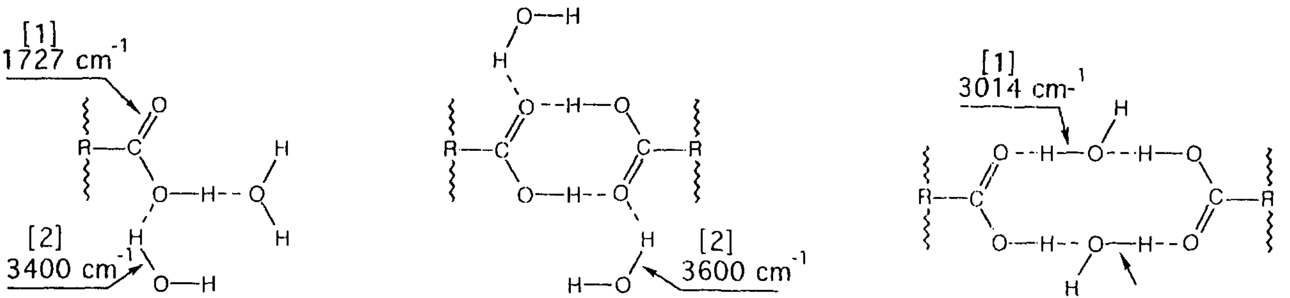
Figure 4 Spectrum of bulk water (1) and difference spectra at 1600–1850 cm^{-1} (dry polymer subtracted from water vapour saturated polymer): PAA (2), PVA1 (3) and the PAA/PVA1 1/1 blend (4)

water in this work, we have used ν_{max} for OH stretching and δ_{max} for HOH bending in bulk water. Absorptions corresponding to frequencies lower than the maximum of pure water (3400 cm^{-1}) are assigned to polymeric interactions, while those corresponding to higher frequencies are assigned to dimeric and monomeric structures. In the case of δ_{max} of HOH at 1645 cm^{-1}, polymeric interactions are situated at higher frequencies while dimeric and monomeric structures are situated at lower frequencies[3,19–21]. The d.s.c. study of the vaporization of the sorbed water and polymer crystallinity is used as a complementary method to identify these interactions[23]. D.s.c. scans of water vapour-saturated samples did not reveal the presence of endotherms or exotherms corresponding to melting or crystallization of water between −20 and 0°C. This indicates the absence of free and intermediate water; only polymer-bound water (non-freezing water) is involved. The crystallinity of PVA1 and its blends has been determined by both d.s.c. and *FT*i.r., as explained in the Introduction. The experimental results are summarized in *Tables 1–4*.

Poly(vinyl alcohol)

Water–PVA1 interactions. PVA1 saturated with water vapour absorbs 0.66 mol of H_2O/1 mol of PVA1 repeating unit in the non-crystalline region (*Table 1*). *Figure 1* gives the i.r. spectra of initially dry PVA1 and of water-saturated PVA1 in the region of OH stretching. The C–H absorption at 2917 cm^{-1} has been chosen as a reference to normalize the spectra. The position of the maxima corresponding to characteristic absorptions are summarized in *Table 2*. *Table 2* and *Figure 1* show a very small displacement of $\nu_{max\,OH}$ towards low frequencies for water-saturated PVA1, which could indicate a global increase in the strength of interactions between OH groups by comparison with dry PVA1. *Figure 1* also gives the spectrum of water sorbed in PVA1, obtained by difference between the spectra of water-saturated PVA1 and dry PVA1. This spectrum of sorbed water is also given in *Figure 2* (curve 3) in order to compare it with the spectrum of bulk water (curve 1). A main peak at 3186 cm^{-1} and a shoulder at 3500 cm^{-1} are observed for sorbed water (*Table 3*), demonstrating the presence of two states of water corresponding to two degrees of H bonding. The main absorption is situated at a lower frequency than the maximum of bulk water, indicating that most water OH groups are included in polymeric H bonds with PVA1. The spectrum of water in PVA1 in the region of HOH bending (*Figures 3* and *4*, curve 3) confirms this observation: a shift to high frequency (δ_{HOH} = 1666 cm^{-1}) with respect to bulk water (δ_{HOH} = 1645 cm^{-1}) is indeed observed. Absorption at

1. PAA-WATER H-BONDS



a) PAA monomer-water H-bonds. Weak interactions.

b) PAA cyclic dimer-water H-bonds. Weak interactions .

c) PAA cyclic dimer water strong H-bonds. Cyclic structure .

2) PVA-WATER H-BONDS

a) PVA amorphous region. Weak interactions.

b) PVA intermediate region Strong interactions.

[1] this work [2] reference (26) and this work

Scheme 2 Types of polymer–water H-bonds

1720 cm^{-1} in dry PVA1 is due to residual (2%) acetyl groups. We have indicated in the last section that the polymers used in the present work do not contain any free water when saturated with water vapour. We propose that strongly polymeric bound water revealed here by both OH ($\nu_{max} = 3186\,cm^{-1}$) (*Figure 2*, curve 3) stretching and HOH bending ($\nu_{max} = 1666\,cm^{-1}$) (*Figure 4*, curve 3) is situated in the 'intermediate' phase, where it will be more easily integrated to polymeric H-bond chains (*Scheme 2-2b*). The formation of chains of polymeric H bonds is possible only in relatively ordered structures such as the intermediate phase. Water weakly bound to polymer ($\nu_{max} = 3500\,cm^{-1}$ and $\delta_{max} = 1655\,cm^{-1}$) is situated in the amorphous phase (*Table 3, Figures 2* and *4* (curve 3) and *Scheme 2-2a*); it is well known that the crystalline phase is not penetrated by water.

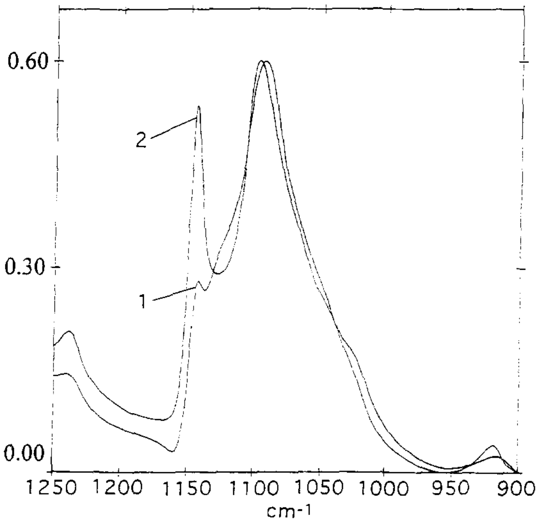


Figure 5 Crystallinity band of PVA1: dry thermally non-treated PVA1 (1) and dry thermally treated PVA1 (2)

Water absorbed in PVA1 can be eliminated by heating. The vaporization curve obtained by d.s.c. (not shown) is a function of water polymer interactions. It is characterized by it maximum (95°C) and by the range of temperatures where vaporization takes place (30–180°C). In the following sections, it will be compared with curves obtained with PAA and its blends.

Effect of water on the crystallization of PVA1. The effect of water on the crystallinity of PVA1 has been studied using the crystallinity band at 1140 cm^{-1}. Indeed, melting endotherms cannot be used in this case since microscopic examination of the birefringence of PVA1 films has shown that crystallization increases by heating the sample up to the melting point. The results are given in *Table 4*. They show that crystallization increases from 18 to 24% in the presence of water. This increase has been difficult to evaluate by d.s.c. Quantitative evaluation of the crystallinity from i.r. spectra has been done by comparing the surface under the peak centred at 1140 cm^{-1} for the various samples. The surface under the peak at 1140 cm^{-1} obtained for thermally treated PVA1 (see the next section) was used as a reference of crystallinity (49.4%) corresponding to the value determined by d.s.c. (*Figure 5* (curve 2) and *Table 4*), using a value of 156 cal g^{-1} for the melting enthalpy of the

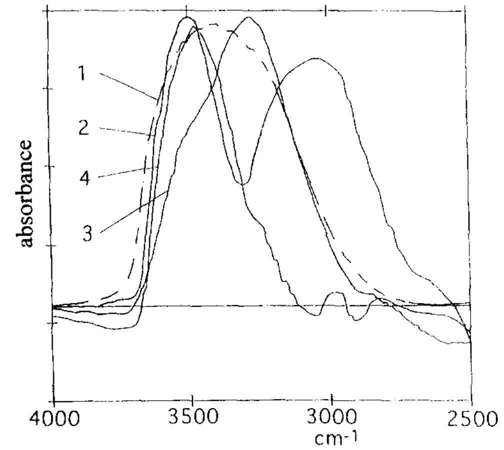


Figure 6 Spectrum of bulk water (1) and the difference spectra for the thermally treated samples at 2000–4000 cm^{-1} (dry polymer subtracted from water vapour saturated polymer): PAA (2), PVA1 (3) and the PAA/PVA1 1/1 blend (4)

100% crystalline sample. Indeed, in this case the crystallinity no longer changes during the heating cycle. When the water-saturated sample is dried again in the standard conditions given in the Experimental part for the initial samples, only a very small decrease in crystallinity (from 24 to 22%) is observed with respect to the water-saturated sample (*Table 4*), indicating that the increase of crystallinity induced by water vapour is mostly irreversible after water removal. Water absorbed by the polymer plasticizes it, inducing mobility of the chains and their reorganization into crystallites. Partly organized water absorbed in the intermediate phase is most probably responsible for the increase of crystallinity; new crystallites are nucleated on the pre-existing crystalline phase.

Thermal treatment of PVA1

(1) Effect of thermal treatment on the absorption of water. Thermal treatment (annealing) consists of heating the initial dry sample for 0.5 h at 180°C in air. Other studies[24] have shown that thermal treatment in these conditions induces the formation of a small number of polyenes (3–10 conjugated double bonds in the approximate concentration of 35×10^{-3} mol dm^{-3}). They are readily identified by u.v. absorption spectroscopy (spectrum not shown) but do not modify the i.r. spectra.

The quantity of water vapour absorbed per gram of polymer by the thermally treated PVA1 is much lower (0.15 g) than that absorbed by the initial polymer (0.27 g) (see *Table 1*). This cannot be due to the small quantity of formed polyenes, but results from the increase of crystallinity due to annealing and measured by i.r. spectroscopy, as discussed in the next section. If only the amorphous region is considered, the quantity of absorbed water remains constant.

(2) Effect of thermal treatment on water–polymer interactions and the crystallinity of PVA1. A modification is observed in the 3500–3000 cm^{-1} region corresponding to ν_{OH} of water sorbed by annealed samples (*Figure 6*, curve 2). The general features (main peak + shoulder, reported for the unannealed spectrum (see *Figure 2*, curve 3)) is preserved, but a shift (+94 cm^{-1}) of the maximum to higher frequencies (see *Table 3*) suggests a decrease in the strength of interactions between water and annealed polymer compared to non-annealed samples. The d.s.c. vaporization curve (not shown) also indicates that sorbed water volatilizes at lower temperatures and is thus less bound to the treated sample than to the untreated sample.

The thermal treatment does not affect significantly the melting point (*Table 4*). In the i.r. absorption region of PVA1, 1000–1200 cm^{-1}, an important increase in crystallinity from 18 to 49.4% is observed for the thermally treated dry sample (see *Figure 5* and *Table 4*). This results from the reorganization of the chains near T_m. This effect is qualitatively comparable but quantitatively much more important than that induced by sorbed water in the unannealed sample (from 18 to 24%). Saturation of annealed PVA1 with water vapour does not increase its crystallinity, indicating that all the crystallizable regions have been organized during the thermal treatment (*Table 4*).

It could be proposed that the thermal treatment induces reorganization and crystallization of the intermediate and amorphous phases, causing a marked decrease in the strength of H bonding between water and PVA1 that is observable in the i.r. spectra.

Poly(acrylic acid)

Interactions of water with PAA. PAA absorbs two molecules of water per acid group, as shown in *Table 1*. D.s.c. studies show that the vaporization of sorbed water proceeds in two steps (not shown). The first one occurs below T_g (120°C) with a maximum at 113°C, and concerns weakly bound water. The second one occurs after T_g as multiple small peaks due to sudden outgasing of the films. It corresponds to more strongly bound water molecules, which require movements of long-chain segments to be eliminated. As in PVA1, water absorbed in PAA can thus be divided into two fractions:

- Water weakly bound to PAA with maxima for water stretching and bending respectively at 3522 and 1634 cm^{-1} (see *Figure 2* (curve 2), *Figure 4* (curve 2) *Figure 7* and *Table 3*). The first values are in the range of absorption (3600–3400 cm^{-1}) proposed by Levy *et al.*[26] and given in *Scheme 2* for weekly interacting PAA–water structures.

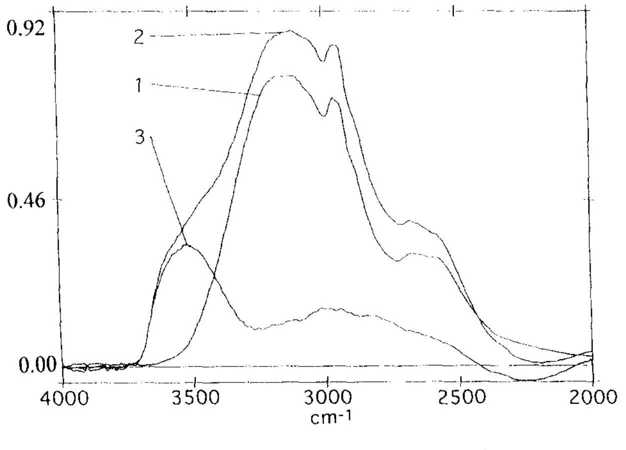


Figure 7 *FT*i.r. spectra of PAA: dry (1), saturated with water vapour (2) and the difference spectrum (curve 2–curve 1) (3) (2000–4000 cm^{-1})

- Water strongly bound to PAA with maxima for water stretching and bending respectively at 3014 and 1672 cm^{-1} (see the figures and tables cited for the first fraction).

Water linked to PAA has to be related to the existence of different states of autoassociation of COOH groups in the polymer: strongly bound COOH in cyclic dimers and free COOH, but also a wide range on non-cyclic dimers (see *Scheme 1*).

The C=O stretching band of PAA gives more information about the strength of H bonding between water and PAA and about the changes in polymer autoassociation induced by the presence of water (*Figure 4*, curve 2). This figure shows that the introduction of water in PAA induces the transformation of some COOH groups from the monomer (appearing as negative at 1750 cm^{-1}) and the cyclic dimer (appearing as negative at 1710 cm^{-1}) to non-cyclic structures interacting with water (positive at 1727 cm^{-1}) (*Scheme 2-1a*). According to Sherman[25], this frequency corresponds to the 'free' C=O of acid functions, the OH groups being bound with water. Another possible structure for water–PAA H-bond association is the cyclic structure (*Scheme 2-1c*) in which the water molecules are intercalated between the COOH groups of the cyclic dimer[26]. Water is associated as strongly bound water to these cyclic structures, and is identified by water absorption at 3014 cm^{-1} (see *Figure 2*, curve 2).

Thermal treatment of PAA and its effect on water vapour sorption. Thermal treatment (180°C for 0.5 h) partly transforms PAA into cyclic anhydrides with C=O stretching absorptions at 1804 and 1757 cm^{-1} (spectrum not shown). A shift of $\nu_{\max \mathrm{OH}}$ of the acid group from 3126 to 3153 cm^{-1} (see *Table 2*) is also observed. It can be related to the partial dissociation of the acid cyclic dimer into less associated structures. Water absorbed after thermal treatment completely hydrolyses anhydrides. The decrease of $\nu_{\max \mathrm{OH}}$ of water from 3522 cm^{-1} in water-saturated untreated initial samples to 3503 cm^{-1} in thermally treated water-saturated films (see *Table 3*) indicates that H bonds of water with annealed PAA are slightly stronger in the last case.

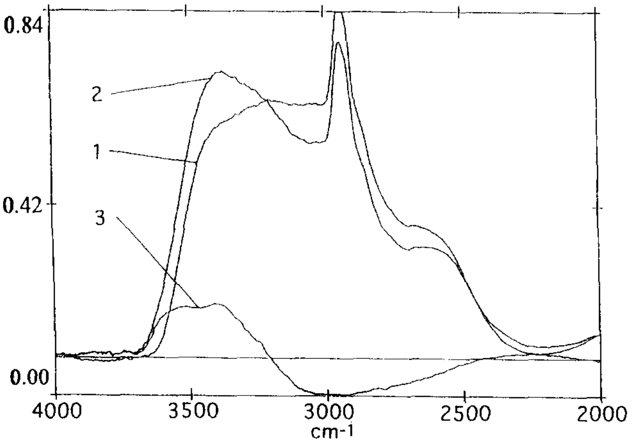


Figure 8 *FT*i.r. spectra of PAA/PVA1 1/1 (equimolar): dry (1), saturated with water vapour (2) and the difference spectrum (curve 2–curve 1) (3) (2000–4000 cm^{-1})

The d.s.c. curves for water vaporization from the water-saturated sample are identical for the thermally treated and untreated samples (curves not shown); anhydrides are formed again during the d.s.c. run. This shows that the transformations initiated by this thermal treatment of PAA are reversible.

Blends

Interactions of water–(PAA/PVA1) in the blends. The equimolar PAA/PVA1 miscible blend (1/1 blend) is not crystalline and absorbs one water molecule per repeating unit (see *Table 1*.) Summation of the number of moles of water absorbed by the same quantities of pure PAA and pure amorphous PVA1 should give a higher value (1.6 water molecules per repeating unit). The interactions of water with the components of the blend will now be specified. If the difference spectra of the OH stretching for the 1/1 blend (see *Figure 2* (curve 4), *Figure 4* (curve 4) and *Figure 8* (curve 3)) are assimilated to the spectra of absorbed water in the blend and compared with the corresponding spectra of absorbed water in PAA and PVA1, the absorption of strongly bound water seems to be displaced to the high frequencies in the blend (see *Table 3*), becoming thus more labile. This is confirmed by the d.s.c. curves (not shown). If the vaporization curve of water absorbed in the 1/1 blend is compared with the corresponding normalized curves for the pure polymers, it readily appears that the proportion of strongly bound water vaporized above T_g in each system is lower in the blend than in the pure polymers.

All these changes can be explained by the competition between interpolymer (PAA–PVA1) and water–polymer interactions. Let us remember that in the autoassociated polymers, strongly bound water interacts with the cyclic dimers of PAA and with OH groups of the intermediate region in PVA1. In the blend, part of these groups are not available since they are involved in interpolymer interactions.

Interactions of water with PAA in the blend can be further clarified by considering the changes in the difference spectrum at 1600–1800 cm^{-1} (see *Figure 4*, curve 4). Water absorbed in the blend dissociates some cyclic PAA dimers (appearing as negative at 1708 cm^{-1}) and also non-cyclic structures (appearing as negative at 1741 cm^{-1}). H bonds of water with the liberated acid

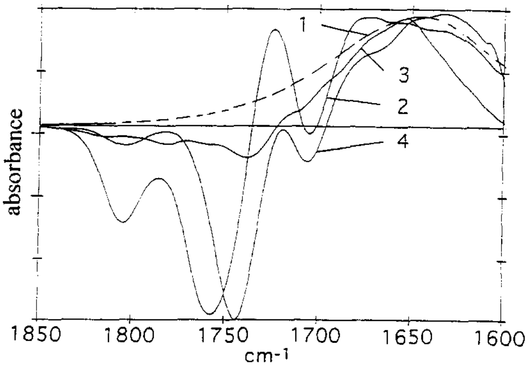


Figure 9 Spectrum of bulk water (1) and difference spectra for the thermally treated samples at 1600–1850 cm^{-1} (dry polymer subtracted from water vapour saturated polymer): PAA (2), PVA1 (3) and the PAA/PVA1 1/1 blend (4)

functions are formed, and appear at $1727\,cm^{-1}$. Indeed, curve 4 of *Figure 4* can only be obtained if a positive absorption at $1727\,cm^{-1}$ is added to the negative contributions just mentioned.

To study the effect of water on melting point and crystallinity, the blend 0.25/1 PAA/PVA1 will be considered. Indeed, the changes in the i.r. absorption of the amorphous part of this blend are similar to those observed for the 1/1 blend, which is not crystalline. In the PVA1-rich 0.25/1 blend, the crystallinity of the PVA1 fraction increases from 2.5 to 15% (*Table 4*) in the presence of water, as shown by the increase of the absorption band situated at $1140\,cm^{-1}$ (not shown). Water penetration in the PAA/PVA1 miscible blend thus induces segregation of a part of the PVA1, which crystallizes, the remaining PVA1 being miscible with PAA in the amorphous phase.

Effect of thermal treatment on water–polymer and polymer–polymer interactions in the blends. The i.r. absorption of anhydrides is lower in the PAA/PVA1 1/1 blend than in pure PAA. The quantity of anhydrides disappearing during water saturation of the thermally treated samples can be deduced from the importance of the negative band at $1804\,cm^{-1}$ assigned to anhydrides in pure PAA (*Figure 9*). Comparison of curves 2 and 4 show that more anhydrides decayed in pure PAA than in the blend. It is proposed that in the presence of PVA1, anhydride formation is inhibited. It has been calculated that under the action of heat, formation of diene in the PVA1 component of the blend liberates enough water to decrease the quantity of anhydrides formed.

Thermal treatment also decreases the number of COOH groups auto-associated as cyclic dimers by transforming them into non-cyclic structures. Indeed ν_{max} of C=O stretching in the 1/1 blend spectrum is displaced from 1710 to $1720\,cm^{-1}$ after thermal treatment (spectra not shown). The main potential partners for H bonding with water in thermally treated samples are thus non-cyclic dimers at $1744\,cm^{-1}$, which appear as negative in curve 4 of the difference spectrum given in *Figure 9*. In the samples which were not thermally treated, both the cyclic and non-cyclic dimers are partners for water. Indeed, in this case, the negative absorption at $1744\,cm^{-1}$ (non-cyclic dimer) and at $1708\,cm^{-1}$ (cyclic dimer) have about the same contribution in the difference spectrum (curve 4 of *Figure 4*).

Concerning the crystallinity of PVA1 in the annealed 0.25/1 blend saturated with water vapour, water penetration does not induce reorganization and crystallization of the chains (*Table 4*). Indeed, the crystallizable part has already been increased from 2.5 to 22.1% during the thermal treatment.

In the amorphous phase, phase separation occurs during thermal treatment. This phase separation is identified by comparing the T_m values of PVA1 in the untreated and thermally treated 0.25/1 blends. In the untreated blend, PVA1 crystallizes, and an important melting point depression is observed (from 221.8 to 192.1°C; *Table 4*). This depression results from miscibility in the amorphous phase. In the thermally treated sample, the melting point depression is lower (from 221.8 to 201.3°C), indicating that crystalline PVA1 is now in equilibrium with a liquid phase which is richer in PVA1 as a consequence of L–L demixing of the amorphous phase of the blend. This demixing is clearly identified by the presence of two glass transition temperatures after 6 h of thermal treatment at 180°C[24].

CONCLUSIONS

The presence of water modifies autoassociation of pure PAA and PVA1 and interpolymer interactions in their blends and thus affects the miscibility of the components. The results obtained by *FT*i.r. and d.s.c. have shown that polymer-bound water (non-freezing) contains two types of molecules: weakly and strongly H bound to the chains. Weakly bound water absorbs between 3500 and $3570\,cm^{-1}$ in the i.r. (ν_{OH}). It vaporizes at temperatures lower than T_g, and is engaged in dimeric H bonds with the OH groups of the amorphous phase of PVA1 and with the acid functions of PAA. Strongly bound water absorbs in the range $3015–3400\,cm^{-1}$ (ν_{OH}), and vaporizes at temperatures higher that T_g. It is intercalated in the polymeric H bonds of the intermediate phase of the autoassociated PVA1 or between the COOH groups of cyclic dimers. Examination of the C=O stretching absorption shows very accurately that the OH group of the acid function participates in H bonds with water in PAA; C=O bonds remain free and absorb at $1727\,cm^{-1}$. In PVA1, absorbed in water increases the mobility of the chains and induces crystallization in the amorphous phase at temperatures below T_g. In the blends, the quantity of strongly bound water is lower than in pure polymers, probably because of competition between polymer–polymer and water–polymer interactions. Thermal treatment affords a decrease in the hygroscopicity of pure PVA1 resulting from the formation of a small quantity of double bonds and mainly from the crystallization of a part of the amorphous phase. In pure PAA, reversible anhydride formation is observed. In the blends, thermal treatment brings about demixing of the amorphous phase followed by crystallization of a part of PVA1.

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