Poly(vinyl alcohol)/Poly(acrylic acid) Blends: Miscibility Studies by DSC and Characterization of Their Thermally Induced Hydrogels

H. VÁZQUEZ-TORRES,[1,2,*] J. V. CAUICH-RODRÍGUEZ,[1] and C. A. CRUZ-RAMOS[1,†]

[1]Centro de Investigación Científica de Yucatán, A. C. Departamento de Polímeros, Apdo. Post. 87, Cordemex, Mérida, Yucatán, México C.P. 97310; [2]Universidad Autónoma Metropolitana-Iztapalapa, Departamento de Física, México, D.F., Apdo. Post. 55-534, México C.P. 09340

SYNOPSIS

Binary blends of poly(vinyl alcohol) (PVA) with poly(acrylic acid) (PAA) and polyacrylamide (PAAm) were characterized by differential scanning calorimetry (DSC), thermal gravimetric analysis (TGA), and infrared spectroscopy (IR). Molecular weight, blend composition, and heating time at 150°C were the variables used. Results obtained by DSC indicated that PAA/PVA blends are miscible in the full range of composition. Similarly, TGA traces showed that thermal stability was higher for blends than for pure polymers. Blends of PVA with high molecular weight PAA exhibited a hydrogel behavior after drying at relatively low temperature (100°C), whereas blends containing low molecular weight PAA behaved as hydrogels only after they were heated at 150°C. Hydrogel character was increased for these two PVA/PAA blends with the heating time at higher temperature (150°C). IR spectra revealed that esterification took place in these blends after thermally treated at this temperature. In contrast, addition of glyoxal in combination with heating was necessary to produce hydrogels from PAAm/PVA blends. Furthermore, the cross-linking degree of these hydrogels was estimated from their absorbency values by applying the Flory–Rehner equation. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

Structural and physical characterization of hydrogels has steadily grown in importance from both academic and industrial points of view.[1-3] This is because these materials can be used as membranes to separate certain liquids or proteins dissolved in water as well as in drug-delivery systems. However, such a characterization has been a difficult task for researchers of physical chemistry.[4] For example, when polyacrylamide hydrogels are obtained by copolymerization of acrylamide and bisethylene acrylamide, which works as cross-linking agent, structural heterogeneity occurs in the polymeric network. This heterogeneity is difficult to control and causes a nonuniformity on the transport properties of the swollen hydrogels.[5] However, these water-absorbing materials can also be prepared by cross-linking a water-soluble polymer, such as poly(acrylic acid) (PAA) or polyacrylamide (PAAm). Cross-linking can be induced in these polymers by either γ-irradiation[6] or thermal treatment,[3,7] as well as by using a cross-linking chemical agent.[8] Alternatively, water-soluble polymer blends, in which components are reactive with each other, can be used to produce hydrogels. In this case, the distribution of cross-links is expected to depend strongly on the state of miscibility of the polymer blend under study, corresponding to a homogeneous distribution of cross-links for totally miscible blends (i.e., blends that are miscible at the segmental level). Thus, it is of paramount importance to determine the miscibility behavior of the polymer blends before the cross-linking takes place in these systems. In this line of thought, blends of poly(vinyl alcohol) (PVA) with PAA have

---

been used as water-soluble packaging films.[3] However, to our knowledge, detailed miscibility studies on this system have not been reported.

In the light of the above discussion, the cross-linking of blends of PVA with PAA, or with PAAm, was considered as a promising route to prepare hydrogels. In this work, the results of miscibility studies by differential scanning calorimetry (DSC) on the PVA/PAA and the PVA/PAAm blends are reported. Infrared (IR) spectroscopy was also applied to detect possible structural changes in the thermally treated blends. The water absorbency of the resulting hydrogels was determined as a function of both the blend composition and the heating time. Furthermore, by applying the Flory–Rehner equation to the absorbency data obtained for the resulting swollen hydrogels, the cross-linking degree for each sample was calculated.

EXPERIMENTAL

Materials

Poly(vinyl alcohol) (PVA), poly(acrylic acid) (PAA), and polyacrylamide (PAAm) were purchased from Polysciences, Inc. (USA); some characteristics of these polymers are described in Table I. Glyoxal (Aldrich Chemical Co., USA) was used as a cross-linking agent. 1-Propanol and chloroform (Merck, México) were used as suspending liquids during the measurement of the blend density. All these materials were reagent grade and they were used as received.

Preparation of Binary Polymer Blends and Their Films

Different weights (0–2.0 g) of both polymers, as were needed for preparing 2 g of each binary blend in the full range of composition, were separately dissolved in 100 mL of distilled water by stirring and heating at 80°C. The resulting solutions of both components were then mixed and stirred at 60°C for 1 h. Each one of these homogenized mixtures was transferred into a Petri dish, which was previously covered in the inside with polyethylene film. Afterward, films were cast from these aqueous solutions by evaporation of water in a drying oven at 60°C for 24 h. Additional sets of the same binary blends, but containing glyoxal as a cross-linking agent, were prepared by adding the glyoxal to the corresponding aqueous mixture of polymers, being 1% by weight for PVA/PAA and 5% for PVA/PAAm, and stirring them for 1 h at room temperature. Films were cast from these mixtures as above. All blends were prepared in duplicate.

Thermal Treatment

Specimens (films of 0.1 g approximately) of each one of the blends were previously heated in a vacuum oven at 100°C for 1 h. Then, samples taken in triplicate from these preheated specimens were further heated by allowing them to stand in a vacuum oven at 150°C for 0, 15, 30, and 45 min, respectively. These samples were further tested for water absorbency.

Thermal Analysis

Sample specimens were tested in duplicate in a Perkin-Elmer thermal gravimetric analyzer (TGA-2) and in a Perkin-Elmer differential scanning calorimeter (DSC-2C). DSC apparatus was calibrated with tin and indium. DSC runs were performed on approximately 12 mg of the sample, using aluminum sample pan holders (Perkin-Elmer) under nitrogen

Table I Characteristics and Nomenclature of the Used Polymers[a]

Polymer	Nomenclature	$\bar{M}_w$	Hydrolysis Extent (%)	Carboxyl Groups (%)
Poly(vinyl alcohol)	PVA(1)	25,000	88	—
	PVA(2)	78,000	88	—
	PVA(3)	125,000	88	—
Poly(acrylic acid)	PAA(1)	1.0×10^6	—	100
	PAA(2)	450,000	—	100
Polyacrylamide	PAAm(1)	$5.0–6.0 \times 10^6$	—	0
	PAAm(2)	200,000	—	70
	PAAm(3)	200,000	—	10

[a] Carboxyl groups in PAAm polymers are in the form of sodium salt.

(flow rate of 20 mL/min) from 40 to 180°C at a heating rate of 10°C/min. The DSC runs on PVA/PAAm blends were carried out from 40 to 200°C. TGA runs were carried out on about 4 mg of sample under nitrogen (flow rate 20 mL/min) and furnace heating rate of 20°C/min from 40 to 500°C. All the thermally analyzed films were previously dried in a vacuum oven at 100°C for 24 h.

Infrared Spectroscopy

IR spectra for thin films of blends (approximately 0.1 mm thick) were obtained with a Perkin-Elmer spectrophotometer Model 683, in the transmittance mode, at scan time of 20 min, between 4000 and 400 cm^{-1}. These films were previously dried in a vacuum oven at 100°C for 24 h and then heated again in a vacuum oven for different lengths of time as above.

Density Measurement[9]

Samples of the blend films (6–8 mg) previously dried in a vacuum oven at 100°C for 24 h, or thermally treated at 150°C for 0, 15, 30, and 45 min, were immersed into 5 mL of chloroform contained in a graduated cylinder glass. Then, drops of 1-propanol were added slowly to the chloroform until the film had floated in the high-half of the volume of the resulting mixture. After each drop was added, the mixture was thoroughly homogenized with a magnetic bar stirrer and the temperature maintained at 20°C. Measurements were taken when the suspended film was floating at rest into the mixed solvents.

Tests of Absorbency

Samples of blends films (0.1 g), which were previously thermally treated at various experimental conditions, were first immersed in distilled water (100 mL) at 25°C for 24 h and then taken out. (In preliminary experiments, it was observed that water retention was practically constant for immersion time longer than 20 h.) The swollen films were weighed after the excess of water lying on the surfaces was absorbed with a filter paper. Afterward, the swollen films were dried at 100°C until a constant weight was attained and weighed again. Water absorbency (WA) was calculated using the following equation:

$$WA = \frac{Wt_s - Wt_{sd}}{Wt_{sd}} \qquad (1)$$

where Wt_s is the weight of swollen film, and Wt_{sd}, the weight of dried film after being swollen.

Extractable Mass during Immersion in Water

The loss of mass experienced by the samples, during the test of absorbency, was determined by the weight difference between the weight of the dried sample used for immersion in water (Wt_0) and that of the same sample after being swollen and dried (Wt_{sd}). Calculation for the amount (in wt %) of extractable mass (EXT) was done using the following equation:

$$EXT = \left[\frac{(Wt_0 - Wt_{sd})}{Wt_0} \right] \times 100 \qquad (2)$$

RESULTS AND DISCUSSION

Preliminary Observations

Pure PAA gave transparent, colorless, flexible films by casting from its aqueous solution. PAAm having carboxyl groups also gave transparent, flexible, but slightly yellowish films. PVA rendered transparent, colorless, but rather rigid films. In contrast, PAAm having no carboxyl groups rendered partially hazy, fairly brittle films.

In general, flexibility and transparency showed by the films of PVA/PAA and PVA/PAAm blends were roughly a combination of those properties of pure components, being more flexible the higher the content of PAA or PAAm having carboxylate groups. Likewise, blends of PVA with PAAm having no carboxylate groups became partially hazy and fairly brittle as the content of PAAm was increased.

Effect of Temperature and Heating Time

Pure Polymers

All the films made of the pure polymers PAA(2), PVA, and PAAm were soluble in water and no swollen gels were observed after immersion in water, even though they were previously heated at 150°C for 45 min. In contrast, films of pure PAA(1) swelled after immersion in water, and a portion of its mass was removed during this test. Both the absorbency of the resulting swollen PAA(1) films and the weight of extractable mass diminished with the time of thermal treatment (Fig. 1). This behavior of PAA(1) is explained by assuming that dehydration took place at these conditions, as has been reported for PAA after being heated at 150°C or higher temperature. This results in the formation of anhydride
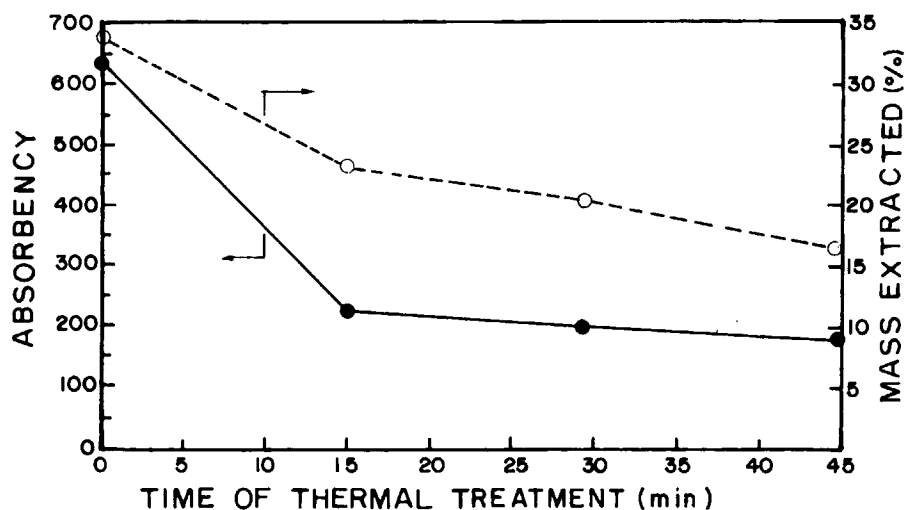
Figure 1 Effect of heating time (———) on the absorbency and (- - -) on the weight of extractable mass of PAA(1) films. Heating condition: at 100°C for 1 h and then at 150°C for the indicated time.

groups along the polymer chains,[10,11] which cause a decrease in their solubility in water. On this basis, both the intramolecular glutaric–anhydride type and the intermolecular isobutyric–anhydride type may occur in PAA under these conditions, making it less soluble the higher the extent of the formed anhydride groups.[10] Although only the intermolecular anhydride moieties can contribute to the gel character of PAA, these two structures would reduce the absorbency of the resulting gels. Interestingly, the absorbency of the PAA(1) gel, which was obtained by heating its films (100°C for 1 h and then from 100°C to 150°C), was comparable in value to those of typical superslurpers that are usually produced by hydrolysis of starch-g-polyacrylonitrile copolymers.[12] The same observation is true for the mass extracted after they were immersed in water.

The cross-linking degree appeared to be high enough to produce gels in PAA(1), due to its higher molecular weight ($\bar{M}_w = 1.0 \times 10^6$), but failed to form a measurable amount of gel in PAA(2) ($\bar{M}_w = 2.5 \times 10^5$). On this basis, the absence of gels in the heated films of PAAm having carboxylate groups can be attributed to their lower molecular weights, as well as to the lesser extent of carboxylate groups, which are diluted by the contained amide groups, in comparison to PAA. Films of pure PVA and PAAm having no carboxylate groups did not experienced any change in their water solubility after heating. These pure polymers were also thermally treated to be used only as controls in the following experiments.

PVA/PAA Blends

Dried films of blends of PAA(1) with PVA(1), PVA(2), and PVA(3), respectively, were partially insoluble in water, in spite of being heated at 100°C for 1 h and then heated for the necessary time (5 min approximately) for the temperature reach 150°C. Insoluble portions of these blends showed the behavior of a swollen gel having significant absorbency values (Table II). This gel behavior may be a result of the highly probable specific interaction in these blends, as has been suggested by Sonenstein[3] and, after studies on this system in solution, by Williamson and Wright.[13] Absorbency values of these films depended upon both the blend composition and the molecular weight of PVA (Table II), at least for the range of molecular weight studied here. Furthermore, though data in Table II are the results of a rough screening, it is worthy to notice that the lowest absorbency values corresponded to blends being intermediate in composition. Interestingly, this composition corresponds to a molar ratio of 1 of carboxyl to hydroxyl groups in these blends. A longer heating time at 150°C produced a drastic reduction in the absorbency values of these blends (Fig. 2) and, as a consequence, the effect of the blend composition was not distinguished clearly. This may be a result of a combination of several factors: the strong tendency of high molecular weight PAA(1) to form gels after being thermally treated, the possible strong specific interaction in PVA/PAA blends, and a probable chemical re-

Table II   Absorbency of PAA(1)/PVA Blends after Immersion in Water[a]

Blend	Blend Composition (Wt %) and Absorbency				
	100/0	75/25	50/50	25/75	0/100
PAA(1)/PVA(1)	630	100	220	500	Soluble
PAA(1)/PVA(2)	630	60	90	320	Soluble
PAA(1)/PVA(3)	630	70	70	120	Soluble

[a] Dried blends were preheated at 100°C for 1 h and heated up to 150°C. Absorbency is given in g of water per g of dried sample of blend. Nomenclature as in Table I.

action between the carboxyl groups of PAA and the hydroxyl groups of PVA.

On the other hand, a rough screening indicated that all the blend films of PAA(2) with PVA(1), PVA(2), and PVA(3), respectively, as well as of pure polymers, were completely dissolved in water even though they were heated at the same conditions (100°C for 1 h and then to 150°C) as those applied on blends having PAA(1). This result allowed us to assume that, under these experimental conditions, effective cross-linking in these blends of PAA(2) was not high enough to produce a measurable quantity of hydrogel due to the low molecular weight ($\bar{M}_w$ = 4.5 × 10^5) of PAA(2). However, after these blends were heated at 150°C for 15, 30, and 45 min, they swelled and partially dissolved in water.

One of the main objectives of the present study was to determine the influence of the heating time, as well as the effect of blend composition, upon the

absorbency showed by films of PVA/PAA blend. Then, taking into account that blends of PVA with PAA(2) rendered gels only after they were heated at 150°C for longer time, we selected the PAA(2)/PVA(2) system to continue this study in more detail, avoiding the masking gel behavior showed by pure high molecular weight PAA.

PAA(2)/PVA(2) System

The effect of heating time at 150°C, as well as of blend composition, on the absorbency values of the resulting gels of the PAA(2)/PVA(2) system is showed in Figure 3. In this figure, it can be appreciated that the effect of blend composition was more distinguishable in the extremes of this diagram for a heating time of 15 min. Also, the lower absorbency values corresponded to intermediate compositions, as in the case of PAA(1)/PVA blends. The same
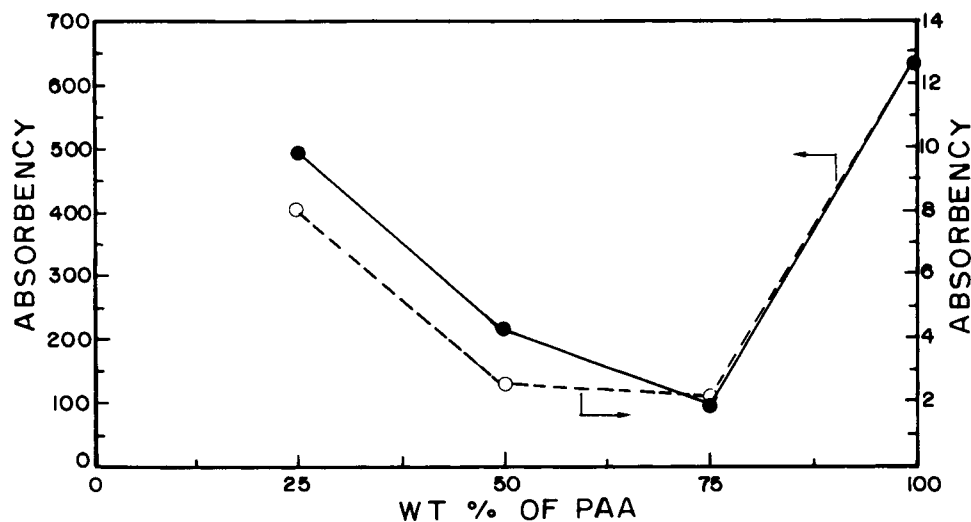
Figure 2   Influence of blend composition and heating temperature on the absorbency of PAA(1)/PVA(3) blends: (——) at 100°C for 1 h and (- - -) at 150°C for 30 min.
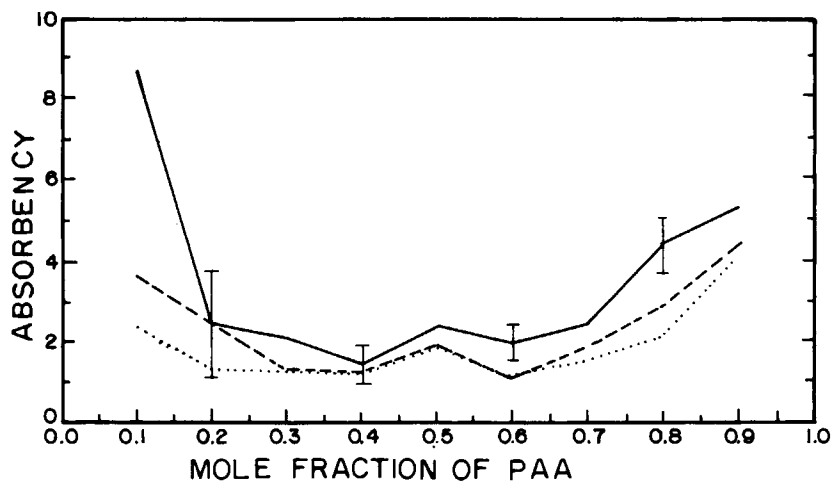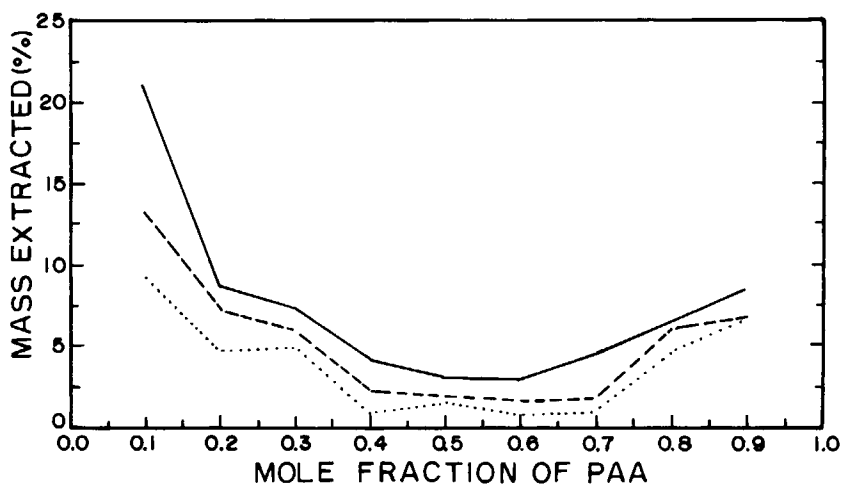
Figure 3 Effect of blend composition and heating time at 150°C on the absorbency PAA(2)/PVA blends. Curves correspond to the blends heated during a time of (———) 15, (- - -) 30, and (· · ·) 45 min, respectively.

observations are true for the mass extracted from these blends after they were immersed in water for 24 h (Fig. 4). These results strengthen the above assumption that thermal treatment at 150°C induced the occurrence of a cross-linking reaction between PAA and PVA, which would take place mainly during the time of 30 min (Fig. 3). This probable reaction may be the esterification of carboxyl groups of PAA with hydroxyl groups of PVA, as assumed above, since it has been reported that PAA experiences this reaction type with glycerol and other poly hydroxylated compounds.[10] Likewise, it has been

claimed that PVA can be cross-linked with citric acid.[14]

PAA(2)/PVA(2)-Glyoxal System

To increase the cross-linking degree in PAA(2)/ PVA(2) blends, glyoxal was added (1 wt % with basis on the blend weight) when the polymer mixture was in solution. After the films were obtained and dried, they were heated at 150°C. The absorbency values and the percent of mass extracted for the PAA(2)/PVA(2)-glyoxal system were then


Figure 4 Effect of blend composition and heating time on the weight of extractable mass of PAA(2)/PVA(2) blends: Heating time was (———) 15, (- - -) 30, and (· · ·) 45 min, respectively.
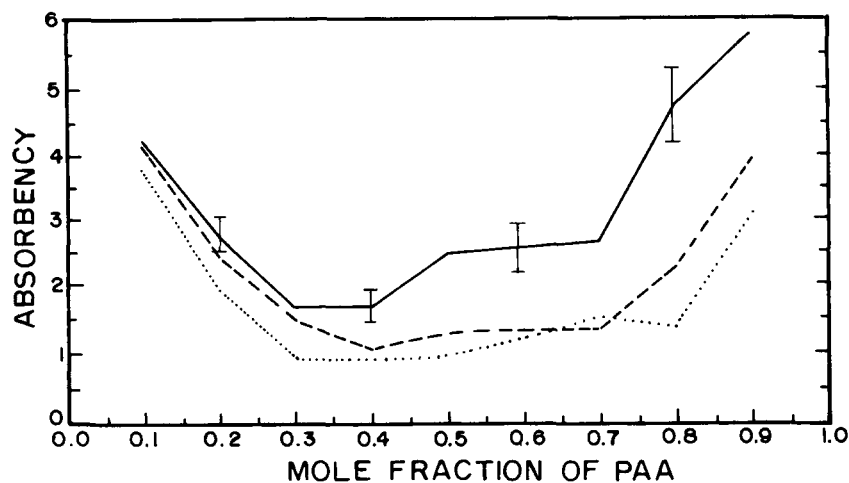
Figure 5   Absorbency of PAA(2)/PVA(2) blends containing glyoxal (1% by weight). Blends were previously heated at 150°C for (———) 15, (- - -) 30, and (· · ·) 45 min, respectively.

determined (Figs. 5 and 6). Regarding this system, four effects are worthy of mention: First, the addition of glyoxal caused a decrease in the absorbency values only for the blends with high content of PVA(2) (Fig. 5). Second, the time of thermal treatment from 30 to 45 min had a measurable effect on the absorbency of blends having a composition of about 50 wt % of PAA (Fig. 5). Third, the amount of mass extracted from the blends with glyoxal and high contents of PVA was lower (Fig. 6) than that for blends without glyoxal (Fig. 3). Fourth, the experimental error on the absorbency data was lower

in blends rich in PVA and containing glyoxal (Fig. 5), in comparison to that of blends having no glyoxal (Fig. 3). This effect of glyoxal can be explained by taking into account that this reagent reacts with two hydroxyl groups of PVA, forming acetal structures.[8] Eventually, the hydroxyl groups that take place in this reaction can belong to different chains, resulting in the formation of cross-links between chains of PVA in this system. However, pure PVA remained water-soluble at a low concentration of glyoxal (1% by weight). This is an indication that the reaction between PVA and glyoxal, at this level
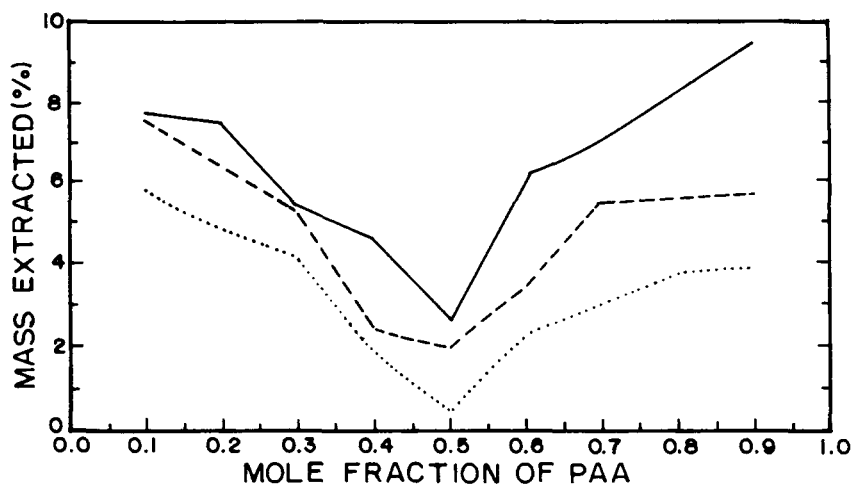
Figure 6   Weight of mass extracted from PAA(2)/PVA(2) blends containing 1 wt % of glyoxal after immersion in water for 24 h at 25°C. Blends were previously heated at 150°C for (———) 15, (- - -) 30, and (· · ·) 45 min, respectively.

of concentration, had a low contribution to the hydrogel behavior, which was shown by PVA/PAA blends after heating. Then, one must necessarily invoke a chemical reaction between both polymers to explain the synergism arising from the combination of these three components and the thermal treatment. This explanation is reinforced by taking into account that 5 wt % of glyoxal, when added to PAA/PVA blends, produced hydrogels showing a very low absorbency values, i.e., highly cross-linked hydrogels, as was observed in preliminary experiments. This was the reason for the use of 1 wt % to cross-link PAA/PVA systems in all the experiments reported here.

PVA/PAAm Blends

In contrast to PVA/PAA blends, all the films of PVA/PAAm blends were soluble in water, despite being heated at 150°C for 45 min. However, a severe reduction of solubility for PVA/PAAm films was achieved by addition of 5 wt % of glyoxal, even though they were only preheated at 100°C for 1 h. The absorbency of the resulting hydrogels of binary blends of PAAm(1) with PVA(1) is shown in Table III. As can be seen, absorbency values for these hydrogels depended upon the blend composition in the range from 25 to 50 wt % of PAAm, but such a dependence was unclear for the blends with a higher content of PAAm(1) (Table III). This indicates that the cross-linking degree was too high for the blends rich in PAAm(1) and, as a consequence, the effect of glyoxal on the blend absorbency might have masked that arising from the blend composition. Likewise, the influence of molecular weight of PVA upon the blend absorbency was not clearly distinguishable when these blends were heated at 150°C. Indeed, the molecular weight effect was noticeable only in blends of 25 wt % of PAAm(1) with glyoxal

Table III   Absorbency of PAAm/PVA(1)–Glyoxal Systems[a]

	Blend Composition (Wt %) and Absorbency		
Blend	75/25	50/50	25/75
PAAm(1)/PVA(1)	3.5	4.3	6.3
PAAm(2)/PVA(1)	23.6	13.6	10.7
PAAm(3)/PVA(1)	13.1	5.2	6.9

[a] Dried films containing 5 wt % of glyoxal were heated at 100°C for 1 h and at 150°C for 15 min. Nomenclature of polymers as in Table I.

after being heated at a relatively low temperature (100° for 1 h). Absorbency for these blends was higher the higher the molecular weight of PVA (Fig. 7). This latter effect is expected because the number of chain terminals is higher in the networks for blends having lower molecular weight PVA and, as was established by Flory,[15] chain terminals do not contribute appreciably to the character of polymer network, nor, of course, to its gel behavior.

The combined effect of both the heating temperature and the addition of glyoxal on the absorbency of the PAAm(1)/PVA(2) blend is shown in Figure 8. As can be observed in this figure, glyoxal induced a hydrogel behavior for pure PVA at a heating temperature of 150°C. The resulting hydrogel showed a low absorbency value (approximately 20), which allows one to infer that a relatively high cross-linking degree was produced in this blend. This result reinforces the above assumption regarding the probable acetalization of PVA with glyoxal, which became evident at this higher level (5 wt %) of glyoxal content. The effect of heating temperature on the absorbency of this blend can be appreciated in the PVA(1)/PAAm(1) blend containing 25 wt % of PAAm(1): This blend shows a lower absorbency value (ca. 6) when heated at 150°C (Fig. 8) than that of the same composition but heated only at 100°C (ca. 8) (Fig. 7). Although this latter effect was present to a small extent, it is evident that the combination of both the presence of glyoxal and the high temperature (150°C) favored the formation of hydrogels. The former is the most important factor since, as discussed above, PVA/PAAm blends without glyoxal did not show a hydrogel behavior, even though they were heated at 150°C. In these conditions, these two combined factors were dominant on the possible effect arising from the heating time, as can be inferred after inspection of curves depicted in Figure 8. Indeed, these three curves for the samples heated for 15, 30, and 45 min are very close to each other, their differences within experimental error.

PVA/PAAm–sodium Carboxylate

Blends of PVA with low molecular weight PAAm containing two different percentages of sodium carboxylate groups (10 and 70%, respectively), without glyoxal, remained soluble in water even after being heated at 150°C, like those with PAAm having no carboxyl groups. However, a hydrogel behavior was evident for these blends after adding glyoxal and heating at 100 or 150°C (Table III). As in the case
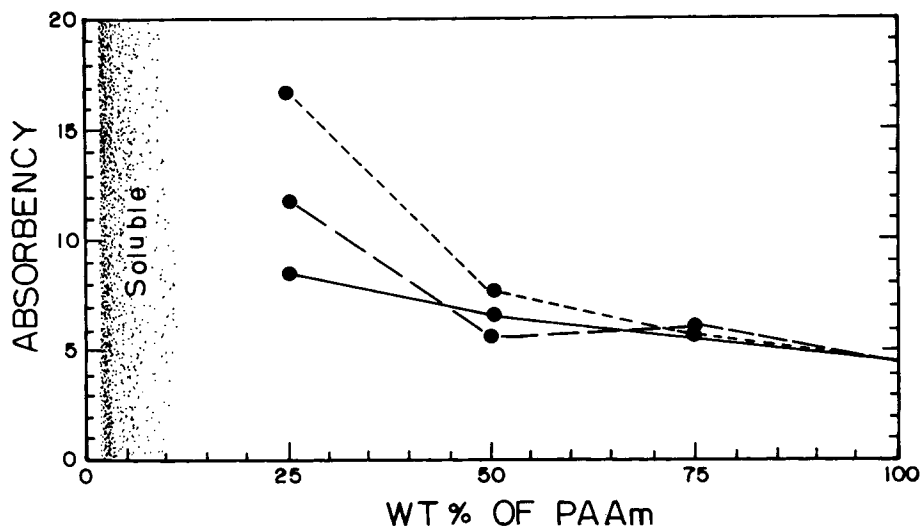
Figure 7   Absorbency of high molecular weight PAAm(1) with (———) PVA(1), (– –)
PVA(2), and (- - -) PVA(3), respectively, as a function of blend composition.

of blends of PAAm without carboxylate groups, the dependence of absorbency on blend composition was not clearly observed. This behavior may result from the probable immiscibility of these systems. Unfortunately, as will be discussed below, conclusive DSC results were not achieved for these systems. Nevertheless, pure PAAm–sodium carboxylate also showed a hydrogel behavior after glyoxal addition and being heated (Table III). Since these hydrogels exhibited a very low absorbency, a chemical reaction must be invoked to explain this result. Such a reaction may be of the type reported to occur between

amide and aldehyde groups, resulting in the formation of acetylated amine–alcohols.[16] Because of their complexity, these systems containing PAAm require a more detailed study in order to understand the preliminary results reported here.

Estimation of Cross-linking Degree in PVA/PAA Blends

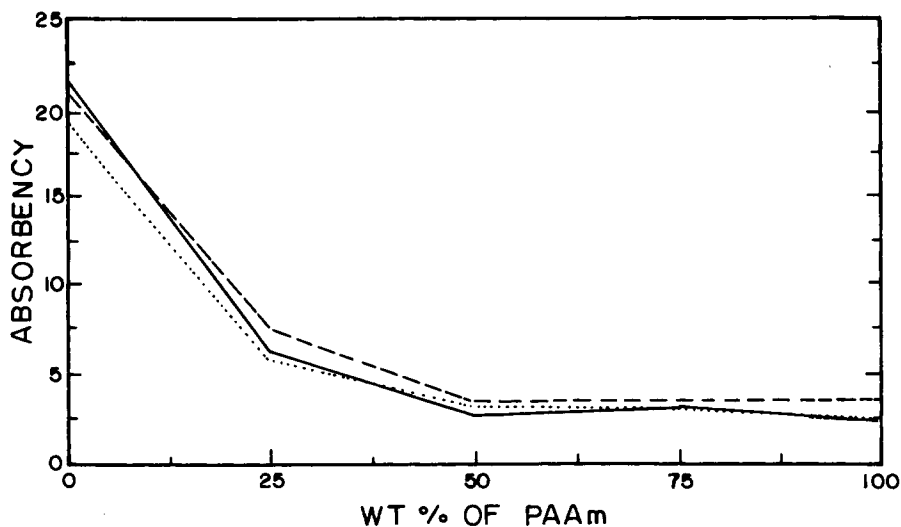Cross-linking degree (CD) was estimated in PVA(2)/PAA(2) blends using the following Flory–Rehner equation[8,17]:

Figure 8   Absorbency vs. composition for the PVA(2)/PAAm(1)–glyoxal system after
being heated at 150°C for (———) 15, (- - -) 30, and (· · ·) 45 min, respectively.

$$\nu = \frac{-[V_p + \chi V_p^2 + \ln(1 - V_p)]}{\rho_p V_0(V_p^{1/3} - \frac{1}{2}V_p)} \quad (3)$$

where ν is the moles of cross-linked units per gram of polymer, which is inversely related to the molecular weight value of segmental chains between cross-links; V_p, the ratio of the swollen polymer volume to the total volume of the cross-linked polymer; V_0, the molar volume of solvent ($18 \text{ cm}^3/\text{mol}$ for water as a swelling liquid); ρ_p, the density (g/cc) of polymer; and χ, the polymer–solvent interaction parameter. For water-swellable polymers (hydrogels), eq. (3) can be simplified by expressing V_p as follows[8]:

$$V_p = \frac{1}{1 + q} \quad (4)$$

where $q = Wt_s/Wt_g$, where Wt_s and Wt_g are the weight of swelling liquid (water) and the polymer weight in the hydrogel, respectively.

To apply this equation, the specific gravity of the PVA(2)/PAA(2) blend was determined in the full range of composition. The obtained density values followed approximately the additivity rule for blend composition when glyoxal was not added, but PVA(2)/PAAm(2) blends having 1 wt % of glyoxal showed a small, positive deviation from this linear behavior (Fig. 9).

On the other hand, the inaccuracy of the Flory–Rehner equation arises primarily from the assumption that χ is constant for any solvent–polymer composition of each system. However, as has been pointed out,[15] χ is a free-energy-type function; thus, it depends on the pressure, p, the temperature, T, and the composition, ϕ (volume fraction of components) in a particular studied system. Unfortunately, there is no universal equation for the function $\chi = (p, T, \phi)$, nor has an empirical equation for χ has been obtained for any hydrogels of interest. Furthermore, if the studied hydrogel is made by copolymerization of two or more comonomers, or by cross-linking two or more homopolymers previously mixed, it is mandatory to express the interaction parameter χ as a contribution of three or more components. Thus, for hydrogels being either copolymers or binary mixtures, χ is usually expressed as follows[18]:

$$\chi = \phi_1\chi_{1s} + \phi_2\chi_{2s} - \phi_1\phi_2\chi_{12} \quad (5)$$

where ϕ is the volume fraction of the component and the subindexes 1 and 2 refer to components 1 and 2, respectively; s refers to the swelling liquid (water for hydrogels). Equation (5) was used to calculate the parameter χ of the PVA/PAA–water system. The χ_{12} was, in turn, calculated by applying the following equation[19]:

$$\chi_{12} = (V_r/RT)(\delta_1 - \delta_2) \quad (6)$$
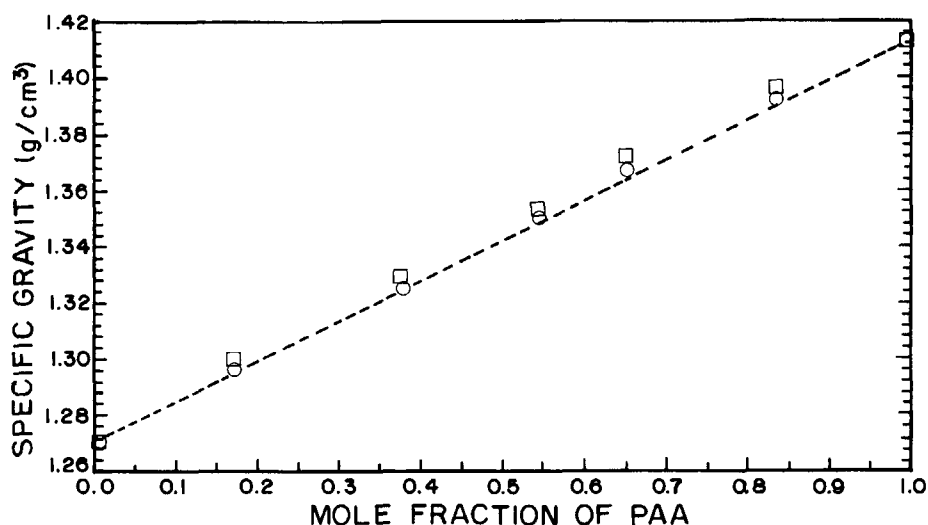
Figure 9 Specific gravity for PAA(2)/PVA(2) blends as a function of blend composition (O) without glyoxal and (□) containing 1 wt % of glyoxal. Theoretical curve (---) is also included, which was obtained on the assumption that the blend density follows the additivity rule contribution from that of their components.

Here, V_r is the reference molar volume, which corresponds to that of the polymer showing its smallest value (V_{PAA} = 51.02 cm^3/mol and V_{PVA} = 35.00 cm^3/mol).[20] The reported solubility parameter[20] for PVA is 25.78 (J/cm^3)$^{1/2}$ and that of PAA was calculated [δ_{PAA} = 23.68 (J/cm^3)$^{1/2}$] taking into account the contribution of the three solubility parameters, which arise from dispersion and polar forces and from hydrogen bonding. These values were, in turn, estimated from the groups' contribution.[20] As was mentioned above, in the case of hydrogels made of polymer blends, it is necessary to know the state of miscibility occurring in those blends, since the absorbency of such hydrogels is obviously dependent on the extent of uniformity and the level at which their components are mixed.

Using eqs. (3) and (4) in combination with both the absorbency and the specific gravity values of the 50/50 mol % PVA(2)/PAA(2) blend, the cross-linking degree (CD) was estimated for this blend thermally treated at 150°C for different lengths of time (Fig. 10). Absorbency values are also included in this figure for comparison. As expected, the CD increased with the heating time (up to 3.2 × 10^{-3} for 45 min of heating), presumably as a result of the esterification reaction between the two blended polymers. Also, glyoxal produced an additional increase in CD (up to about 5.2 × 10^{-3}) for the PVA(2)/PAA(2) blend, which was heated at the same conditions (Fig. 10). Such an increase was too large (ca. 2.0 × 10^{-3}) in comparison with the expected maximum value of about 1.7 × 10^{-4}, which

was estimated by assuming that all the added amount of glyoxal (1 wt %) reacted with the blend components. This result supports the idea that some type of cross-linking chemical reaction, beside esterification, took place between the two blended components of this system containing glyoxal.

Thermal Analysis

The DSC curves of PVA/PAA blends were highly reproducible after the first run, which showed an endothermal peak immediately above its T_g (Fig. 11). This peak corresponds to an enthalpic relaxation experienced by the PAA in the blend. A similar enthalpic relaxation was shown by the pure PAA in these studies and has also been reported by Maurer et al.[21] The DSC thermograms of either pure or blended PAA did not show thermal events that might be attributable to some traces of water, in contrast to the DSC results reported by Maurer et al.[21] This indicates that the drying procedure used in the present study was very efficient. In turn, DSC thermograms obtained for all the PVA/PAA blends exhibited a single T_g, which was composition-dependent, as can be appreciated from Figure 12, which showed a significant deviation from the linear behavior. Such a deviation is similar to that shown by miscible blends in which enthalpic contributions are responsible for miscibility.[22] Thus, it is highly probable that strong specific interactions are taking place in the PVA/PAA blend, as assumed above. Furthermore, PVA/PAA blends having glyoxal exhib-
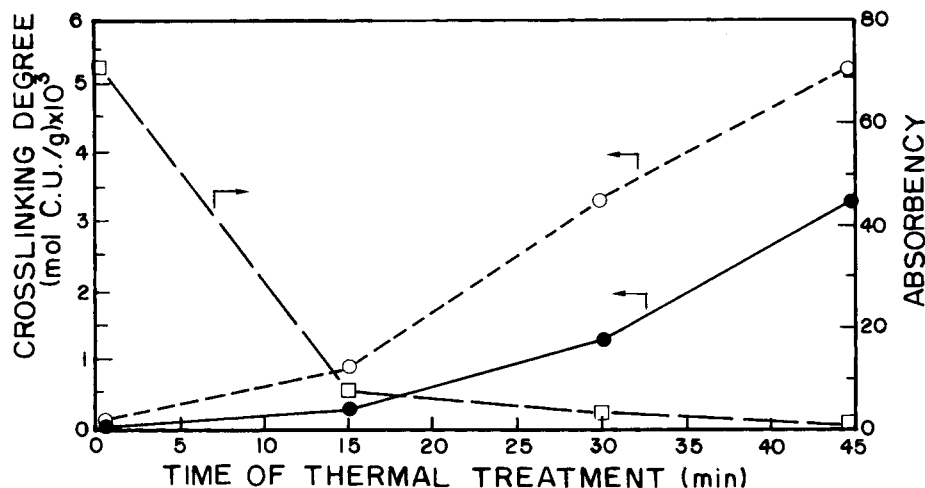
Figure 10   Cross-linking degree (CD) of the 50/50 mol % PVA(2)/PAA(2) blend, as a function of heating time, (——) without glyoxal and (- - -) with 1 wt % of glyoxal as an additive. Absorbency values of the blends having no glyoxal (– –) is also included to illustrate that this parameter is inversely related to CD.
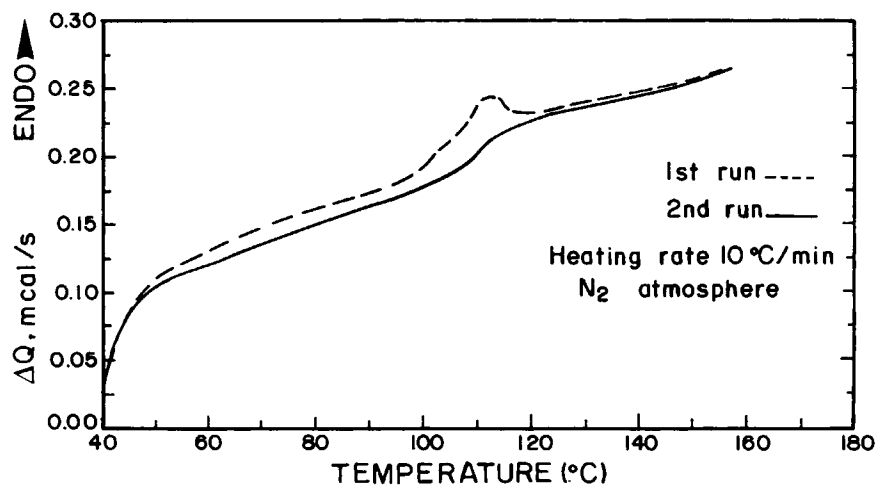
Figure 11 Typical DSC thermograms for PAA/PVA blends. Thermograms correspond to the PAA(2)/PVA(2) blend being 50/50 mol % in composition.

ited a T_g higher in value than that for blends without glyoxal, which reinforces the assumption that cross-linking reactions took place in this blend with glyoxal, either during the drying process or during the first run in DSC experiments.

On the other hand, it is a well-known fact that fully hydrolyzed PVA markedly differs in some properties from those of partially hydrolyzed PVA: The former is a semicrystalline polymer and partially dissolves in water, whereas the latter is amorphous in nature and easily dissolves in water.[23] Though, from our knowledge, thermally induced crystallization has not been reported for partially

hydrolyzed PVA used here, it might be suspected that the unusual high cross-linking degree showed by its blends with PAA has a substantial contribution from physical cross-linking. Such a physical cross-linking would arise from this hypothetical crystallization after the imposed heating conditions in this study (150°C, 6 h). To check if there was any crystallization in pure PVA and PVA/PAA blends when heated at these conditions, DSC runs were carried out on respective samples from 50 to 250°C. The obtained DSC thermograms were very similar in shape to the so-called second run in Figure 11, in which endothermal peaks were absent. This
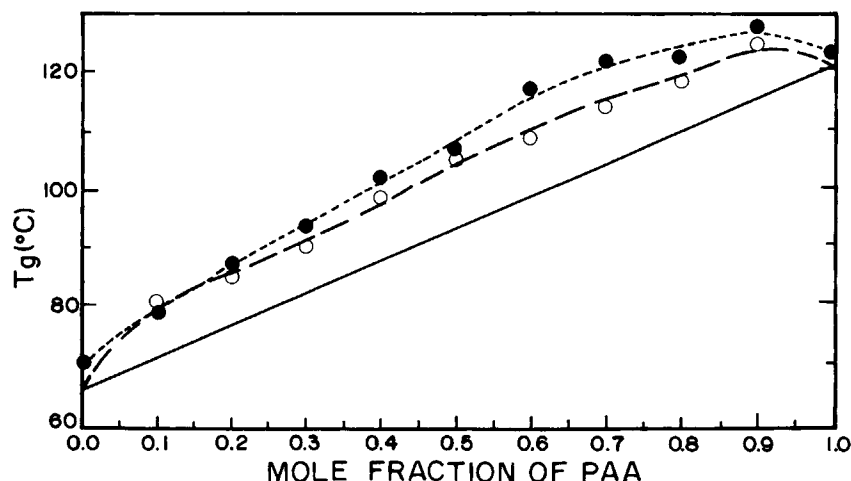

Figure 12 Dependence of the glass transition temperature on the blend composition for the PAA(2)/PVA(2) system (- -) without glyoxal and (---) containing 1 wt % of glyoxal, respectively. The continuous line (——) was obtained assuming that the T_g follows the additivity rule with the blend composition.

is clear evidence that thermally induced crystallization did not take place in the PVA/PAA system and any contribution of physical cross-linking must be therefore discarded. There were, however, two changes in these thermograms, which are worthy of mention, as results of heating for 6 h: (a) The T_g for this system increased in comparison to that of the system heated for 15 min; the maximum increase was observed for the 50/50 blend (20°C approximately). (b) The ΔC_p at the T_g decreased in value; the highest decrease in ΔC_p (approximately 60%) was observed for the 50/50 blend. These results hold up the assumption that a cross-linking chemical reaction took place, as mentioned above. Since it is well established that translational degrees of freedom strongly contribute to the ΔC_p of polymer chains in the liquid state,[24] the presence of cross-links causes a reduction on polymer chain mobility and, in turn, on the ΔC_p at the T_g of cross-linked polymer systems. Interestingly, when revising the first version of the present paper, results of miscibility studies on the PVA/PAA blends were published, in which 98% hydrolyzed PVA was used.[25] This system was reported to be miscible in the full range of composition. The melting point for this pure PVA was of 219°C and a melting-point depression was observed (of about 20°C for the 50/50 blend) as a result of dilution effects of PAA. On this basis, any eventual crystallization induced in the blend studied here would have been observed in the range from 50 to 250°C, which was applied on the DSC runs. In the light of the results reported for PVA/

PAA in the present work, it seems mandatory to check for the presence of cross-links in the reported PVA/PAA blends[25] in which the 98% hydrolyzed PVA was used. Cross-linking is highly likely to occur in this system during the applied annealing conditions, which are required in order to use the Hoffman–Weeks method for thermodynamic studies of melting-point depression on polymer blends. If this is the case, the recrystallization process is affected and, as a consequence, the observed melting-point depression could have two contributions: one arising from thermodynamic miscibility and the other one due to a decrease in mobility of cross-linked chains.

In contrast to the results obtained for PVA/PAA, the DSC thermograms for PVA/PAAm(1) showed two T_g and, judging from the lacking of good reproducibility of these values, one can suspect that these systems, if partially miscible, were affected by the rate of evaporation of the used solvent (water). Likewise, DSC experiments gave ambiguous results for the PVA/PAAm–sodium carboxylate blends: When samples of 15 mg were used for DSC runs, the obtained thermograms did not show a measurable T_g, whereas larger samples rendered irregular DSC thermograms and the samples looked like foam after the pan was opened and visually examined. This may be a result of a probable decomposition of PAAm contained in the blend.

On the other hand, TGA thermograms of PVA(2)/PAA(2) blends (Fig. 13) indicate that the thermal stability of this system was significantly enhanced by addition of glyoxal. Indeed, the loss
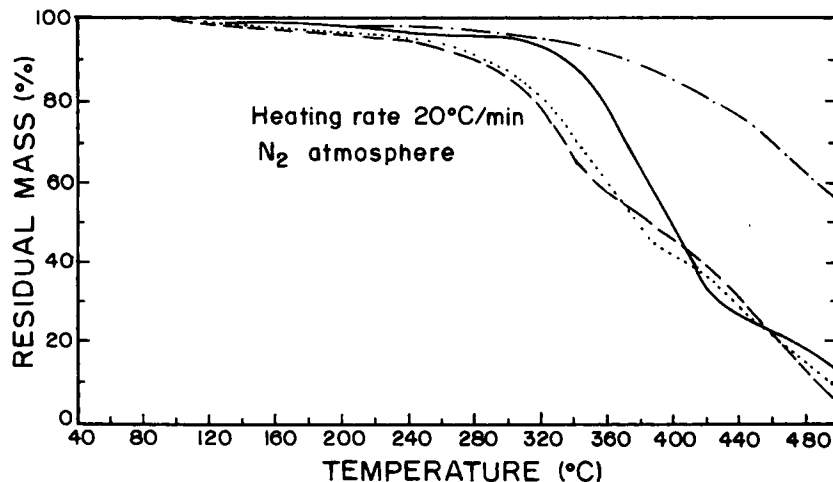

Figure 13   Typical TGA thermograms for PAA(2)/PVA(2) blends. Curves correspond to the blend being 50/50 wt % in composition (· · ·) without glyoxal and (– ·–) containing 1 wt % of glyoxal. TGA traces for (– –) pure PAA(2) and (——) pure PVA are included for comparison.

mass of this blend diminished from almost 90% to 45% by addition of glyoxal (Fig. 13) after being heated up to 500°C in the TGA apparatus. This finding agrees with the assumption made above regarding the role of glyoxal as a cross-linking agent in these blends.

Infrared Studies

The IR spectra of PVA/PAA blends, as well as of that of pure PVA, which were heated at 150°C for 45 min, did not show changes that might be attributable to some chemical reaction. However, the IR spectrum of pure PAA film heated at the same temperature for 30 min showed a shoulder at 1805 cm^{-1}. This shoulder can be assigned to anhydride groups, on the basis of studies previously reported.[20] To in-

duce some detectable changes in the PVA/PAA system, both the blend and the pure components were heated at 150°C for three successive periods of 2 h and their infrared spectra were obtained (Fig. 14). Also, the relative intensity of the shoulder at 1805 cm^{-1} (anhydride groups) in the spectrum of PAA remained constant even though this heating temperature was maintained for 6 h, while the same conditions did not cause a detectable formation of these anhydride groups in PVA/PAA blends. On this basis, one must discard these groups as being responsible for the cross-linking in the above PVA/PAA hydrogels. On the other hand, it can be observed that the band intensity in the 1700–1770 cm^{-1} region (carbonyl groups) and that in the 1190–1260 cm^{-1} region (ester groups) are higher in the IR spectrum of the PVA/PAA blend than in those of pure components, either in each one alone or in su-
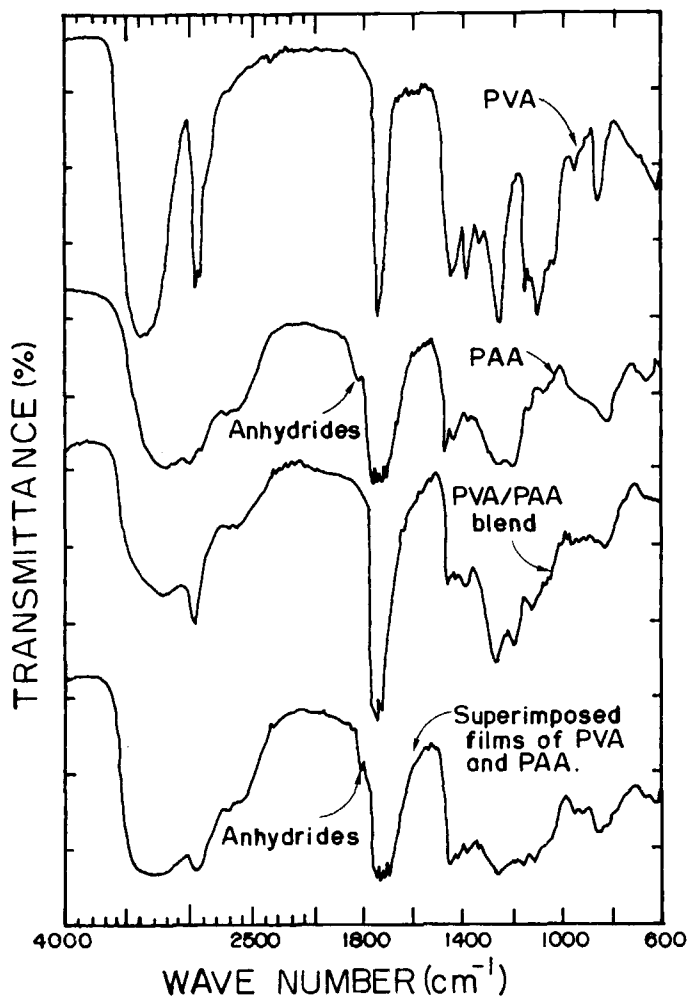
Figure 14 IR spectra for PAA(2)/PVA(2) blend and its components. The IR spectrum obtained on the superimposed films of pure PVA and pure PAA is included for comparison.

perimposed films (Fig. 14). This is strong evidence that an esterification reaction took place in these blends, as assumed above, involving some hydroxyl and carboxyl groups of PVA and PAA, respectively. Since these features were not observed in the IR spectrum of the PVA/PAA blend heated for 45 min, despite this system showing a hydrogel character, one can assume that esterification took place to so little an extent that was not detectable by conventional IR spectroscopy. This assumption agrees with the above observed reduction of water absorbency for these PVA/PAA blends with the heating time.

Regarding PAAm, it can be observed (Fig. 15) that the band at 1590–1770 cm^{-1} is broader for PAAm having glyoxal than that for PAAm without this additive. This result reinforces the idea that a chemical cross-linking was produced by glyoxal in this polymer, as well as in its blends with PVA, after being heated at 150°C. However, systematic studies should be carried out to elucidate the chemical structure of such cross-links, varying the concen-

tration of the cross-linking agent and applying different combinations of heating temperature and heating time. More powerful spectroscopic techniques than those used here should be applied to quantify the cross-linking degree and to correlate it with the absorbency values showed by the resulting hydrogels.

CONCLUSIONS

The PVA/PAA system was miscible in the full range of composition, as revealed by DSC studies, and their blends showed a hydrogel behavior. Water retention (absorbency) of these hydrogels was reduced by thermal treatment and their values depended upon both the heating time and the blend composition. Esterification was revealed from infrared spectroscopy in these blends only after a heating time of 6 h. Then, it can be assumed that the cross-linking in these blends is a result of the esterification reaction
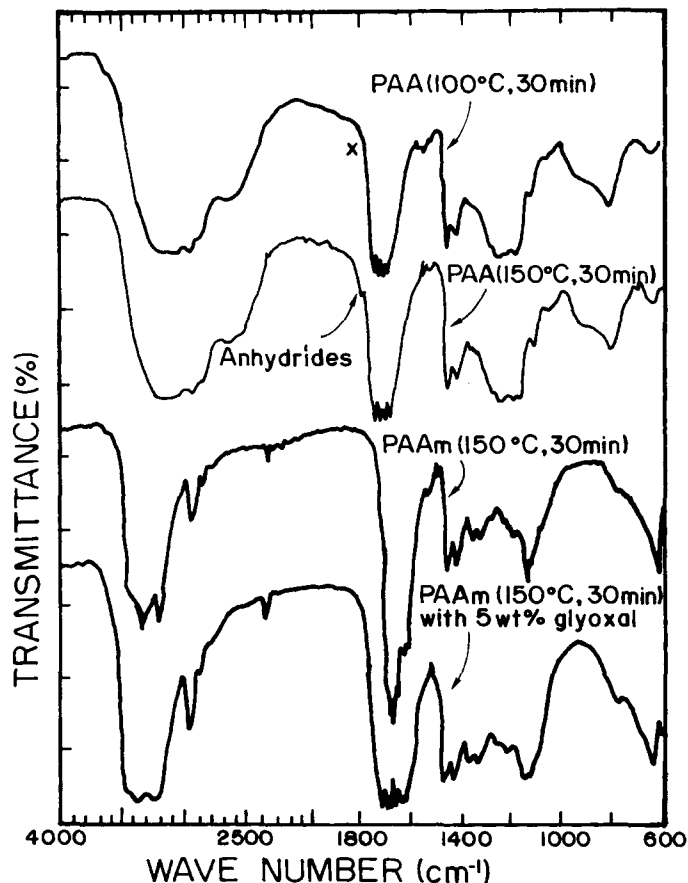
Figure 15   IR spectra for the thermally treated polymer films of PAA and PAAm–70% sodium carboxylate.

between the carboxyl groups of PAA and the hydroxyl groups contained in PVA. The addition of glyoxal in the blends, before their films were cast, increased even more the effect of heating time on the absorbency values. In contrast, PVA/PAAm systems rendered hydrogels only when they had glyoxal as a cross-linking agent. The results obtained by infrared studies on this latter system were not sufficiently clear to address the origin of cross-linking in the hydrogels formed by this system.

The cross-linking degree was estimated for the PVA/PAA hydrogels by using their absorbency values in the Flory–Rehner equation. Based on this calculation, the cross-linking degree was higher the longer the heating time for a given blend composition. Cross-linking degree values were also increased by addition of glyoxal in these blends. This additive improved the thermal stability of PVA/PAA blends.

REFERENCES

1. O. Wichterle, in *Encyclopedia of Polymer Science and Technology*, H. F. Mark, N. G. Gaylord, and N. M. Bikales, Eds., Wiley, New York, 1971, Vol. 15, pp. 273–291.
2. T. Tanaka, in *Encyclopedia of Polymer Science and Engineering*, 2nd ed., H. F. Mark, N. M. Bikales, Ch. G. Overberger, and G. Menges, Eds., Wiley, New York, 1987, Vol. 7, pp. 515–531.
3. G. G. Sonenstein, Ger. Pat. Appl. DE 31 48931 A1 (June 1982).
4. (a) R. Whistler, *Tappi*, **60**, 65 (1977); (b) T. Tanaka, I. Nishio, S. Sun, and S. Ueno-Nishio, *Science*, **218**, 467 (1982); (c) J. Bastide and L. Leibler, *Macromolecules*, **21**, 2647 (1988).
5. (a) J. L. Nieto, J. Baselga, I. Hernández-Fuentes, M. A. Llorente, and I. F. Piérola, *Eur. Polym. J.*, **23**, 551 (1987); (b) J. Baselga, I. Hernández-Fuentes, I. F. Piérola, and M. A. Llorente, *Macromolecules*, **20**, 3060 (1987); (c) T.-P. Hsu and C. Cohen, *Polymer*, **25**, 1419 (1985); (d) J. Baselga, I. Hernández-Fuentes, R. M. Masegosa, and M. A. Llorente, *Polym. J.*, **21**, 467 (1989); (e) P. E. Grimshaw, A. J. Grodzinsky, M. L. Yarmush, and D. M. Yarmush, *Chem. Eng. Sci.*, **44**, 827 (1989), and references cited therein.
6. (a) K. J. Buchanan, B. B. Hird, and T. Letcher, *Polym. Bull. (Berlin)*, **15**, 325 (1986); (b) A. R. Shultz, in *Encyclopedia of Polymer Science and Technology*, H. F. Mark, N. G. Gaylord and N. M. Bikales, Eds., Wiley, New York, 1966, Vol. 4, pp. 350–446.
7. A. H. Clark, R. K. Richardson, S. B. Ross-Murphy, and J. M. Stubbs, *Macromolecules*, **16**, 1367 (1983).
8. C. A. Finch, in *Chemistry and Technology of Water-soluble Polymers*, C. A. Finch, Ed., Plenum Press, New York, 1985, Chap. 5, pp. 81–111.
9. L. R. Miller, in *Encyclopedia of Polymer Science and Technology*, H. F. Mark, N. G. Gaylord, and N. M. Bikales, Eds., Wiley, New York, 1966, Vol. 4, pp. 449–528.
10. R. L. Davidson, *Handbook of Water-Soluble Gums and Resins*, McGraw-Hill, New York, 1980, Chap. 17, p. 8.
11. A. Eisenberg, T. Yokoyama, and E. Sambalido, *J. Polym. Sci. Part A-1*, **7**, 1717 (1969).
12. (a) Z. Reyes, C. E. Rist, and C. R. Russell, *J. Polym. Sci. Part A*, **4**, 1031 (1966); (b) G. F. Fanta and W. M. Doane, in *Modified Starches: Properties and Uses*, O. B. Wurzburg, Ed., CRC Press, Boca Raton, FL, 1986, Chap. 10, pp. 149–178.
13. G. R. Williamson and B. Wright, *J. Polym. Sci. Part A*, **3**, 3885 (1965).
14. B. G. Harper, R. N. Bashaw, and B. L. Atkins, U.S. Pat. 3,810,468 (1974).
15. P. J. Flory, *Macromolecules*, **15**, 99 (1982).
16. J. March, *Advanced Organic Chemistry*, 3rd. Ed., Wiley, New York, 1985, p. 798.
17. P. J. Flory and J. Rehner, *J. Chem. Phys.*, **11**, 521 (1943).
18. Z. S. Petrovic, W. J. MacKnight, R. Koningsveld, and K. Dusek, *Macromolecules*, **20**, 1088 (1987).
19. S. Krause, in *Polymer Blends*, S. Newman and D. R. Paul, Eds., Academic Press, New York, 1978, Vol. I, pp. 15–41.
20. D. W. Van Krevelen, *Properties of Polymers: Their Estimation and Correlation with Chemical Structure*, Elsevier, Amsterdam, 1980, pp. 51–78.
21. J. J. Maurer, D. J. Eustace, and C. T. Ratcliff, *Macromolecules*, **20**, 196 (1987).
22. O. Olabisi, L. M. Robeson, and M. T. Shaw, *Polymer-Polymer Miscibility*, Academic Press, New York, 1979, pp. 117–189.
23. J. G. Pritchard, *Poly(vinyl alcohol): Basic Properties and Uses*, Gordon and Breach. London, 1970.
24. B. Wunderlich and H. Baur, *Adv. Polym. Sci.*, **7**, 151 (1970).
25. L. Daniliuc, C. Dekesel, and C. David, *Eur. Polym. J.*, **28**(11), 1365 (1992).