Poly(vinyl alcohol) Modified with Carboxylic Acid Anhydrides: Crosslinking Through Carboxylic Groups

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ABSTRACT: The reaction of carboxylic acid anhydride with poly(vinyl alcohol)(PVA) leads to vinyl alcohol–vinyl ester copolymers which contain carboxylic acid groups. Esterification enables degrees of modification to be reached which depend on the chemical structure of the anhydride introduced and the ratio of the reagents in the feed. The copolymers obtained were characterized by spectroscopic techniques, elemental analysis, and thermal methods. These half-esters reacted in a second step with aromatic diglycidyl ethers to obtain tridimensional networks. This crosslinking reaction through the carboxylic groups was studied by differential scanning calorimetry. The water absorption of the linear and crosslinked polymers was determined gravimetrically as a function of time at room temperature. © 1997 John Wiley & Sons, Inc. J Appl Polym Sci **65:** 1643–1651, 1997

Key words: poly(vinyl alcohol); crosslinking

INTRODUCTION

The modification of conventional organic polymers is an important technique in the preparation of new materials with improved properties. Poly-(vinyl alcohol)(PVA) is useful in practical investigations of functional polymers because it can be easily modified through its hydroxylic groups. The chemistry of PVA is largely concerned with ester formation by reaction with acid chlorides or acid anhydrides. When anhydride is a cycle, a carboxylic group is incorporated into the resulting polymer. These PVAs which contain different numbers of carboxylic groups are of great interest to the paper industry, as modifiers of thermosetting resins, in plywood manufacture, and as pressure-sensitive adhesives.[1]

Moreover, those polymers containing carboxyl groups can react with difunctional compounds in a further step, leading to a tridimensional network. The use of PVA as a membrane has been intensively studied because of its film-forming, highly hydrophilic, and chemical-resistant properties. Membrane selectivity can, in general, be increased by modifying the chemical structure of polymers by crosslinking, grafting, etc.

Along the same lines, the preparation of crosslinked PVA derivatives have been reported[2,3] by reacting their hydroxylic groups with dianhydrides and diisocyanates. The aim of this work was to obtain networks with longer chains between crosslinks. So, PVA first reacted with two cyclic anhydrides (phthalic and succinic anhydrides) which enabled a carboxylic group to be introduced into the side chain, not directly attached to the main chain but by means of either an aromatic or aliphatic spacer. These half-esters reacted in a second step with the aromatic diglyci-

dyl ethers 4,4′-diphenyldiglycidyl ether, 4,4′-thiodiphenyldiglycidyl ether, and 4,4′-oxydiphenyldiglycidyl ether which led to crosslinking.

Similar half-esters have been reported[4] using ethylene–vinyl alcohol copolymers (with a low alcohol content) and low conversions in the cure of epoxy resins (derivatives of bisphenol A). Analogous PVA reactions increase the number of carboxylic groups and therefore the final network has a greater density of crosslinking. Moreover, depending on the amount of both anhydride and hardener used, different degrees of crosslinking can be obtained, giving materials with different polarities due to the remaining carboxylic and hydroxylic groups.

In this study, modified PVA containing several carboxylic groups was obtained by using different ratios of phthalic and succinic anhydrides. The modification degree of the synthesized linear polymers was determined by elemental analysis and ^{1}H-NMR. Polymers were characterized by spectroscopic techniques and their thermal properties were studied by DSC and TGA.

Crosslinking reactions were carried out on polymers with a high degree of modification using the above-mentioned hardeners. Thermal characterization of the resulting products was studied by DSC and TGA and their capacity to absorb water was evaluated at room temperature.

EXPERIMENTAL

Materials

Poly(vinyl alcohol) (PVA; Fluka) had a degree of hydrolysis of 86–89% and a degree of polymerization of 300. Phthalic anhydride (Fluka) and succinic anhydride (Fluka) were purified by recrystallization. Pyridine (Panreac), 4-dimethylaminopyridine (DMAP; Fluka), benzyltrimethylammonium chloride (BTMA; Aldrich), tetrahydrofuran (THF; SDS), and dimethyl sulfoxide (DMSO; SDS) were used as received. 4,4′-Diphenyldiglycidyl ether (A), 4,4′-thiodiphenyldiglycidyl ether (B), and 4,4′-oxydiphenyldiglycidyl ether (C) were synthesized as previously reported.[5]

Esterification Reaction

PVA (0.05M of hydroxyl group) was dissolved by stirring in DMSO (25 mL) and heating to 60–80°C. Different ratios of carboxylic anhydride (OH/acyl group 1/2, 1/1, and 1/0.50) and pyridine (0.05M) were added at room temperature. The reaction was then stirred for 5 days at room temperature. The polymer was obtained by precipitation into distilled water/HCl. The reaction product was purified by reprecipitating three times from THF into water and then dried *in vacuo* at 50°C.

Crosslinking with Diglycidyl Ether Compounds

The polymer (4 mmol of acid group) was dissolved in the minimum amount of DMSO (10 mL) and both BTMA (20 mol %) and DMAP (10 mol %) were added at room temperature. The diglycidyl ether compound was slowly added. The reaction was then stirred for as long as possible (3–10
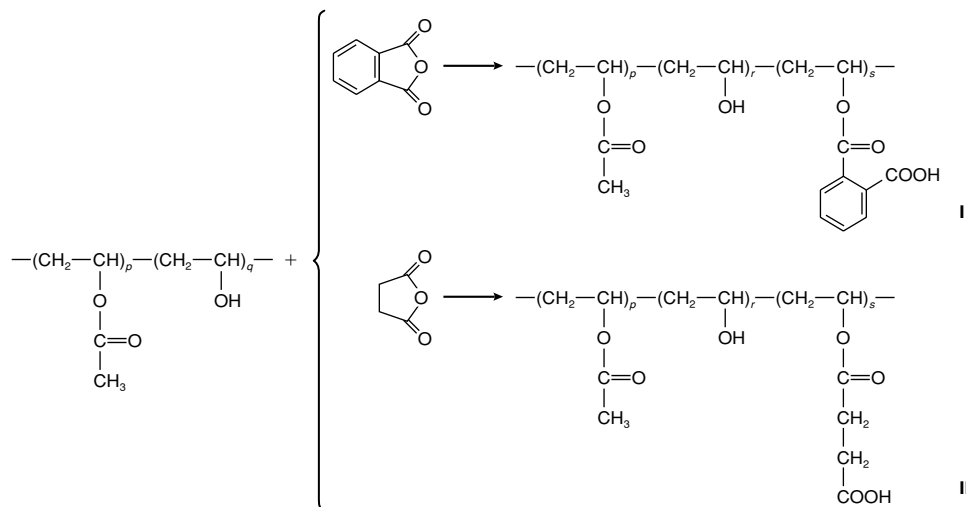
Scheme I   Esterification reaction of PVA with phthalic anhydride (**I**) and with succinic anhydride (**II**).

Table I   Characterization of Vinyl Alcohol–Vinylphthalate (I) and Vinyl Alcohol–Vinylsuccinate (II) Copolymers

	Polymer					
	Ia	**Ib**	**Ic**	**IIa**	**IIb**	**IIc**
Ratio OH/anhydride	1/2	1/1	1/0.5	1/2	1/1	1/0.5
Elemental analysis (%)						
C	62.02	61.03	57.51	51.88	51.53	52.05
H	4.81	4.94	6.75	6.39	6.42	6.85
Degree of substitution (%)[a]	72	54	13	50	47	34
Yield (%)[b]	89	78	22	86	69	23
T_g (°C)[c]	71	53	48	29	32	59
Inherent viscosity (g/dL)						
(NMP, 30°C)	0.49	0.46	0.35	0.23	0.24	0.31

[a] Calculated from [1]NMR and elemental analysis.
[b] Calculated taking into account the degree of substitution.
[c] Obtained by DSC at 20°C/min.

days). The polymers were repeatedly washed with water, filtered, and washed with THF. The filtered products were dried with phosphorus pentoxide under a vacuum for 2 days and then *in vacuo* at 50°C.

Water-absorption Measurements

The dynamic absorption water measurements of the samples were determined by the gravimetric method. A polymer sample of 15–20 mg was

Table II   ^{1}H- and ^{13}C-NMR Spectroscopic Data for Vinyl Alcohol–Vinylphthalate (I) and Vinyl Alcohol–Vinylsuccinate (II) Copolymer

^{1}H-NMR Data		^{13}C-NMR Data	
Resonances	Assignment	Resonances	Assignment
1.1–1.9	a, a′, a″	20	e
2.3	e	29.8	l, m
2.6	l, m	39.1–39.8	a, a′, a″
3.5–4.8	b, b′, c	66.2–68.9	b, b′, b″
5–5.4	b″	139–142	g, h, i, j
11.5	n	167.5	f
12	k	169	k
		170	d
		172	n
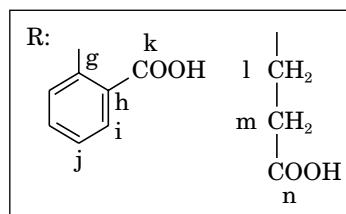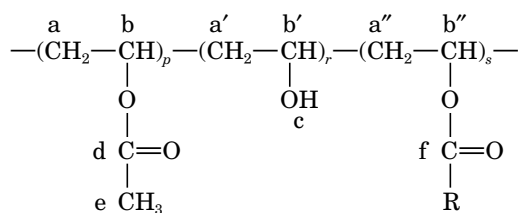
placed in a desiccator over P_2O_5 for 36 h to establish constant weight. The sample was accurately weighed and then placed in a closed chamber containing a saturated aqueous solution of potassium nitrate which provided a relative humidity of 93% (16 mmHg water-vapor pressure in the atmosphere). The experiments were carried out at room temperature (25°C). The samples were weighed at different time intervals and until the hydrated weight reached a constant value. Absorbency was calculated as grams of water per gram of dry polymer.

Instrumentation

^{1}H- and ^{13}C-NMR spectra were obtained using a Gemini 300 spectrometer with DMSO-d_6 as the solvent. IR spectra were recorded on a MIDAC GRAMS/386 FTIR spectrometer. Elemental analyses were carried out using a Carlo Erba 1106 device. Inherent viscosities (η_{inh}) were measured in 1-methyl-2-pyrrolidone (NMP) solutions (ca. 2 g/L) at 30°C on a Schott-Geräte AVS 310 viscosimeter. T_g data were evaluated on a Metler DSC-30 thermal analyzer, using modified PVA samples of known weight (ca. 5 mg) in covered aluminum pans under a nitrogen atmosphere at a heating rate of 20°C/min. Thermogravimetric analyses were carried out with a Perkin-Elmer TGA-7 system in N_2 at a heating rate of 20°C/min.

The equilibrium absorption of water was measured at room temperature for all the samples using an electronic microbalance (Mettler AB204) with an accuracy of $\pm 10^{-4}$ g. Reported values of equilibrium water uptake are averaged over nine measurements, and for each type of sample, water absorption was replicated three times.

RESULTS AND DISCUSSION

Esterification Reaction

PVA was esterified with anhydrides (Scheme I) in a homogeneous medium by solution in DMSO in the presence of pyridine and using different amounts of anhydride. Polymers were precipitated in water acidified with HCl. To fix the reaction time, several samples were taken out and their solubility tested in the precipitation mixture. Times of 4–5 days were necessary in all cases to obtain a considerable precipitate.

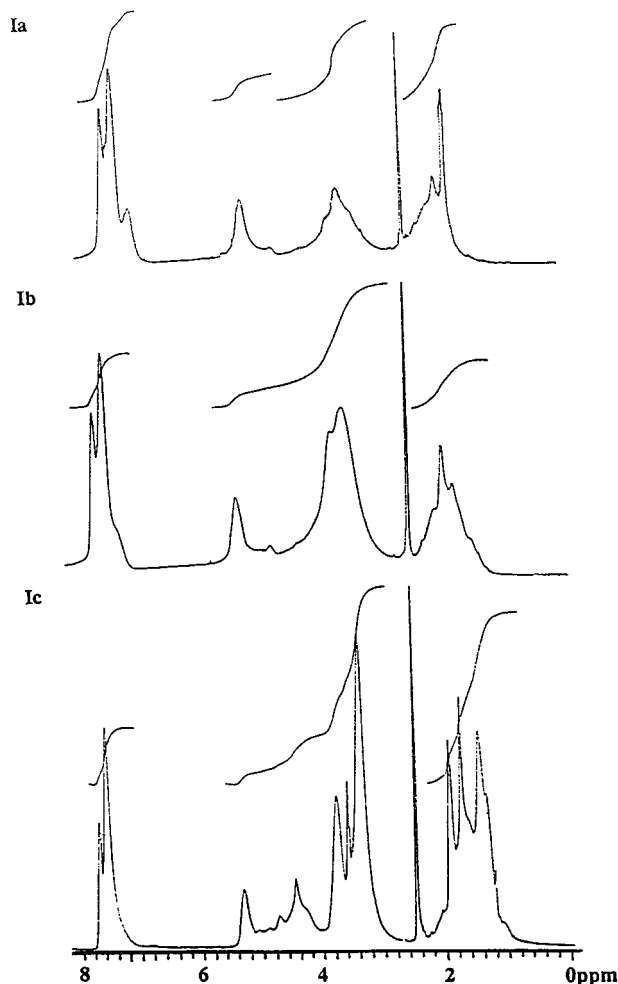Table I summarizes some characteristics of these half-esters. The polymers with a higher de-

Figure 1 ^{1}H-NMR of vinyl alcohol–vinylphthalate copolymer (**I**): (**Ia**) OH/anhydride 1/2; (**Ib**) OH/anhydride 1/1; (**Ic**) OH/anhydride 1/0.5 in DMSO-d_6.

gree of esterification were more easily isolated. Yields, calculated by taking into account the degree of modification reached, increased with the modification, probably due to greater insolubility in the precipitation mixture. The degree of substitution was calculated by elemental analysis and ^{1}H-NMR spectra and both results were very close. Although this degree was higher when the OH/anhydride ratio was 1/2, it did not coincide with the ratio of the reactives in the feed. The degree of substitution was only higher than 50% when the OH/phthalic anhydride ratio was 1/2 and 1/1. The partial esterification was confirmed by IR spectroscopy, since in all cases, characteristic bands about 3200–2400 cm^{-1} (COOH st) and 3340 cm^{-1} (OH st) were observed.

Table II summarizes the NMR data of the two series of copolymers. Figure 1 shows partial ^{1}H-
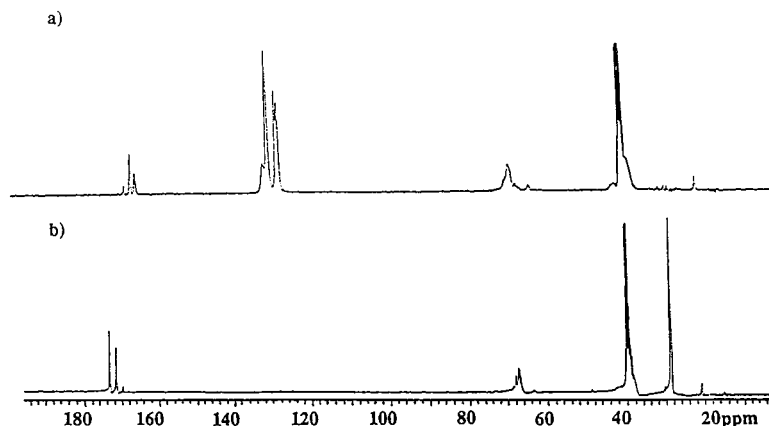
Figure 2 ^{13}C-NMR of (a) vinyl alcohol–vinylphthalate copolymer and (b) vinyl alcohol–vinylsuccinate copolymer in DMSO-d_6.

NMR spectra of copolymers **Ia–c** in which differences can be observed depending on the degree of substitution. Signals caused by the methylene units appear between 1.1 and 1.9 ppm. The signal centered at 1.3 ppm which is assignable to the methylene of the dyad sequence VOH, VOH [VOH = —CH(OH)—CH$_2$—CH(OH)—] (Ref. 6) diminishes and shifts downfield, overlapping with the initial dyads VOH, VA[VA = —CH(OAc)—CH$_2$—CH(OH)—] when esterification increases. A methine signal corresponding to the VOH, VA sequences appears around 3.5 ppm, whereas the signal corresponding to the VOH, VOH methine sequences appears centered at 3.8 ppm. Hydroxyl group signals appear between 4 and 5 ppm and a methine signal corresponding to the VE, VE [VE = —CH(OCOR)—CH$_2$—CH (OCOR)—] sequences appears around 5.4 ppm. All signals in the interval 3.5–5.4 ppm shift downfield after modification. In addition, the aromatic proton signals at 7–8 ppm and a broad band centered at 11.5 ppm due to the carboxylic proton were observed. Copolymers of vinyl alcohol–vinylsuccinate showed analogous variations in the signals depending on the esterification degree.

In the corresponding ^{13}C-NMR spectra, expected variations,[7,8] methine downfield and methylene upfield shifts, were observed according to the degree of modification. Figure 2 shows spectra of the more modified polymers of the two series as an example. As can be seen, there are three different carbonyl signals which correspond to the initial acetate, the newly formed ester, and the free acid groups.

Data on the inherent viscosity and the glass transition temperature (T_g) were determined and are summarized in Table I. The PVA hydroxyl groups are highly interconnected by hydrogen bonding which contributes to a high T_g (46°C in the initial PVA). The introduction of other functional groups breaks this bonding and the resulting T_g value is affected by both the degree of modification and the character of the substituent. So, in the case of vinyl alcohol–vinylphthalate copolymers, the T_g value increased with the number of phthalate groups according to the rigidity introduced, whereas in vinyl alcohol–vinylsuccinate copolymers, the opposite occurred since flexible moieties were introduced in these cases.

The thermal stability of all half-esters was evaluated by thermogravimetric analysis (TGA). Results are summarized in Table III. T_i, $T_{10\%}$, and T_{max} are higher in succinate derivatives and slightly decrease in both series when the carboxylic group content increases. This may be due to a degradation initiated by decarboxylation which is more likely in an aromatic acid.

Crosslinking Reaction

To obtain crosslinked polymers, three diglycidyl ether compounds of different rigidity and reactivity were used to react with copolymers **Ia** and **IIa**. Diglycidyl compounds react with the free acid group present in the modified PVA, giving a network with different polar groups, as is shown in Scheme II.

Reactions were carried out in DMSO at room temperature, using BTMA and DMAP as catalysts. The reaction mixture was stirred until a bulk was formed. Products were insoluble in all solvents tested, which confirmed that crosslinking

Table III   TGA Data of Vinyl Alcohol–Vinylphthalate (I) and Vinyl Alcohol–Vinylsuccinate (II)[a] Copolymers
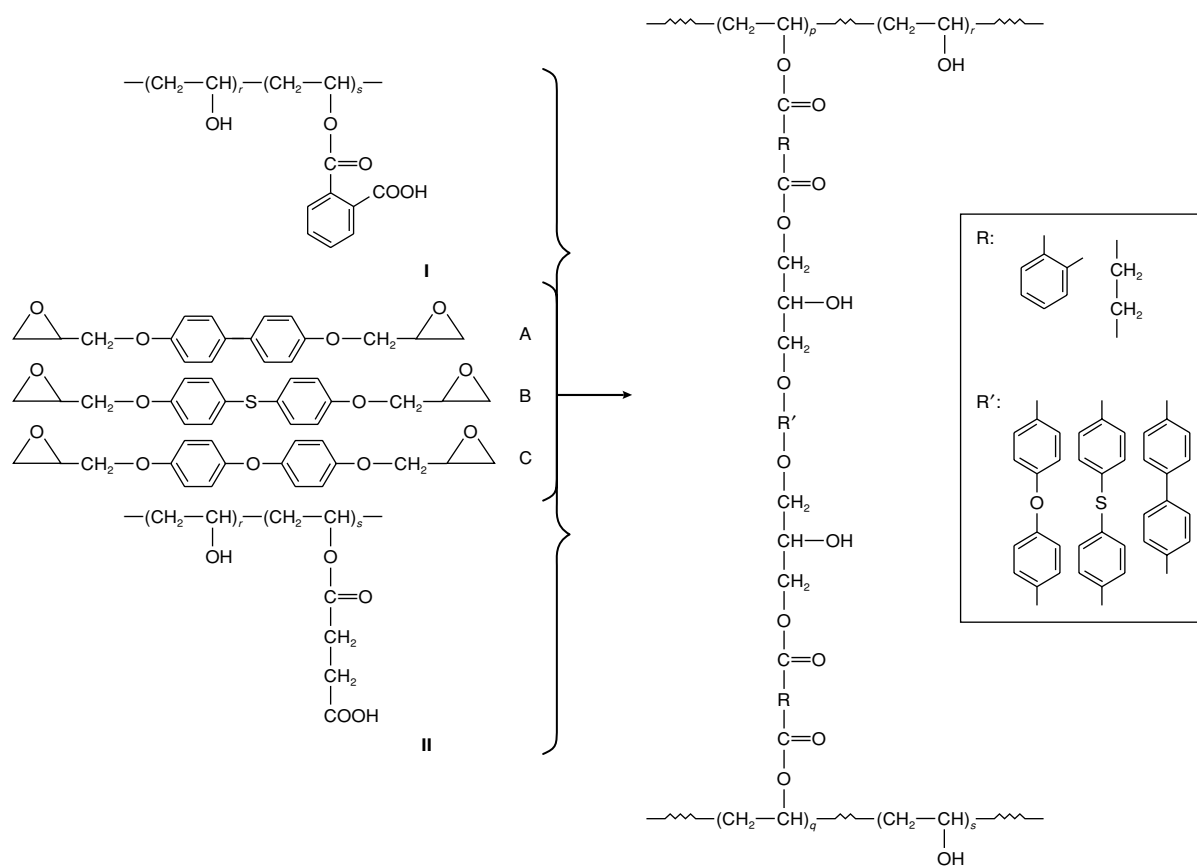
	Polymer					
	Ia	**Ib**	**Ic**	**IIa**	**IIb**	**IIc**
T_i (°C)	215	232	240	281	279	270
$T_{10\%}$ (°C)	242	246	269	297	300	306
T_{max} (°C)	259	267	287	334	337	367
dW/dt (%/min)	15	13	15	16	18	16
$T_{500°C}$ (%)	11	3	2	10	9	7

[a] Obtained at 20°C/min.

had occurred. Networks derived from vinylsuccinate copolymers showed a greater capacity for swelling in DMSO, NMP, and water than did the networks derived from vinylphthalate. No significant differences were observed when the diglycidyl compound was used as a hardener.

Gels in DMSO from vinyl alcohol–vinylsuccinate copolymers were obtained and were suitable for recording ^{13}C-NMR spectra. In spite of the poor resolution of these spectra, the more significant signals were recognized. So, aromatic carbons from the hardener appeared in the zone between 140 and 118 ppm, and methylene carbons of succinate moiety were centered at 30 ppm, and carbonylic carbons, between 178 and 168 ppm. All signals were broad as a result of the different envi-

Scheme II   Crosslinking reaction of copolymers (**I**) and (**II**) with diglicidyls A, B, and C.

Table IV T_g Data[a] and TGA Data[b] of Vinyl Alcohol–Vinylphthalate (I) and Vinyl Alcohol–Vinylsuccinate (II) Copolymers Crosslinked with Diglycidyl Compounds A, B, and C

	Polymer					
	IA	**IB**	**IC**	**IIA**	**IIB**	**IIC**
T_g (°C)[a]	121	134	130	98	62	82
ΔT_g (°C)	+58	+81	+77	+66	+30	+50
T_i (°C)[b]	225	222	219	318	272	266
$T_{10\%}$ (°C)[b]	264	260	259	355	292	278
T_{max} (°C)[b]	409	408	401	396	373	402
dW/dt (%/min)[b]	12	11	13	15	16	12
$Y_{500°C}$ (%)[b]	15	16	13	18	9	10

[a] Obtained by DSC at 20°C/min.
[b] Obtained by TGA at 20°C/min.

ronments that functional groups undergo in the network.

Table IV summarizes the thermal parameters of all crosslinked polymers. These data can be compared if the two series are considered separately since the degree of modification of the polymer precursor in each series is different. The T_g values for series I can be seen to be higher either because of the higher number of crosslinkable sites or the presence of aromatic rings in the starting polymer. However, increases in T_g's are difficult to rationalize since the differences may be due to either the degree of crosslinking reached or the hardener used in each case. Of the other values, it need only be pointed out that the in-

crease in T_{max} after crosslinking is greater in the phthalate series (see Tables III and IV).

Finally, it seems interesting to evaluate the ability of crosslinked PVA derivatives and linear polymer precursors to absorb water, which has been compared to that of starting PVA. The formation of modified linear or crosslinked polymers involves a decrease in hydroxyl groups and the introduction of units of different hydrophilicity. Therefore, lower absorption of water must be expected.

The water absorption of the polymer sample was determined gravimetrically as a function of time. Figure 3 shows PVA and linear polymer data and confirms that PVA has a higher water absorption capacity at room temperature, whereas the vinyl
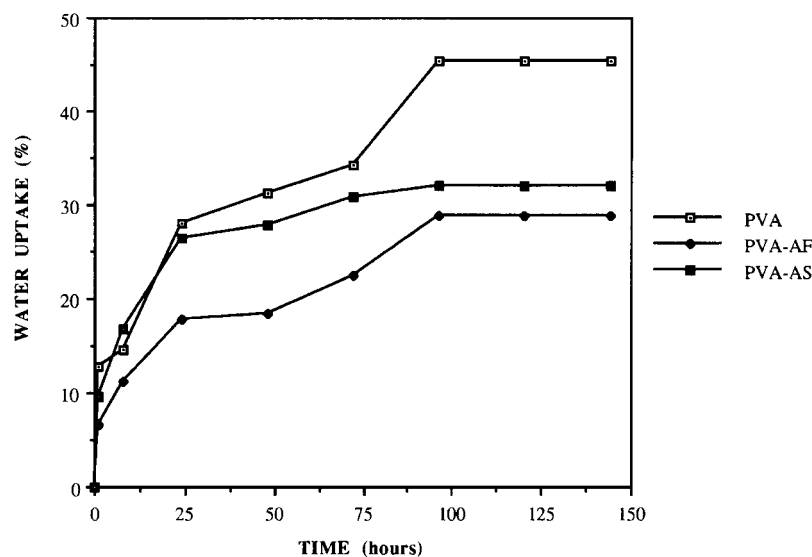

Figure 3   Water uptake as a function of time for PVA, vinyl alcohol–vinylphthalate copolymer (PVA–AF) and vinyl alcohol–vinylsuccinate copolymer (PVA–AS).
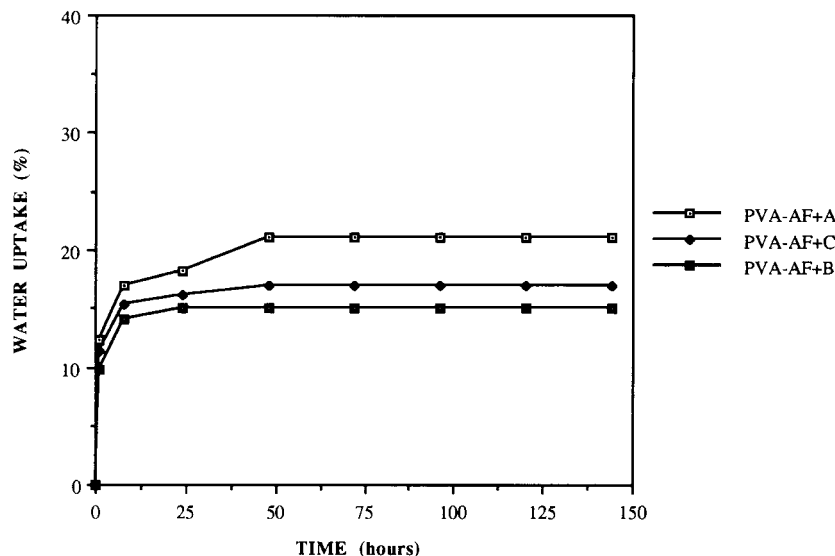
Figure 4   Water uptake as a function of time for vinyl alcohol–vinylphthalate copolymer (PVA–AF) crosslinked with diglycidyl ethers A, B, and C.

alcohol–vinylphthalate copolymer (72% of carboxylic groups) shows lower absorption than does the vinyl alcohol–vinylsuccinate copolymer (50% of carboxylic groups). It was confirmed that the weight of all the samples was saturated after 96 h, and so this value was used as the equilibrium value.

Figures 4 and 5 show plots of the crosslinked vinyl alcohol–vinylsuccinate copolymer and vinyl alcohol–vinylphthalate copolymer, respectively. As can be seen, succinate derivatives have, in general, a higher water uptake than that of the phthalates. However, although the degree of water absorption is affected by the hardener, a clear relation between these hardeners and the water uptake has not been found since different hardener effects occur in each series. The first stage of water absorption was complete after 8 h, but at least 48 h of exposure was necessary to establish the equilibrium value. So, all the samples reached an equilibrium state within 48 h.
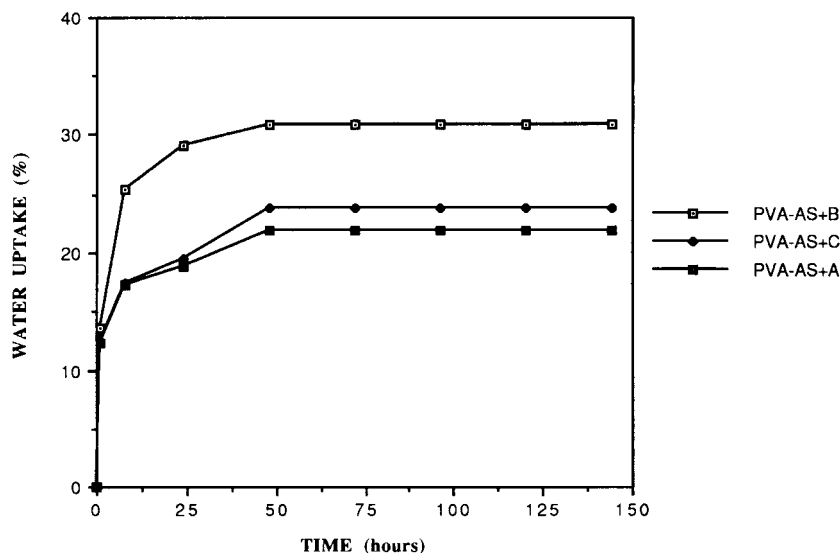
The equilibrium water-uptake percentage as a

Figure 5   Water uptake as a function of time for vinyl alcohol–vinylsuccinate copolymer (PVA–AS) crosslinked with diglycidyl ethers A, B, and C.
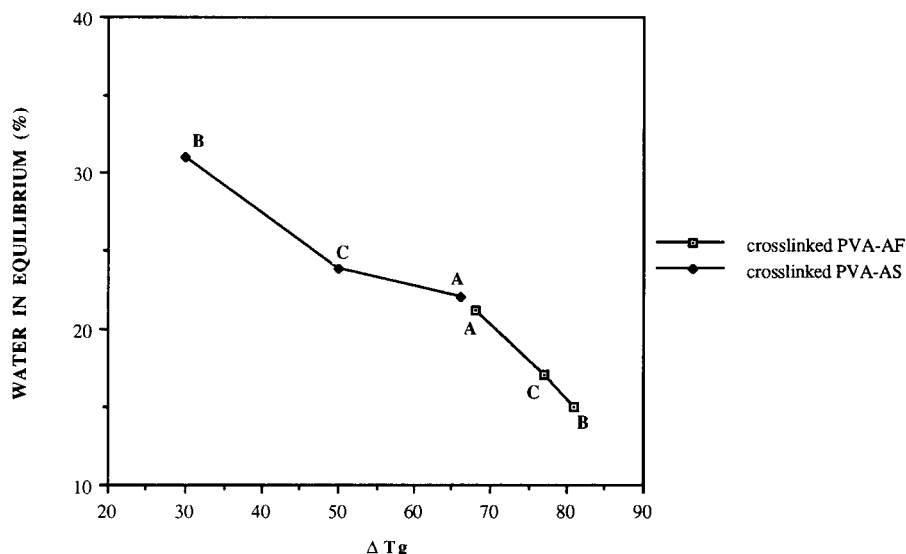
Figure 6 Water in equilibrium as a function of the increase in T_g for vinyl alcohol–vinylphthalate (PVA–AF) and vinyl alcohol–vinylsuccinate (PVA–AS) copolymers crosslinked with diglycidyl ethers A, B, and C.

function of the increase in T_g after crosslinking is shown in Figure 6. As can be seen, in the case of crosslinked vinyl alcohol–vinylphthalate copolymers, in which crosslinking has progressed to a greater extent than for vinyl alcohol–vinylsuccinate copolymers, water absorption is lower for all hardeners tested.

Linear polymers have a great capacity for absorption. By comparing this absorption of crosslinked polymers with that of corresponding linear precursors, a greater difference is observed in the case of phthalate derivatives than in the succinates. This can be explained by the greater crosslinking in these polymers, which makes it difficult for the water molecules to have access to the polar sites.

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