Crosslinking of Poly(vinyl alcohol) Using Dianhydrides as Hardeners

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SYNOPSIS

The crosslinking reaction of poly(vinyl alcohol) (PVA) with 3,3',4,4'-tetracarboxybenzophenone dianhydride, pyromellitic carboxylic acid anhydride, and Epiclon B-4400 as hardeners was studied either in solution or by differential scanning calorimetry. A catalyst agent had to be used in all cases. Depending on the concentration of hardener and catalyst, differences are observed. T_g values increase with the ratio of hardener and catalyst, while activation energies decrease with the amount of catalyst but little changes can be seen when different dianhydride amounts are used. The thermal properties of the final products were unaltered by the hardener used. The decomposition temperature is initiated at a similar temperature in linear and crosslinked PVA, but while uncured PVA undergoes a complete degradation in one step, crosslinked PVA degrades in several steps. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

Poly(vinyl alcohol) (PVA) is one of the few completely biodegradable synthetic polymers and so can be potentially useful for releasing biological and medical material in a controlled way. Moreover, PVA has been intensively studied as a membrane in various ways 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.

As is known, several crosslinking methods have been published in the literature for different uses, since as a rule, all multifunctional compounds capable of reacting with hydroxyl groups can be used. Thus, recently, the crosslinking of PVA with dialdehydes[1-3] or dicarboxylic acids[4,5] has been used in fiber manufacture or for membrane applications, among others. However, no references have been found for the crosslinking of PVA with hardeners such as carboxylic acid dianhydrides which have been widely used with other hydroxylic compounds (for instance, epoxy resins) to obtain tridimensional polymers. So, we recently studied the crosslinking of a epoxy prepolymer containing hydroxylic pendant groups with Epiclon B as a hardener[6] and the results obtained encouraged us to test this dianhydride among others with PVA. So, the aim of the present work was to study the crosslinking of PVA with several dianhydrides leading to networks containing polar groups which allow an interaction with polar solvents.

EXPERIMENTAL

Materials

Poly(vinyl alcohol) (PVA) (Fluka) had a degree of hydrolysis of 86–89% and a degree of polymerization of 300. 3,3',4,4'-Tetracarboxybenzophenone dianhydride (Aldrich) (A), pyromellitic carboxylic acid anhydride (Fluka) (B), and Epiclon B-4400 (MERCK-Schuchardt) (C) were purified by recrystallization in acetic anhydride. Dimethyl sulfoxide (DMSO) (Panreac) and pyridine (Panreac) were used without previous purification. 4-Dimethylaminopyridine (DMAP) (Fluka) was used as received.

Crosslinking in Solution

PVA ($0.02M$) was dissolved by stirring in DMSO (20 mL). The dianhydride in different ratios (OH/anhydride group 1/1, 1/0.75, 1/0.5, and 1/0.25) and DMAP (20 parts per hundred of resin [phr]) were dissolved in pyridine (20 mL). This solution was added to the PVA solution at room temperature. An increase in the viscosity of the mixture was observed after approximately 1 h and the reaction continued as long as stirring was possible. The polymers were repeatedly washed with water. The filtered products were dried with phosphorus pentoxide under vacuum for 1 week and then at 50°C under vacuum for 96 h. The polymers obtained were insoluble solids but could be swollen in polar solvents, such as water, DMSO, and NMP.

Crosslinking by DSC

PVA was mixed at room temperature with the dianhydride and DMAP previously dissolved in dichloromethane to obtain an homogeneous sample. Dichloromethane was evaporated and the sample was dried at 50°C under vacuum for 24 h. The corresponding dianhydride was used in a 1 : 1 equivalent ratio and dianhydride C was also used in different ratios (OH/anhydride group 1/1, 1/0.75, 1/0.5, 1/0.4, and 1/0.25). The DMAP concentrations used were 0.5, 1, 5, 20, and 30 parts per hundred of resin (phr). Approximately 5 mg samples of the mixture were weighed accurately in an aluminum DSC sample pan.

Instrumentation

^{1}H- and ^{13}C-NMR spectra were obtained using a Gemini 300 spectrometer with DMSO-d_6 as the solvent and TMS as the internal standard. IR spectra were recorded on an MIDAC GRAMS/386 FTIR spectrometer or on a Nicolet 5ZDX FTIR spectrometer.

Calorimetric studies were carried out on a Mettler DSC-30 thermal analyzer in covered Al pans under N_2, at various heating rates (5–20°C/min). Samples of known weight (about 5 mg) of unmodified PVA or the PVA mixture with the suitable amount of hardener were put in an aluminium pan. T_g and the enthalpy of curing were tested in dynamic experiments. Thermogravimetric analyses were carried out with a Perkin-Elmer TGA-7 system in N_2 at a heating rate of 20°C/min.

RESULTS AND DISCUSSION

Curing PVA with Dianhydrides as Hardeners

The crosslinking mechanism involves the ring opening of the anhydride by means of a nucleophilic agent. The fact that there is a large number of hydroxylic groups in the PVA seems, in principle, to favor this reaction. When the hydroxylic group reacts with the anhydride, an ester is formed, leaving a free carboxylic acid in the network which could react in a subsequent step. This latter reaction requires a higher activation energy, so the use of a dianhydride helps the curing reaction to go through
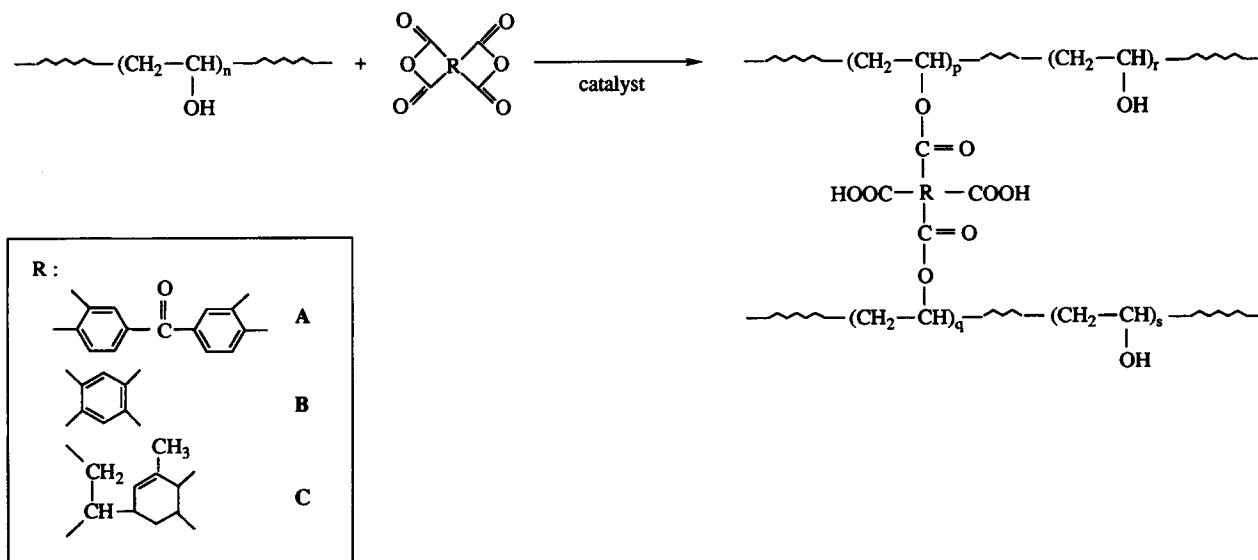
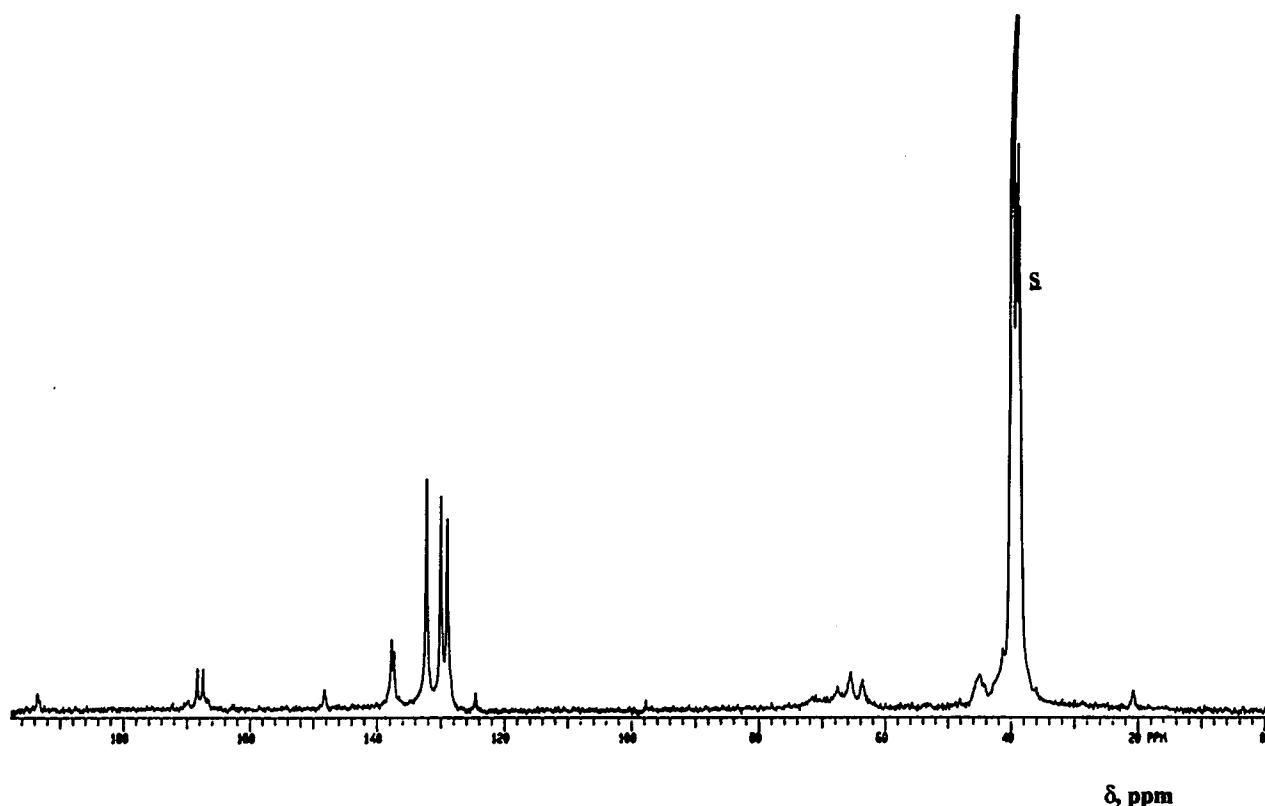**Scheme 1**   Crosslinking PVA with carboxylic acid dianhydrides.

Figure 1 ^{13}C-NMR of PVA crosslinked with dianhydride A as hardener (OH/anhydride 1/1) and DMAP as catalyst (20 phr) in DMSO-d_6.

the most reactive anhydride groups. Therefore, our first experiments were carried out without a catalyst and using three different commercial dianhydrides: 3,3′,4,4′-tetracarboxybenzophenone dianhydride (A) and pyromellitic carboxylic acid anhydride (B), both widely used as hardeners in the obtention of thermosets, and Epiclon B-4400 (C), an unsymmetrical dianhydride whose lower melting point may be advantageous in the curing process (Scheme 1).

Two series of experiments were carried out parallelly, and the crosslinking was followed either by DSC or by spectroscopic techniques. Using DSC, it was observed that a catalyst was needed for the reaction to progress. Therefore, DMAP was always used as a catalyst.

Crosslinking PVA in Solution

PVA (88% hydrolized) was crosslinked in a solution of DMSO/pyridine 1/1 (v/v) using different ratios of dianhydrides (OH/anhydride group 1/1, 1/0.75, 1/0.5, and 1/0.25). Pyridine in this case acts as a catalyst and additional amounts of DMAP did not cause a significant increase in the reaction rate.

Several reaction temperatures were tested but he best results were obtained at room temperature.

The IR spectra of these compounds show OH stretching in all cases, indicating that only a partial curing was achieved even when the stoichiometric ratio was used. Moreover, a significant absorption at about 3500–2500 cm^{-1} due to carboxylic acid is observed. The carbonyl region shows several absorbances due to ester, acid, and probably unreacted anhydride groups. Characteristic bands due to the different dianhydride moieties incorporated in the network are also observed.

^{1}H-NMR spectra were recorded but their poor resolution only shows us that the methylene and methine protons of the unmodified PVA main chain which appear at 1.2–1.8 and 3.6–4.0 ppm, respectively,[7] are affected by interaction between the substituents and are shifted downfield when esterification takes place.[8,9] Moreover, the signals corresponding to the anhydride introduced are also observed.

The PVA modification can be seen in the ^{13}C-NMR spectra: Methylene and methine carbons are split, and while the former is shifted upfield, the

Table I   Tg Data of PVA Crosslinked with Carboxylic Acid Dianhydrides[a]

	Ratio OH/Dianhydride			
	1/1	1/0.75	1/0.50	1/0.25
A	52.8	39.6	26.9	19.6
B	64.0	40.1	27.5	19.8
C	73.2	50.7	31.8	19.9

[a] Obtained at 20°C/min.

latter goes downfield in a similar way to acetylated PVA.[10] Figure 1 shows the PVA crosslinked with the dianhydride A spectrum. At around 20 ppm, the methyl carbon resonance of the acetate groups present can be seen. Because of the presence of these acetate groups, a small resonance due to methylene flanked by an acetyl is expected around 40–43 ppm,[11] but in the spectrum, it appears overlapped with the new esterified methylene carbons. Moreover, in this zone, the unmodified PVA methylene appears, which confirms that it is only partially esterified. Between 60 and 72 ppm, the broad resonances are assigned to the different methine carbons, and in spite of their low resolution, it seems that the three resonances upfield may be attributable to isotactic, heterotactic, and sindiotactic triads, ascending from low to high fields, of split methine resonances flanked by the hydroxylic group.[8] The methine linked to ester groups appears downfield and probably overlaps with the above signal. All the resonances between 124 and 158 ppm correspond to the two aromatic rings of the substituent introduced. The lines at 165–167 ppm can be assigned to the carbonyl groups of the ester linkage and the probably free carboxylic acid. The low-intensity resonance of the acetate group C=O can also be seen at around 170 ppm. Finally,

the ketonic C=O of the dianhydride A appears at 192 ppm. All the spectra of the polymers modified with anhydrides B and C showed analogous signals and only the hardener resonances varied.

T_g is a sensitive and practical parameter for assessing the crosslinking of thermosetting systems, since T_g values increase as the process continues. Therefore, T_g values for the polymers cured with different PVA/dianhydride ratios were obtained. The data are listed in Table I. It can be seen in all cases that the higher the percentage of hardener the higher the T_g values, which confirms the increase in crosslinking. However, in comparison with unmodified PVA with T_g = 46°C, only the most crosslinked have a greater T_g, which can be explained by the high rigidity of PVA due to the large amount of hydrogen bonding. Introducing substituents makes these interactions less likely and only when the percentage of modification is high enough is the loss of hydrogen bonding compensated.

The thermal analysis data obtained by TGA are summarized in Table II. Decomposition temperatures (T_i, onset of the curve weight loss vs. temperature) are not greatly dependent on the chemical structure of the hardener used. However, the increase in the percentage of this hardener has an appreciable influence, especially when the PVA/dianhydride ratio is increased from 1/0.25 to 1/0.5 or 1/0.75. The recorded thermogravimetric plots for all samples show two degradation steps, suggesting the coexistence of more than one degradation process. The maximum weight loss temperatures (T_{max}) for both steps and the rate of weight loss at these temperatures (dW/dt), obtained from the differential thermogravimetric traces (DTG), are also summarized in Table II. Although in this table the maximum weight loss is observed above 340°C in all cases, a second weight loss also occurs about

Table II   Thermogravimetric Data of PVA Crosslinked with Carboxylic Acid Dianhydrides[a]

	Dianhydride Ratio (OH/anh)											
	A				B				C			
	1/1	1/0.75	1/0.50	1/0.25	1/1	1/0.75	1/0.50	1/0.25	1/1	1/0.75	1/0.50	1/0.25
T_i (°C)	250	268	219	138	233	230	222	161	215	281	175	164
$T_{10\%}$ (°C)	277	297	246	184	262	254	252	244	279	312	247	232
T_{max} (°C)	343	363	340	334	340	334	330	325	349	371	346	338
dW/dt (%/min)	9	8	7	6	15	13	12	12	8	11	10	9
$Y_{650°C}$ (%)	36	38	31	27	29	26	23	17	24	18	6	3

[a] Obtained at 20°C/min.

Table III   DSC Data of PVA Crosslinked with Dyanhydride C as Hardener (OH/Anhydride 1/1) and DMAP at Catalyst[a]

	DMAP (phr)				
	0.5	1	5	20	30
T_m (°C)[b]	165, 202	164, 199	157, 196	147, 187	146, 185
T_{max} (°C)[c]	221	217	215	214	214
ΔH (J/g)	12	19	30	50	63
T_g (°C)	23	41	49	86	89
E_a (kJ/mol)[d]	244	230	200	98	76
E_a (kJ/mol)[e]	246	240	202	96	74

[a] Obtained at 20°C/min.
[b] Maximum temperature of the melting process endotherm(s).
[c] Maximum temperature of the crosslinking process exotherm.
[d] Determined by using dynamic method B and the Ozawa equation.
[e] Determined by using dynamic method B and the Kissinger equation.

420°C. The lower temperature loss may correspond either to the breaking of ester linkages or to the decarboxilation of the free carboxylic acids present in the network, and the second, to the degradation of the cured material.

Crosslinking PVA by DSC

DSC was used to obtain data on the exothermic curing reactions of PVA with dianhydrides. Dianhydride C was chosen to test the behavior of PVA in the presence of a dianhydride because of its lower melting point. At first, the OH/anhydride 1/1 ratio was tested and no thermal variation was observed under the PVA decomposition temperature (about

Table IV   DSC Data of PVA Crosslinked with Dianhydrides as Hardeners and DMAP as Catalyst (30 phr)[a]

	Dianhydride	
	A (1/1)	B (1/1)
T_m (°C)[b]	192, 218	202, 265
T_{max} (°C)[c]	277	299
ΔH (J/g)	10	15
T_g (°C)	63	48
E_a (kJ/mol)[d]	136	59
E_a (kJ/mol)[e]	126	55
A (min^{-1})	$4.9 \cdot 10^{10}$	$9.8 \cdot 10^{10}$

[a] Obtained at 20°C /min.
[b] Maximum temperature of the melting process endotherm(s).
[c] Maximum temperature of the crosslinking process exotherm.
[d] Determined by using dynamic method B and the Ozawa equation.
[e] Determined by using dynamic B and the Kissinger equation.

260°C). However, the sample heated up to 250°C turned out to be insoluble in the common PVA solvents, which suggests that a partial crosslinking could have taken place although the exothermic process was not monitored. Similar results were obtained when the percentage of anhydride was varied. Experiments with the other two dianhydrides led to the same results.

Further experiments were carried out adding DMAP as a catalyst to test how adding catalytic amounts of the amine influences the crosslinking behavior of the PVA/dianhydride system. In preliminary DSC experiments using PVA and dianhydride C (OH/anhydride 1/1 ratio) with 0.5 phr of DMAP, an exotherm peak was observed. Thus, several samples of PVA and dianhydride C in the same ratio and different amounts of DMAP (0.5, 1, 5, 20, and 30 phr) were studied.

In all cases, a first heating showed a transition at 46°C corresponding to the PVA T_g, an endotherm peak at about 150°C associated to the anhydride melting, another endotherm peak at about 190°C due to the polymer melting, and an exotherm peak at about 215°C attributable to the crosslinking process. As can be seen in Table III, both endotherm peaks shift to slightly lower temperatures when the amount of DMAP increases while the maximum of the exotherm peak does not appreciably vary. However, the amount of catalyst has a considerable influence on the reaction enthalpy. In a second dynamic DSC run, an increase in T_g is observed when the amount of catalyst increases, which indicates a greater stiffness due to the crosslinking reached. As has been mentioned above, only the most crosslinked samples have T_g values which are higher than those of uncured PVA.

Table V   DSC Data of PVA Crosslinked in Different Ratios (OH/Anhydride) with C as Hardener and DMAP as Catalyst (20 phr)[a]

| | Ratio OH/Dianhydride | | | |
	1/1	1/0.75	1/0.50	1/0.40
T_m (°C)[b]	142, 185	138, 160	126, 158	111, 133
T_{max} (°C)[c]	200	198	192	—
ΔH (J/g)	55	29	21	—
T_g (°C)	98	83	70	69
E_a (kJ/mol)[d]	106	129	130	—
E_a (kJ/mol)[e]	106	128	129	—
A (min^{-1})	$3.9 \cdot 10^{10}$	$9.4 \cdot 10^{10}$	$7.1 \cdot 10^{10}$	—

[a] Obtained at 20°C/min.
[b] Maximum temperature of the melting process endotherm(s).
[c] Maximum temperature of the crosslinking process exotherm.
[d] Determined by using dynamic method B and the Ozawa equation.
[e] Determined by using dynamic method B and the Kissinger equation.

Curing activation energies were calculated by dynamic method B, based on the fact that the peak exotherm temperature varies in a predictable way with the heating rate. This allows the activation energy to be calculated without previous knowledge of the reaction order. Dynamic method A was not used because crosslinking and degradation temperatures are very close and therefore the total enthalpy of the cured process would not be accurate enough.

From the plot of ln v vs. the reciprocal temperature of the exotherm peak for different series of experiments, the activation energy values were obtained by applying Ozawa and Kissinger equations.[12,13] Kissinger's equations were applied for n = 1, so the activation energy values obtained are only valid for first-order reactions. The activation energies calculated by both methods are very close and so we can assume that this process has a first-order mechanism. The concentration of DMAP appears to have a clear influence on the activation en-

ergy values and a decrease is observed when the amount of amine increases.

PVA was also crosslinked with dianhydrides A and B in a ratio OH/anhydride 1/1 and using 30 phr of DMAP. DSC data are summarized in Table IV. Both cases show two clear endotherm peaks corresponding to the fusion of PVA and dianhydride.

Table VI   TGA Data of PVA and PVA Crosslinked in Different Ratios (OH/Anhydride) with C as Hardener and DMAP as Catalyst (20 phr)[a]

	PVA	1/1	1/0.75	1/0.50	1/0.40
T_i (°C)	261	235	231	224	221
$T_{10\%}$ (°C)	314	262	262	262	256
T_{max} (°C)	364	355	353	333	362
dW/dt (%/min)	38	9	13	15	14
$Y_{500°C}$ (%)	9	24	17	13	9

[a] Obtained at 20°C/min.
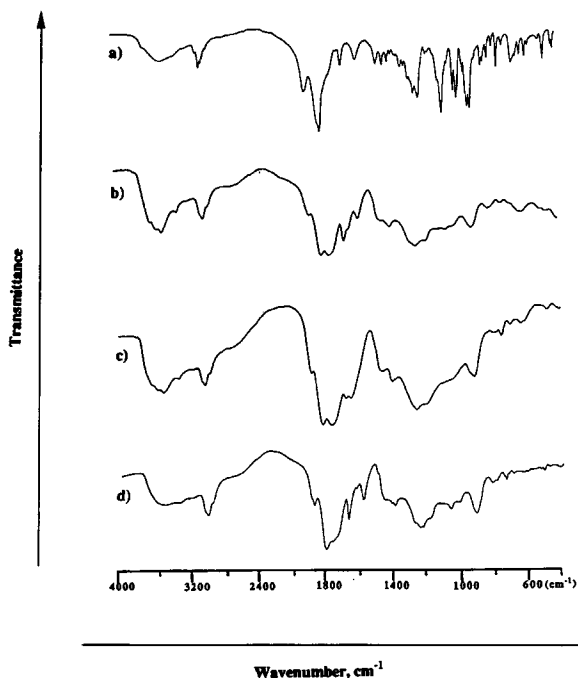
Figure 2   IR spectra of PVA with dianhydride C (OH/anhydride 1/1) and DMAP (20 phr): (a) initial mixture; (b) mixture at 200°C 1 h; (c) mixture at 200°C 24 h; (d) mixture crosslinked in dynamic DSC run up to 200°C.

The maximum temperature of the exotherms is very near to the degradation temperature of PVA, and for this reason, it can be predicted that crosslinking and degradation processes overlap. In another dynamic DSC run, samples were only heated to below the degradation temperature of PVA in order to test if a partial crosslinking took place. Thus, it is observed that the inflection corresponding to T_g undergoes a slight increase, which suggests that a low crosslinking may have taken place. The activation energy values were calculated as before by Ozawa and Kissinger equations, leading to very similar values. As can be seen (Tables III and IV), the crosslinking with Epiclon (C) takes place at a lower temperature (below the degradation temperature of PVA) and therefore the presumable overlapping of both processes is prevented. For this reason, dianhydride C was only used in further experiments with different amounts of hardener and 20 phr of DMAP (no substantial differences were observed between 20 and 30 phr). The data obtained are summarized in Table V. Clear endotherm peaks are only observed when an OH/anhydride 1/1 ratio was used. In the other cases, the two endotherm peaks are closer together and at lower temperatures, which suggests that the mixture is highly homogeneous. The maximum temperature of the crosslinking process hardly changes but the enthalpy of this process decreases with the amount of hardener. Thus, at an OH/anhydride 1/0.40 ratio, no exotherm was detected although some crosslinking must have taken place, since in a second DSC dynamic run, a T_g higher than the uncured PVA's T_g was observed. As can be seen, from the T_g values, the crosslinking increases with the amount of hardener. The same table shows the activation energies calculated by Ozawa and Kissinger equations and preexponential factors.

The thermal stability assessed by TGA (see Table VI) did not show noteworthy differences for the different amounts of hardener used, which seems to suggest that degradation is initiated by ester elimination, leading to an unsaturated chain which is similar to the one obtained by dehydrating uncured PVA. However, although this main degradation is initiated at similar temperatures, the crosslinked polymers only undergo a partial degradation since further degradation steps are observed.

Isothermal experiments by DSC did not allow us to follow the crosslinking process because the enthalpy was not detected. An isothermal approach was used with samples prepared in a similar way as before and heated in an oven, at 200°C, at different reaction times. The changes detected by IR spectroscopy are shown in Figure 2. The most significant feature was the appearance of the OH absorption of carboxylic acid groups and C=O and C—O bands due to the ester and acid groups formed. It should be pointed out that the appearance of an absorption about 1620 cm^{-1} may be attributed to C=C stretching, which would confirm the elimination detected by TGA.

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