

Hydrogels from Glycidyl Derivatives of Poly(vinyl alcohol)

J. Ruiz, A. Mantecón, V. Cádiz

Universitat Rovira i Virgili, Departament de Química Analítica i Química Orgànica, Facultat de Química, Plaça Imperial Tàrraco 1, 43005 Tarragona, Spain

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ABSTRACT: Poly(vinyl alcohol) (PVA) was modified with phthalic anhydride to obtain half esters with carboxylic acid groups, which made the reaction with epichlorohydrin easier. The oxirane ring underwent a further crosslinking that led to crosslinked polymers with polar groups capable of interacting strongly with water and therefore with properties of hydrogels. The curing kinetics of the crosslinking were studied by differential scanning calorimetry, and the dependence of the activation energy on conversion degree

was studied by isoconversional kinetic analysis. Water absorption was determined gravimetrically as a function of time at room temperature. The swelling behavior of these hydrogels was related to the degree of crosslinking. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 87: 693–698, 2003

Key words: poly(vinyl alcohol); hydrogel; crosslinking; isoconversional kinetic analysis

INTRODUCTION

Hydrogels are polymers that can retain a large amount of water when they swell in an aqueous environment, but they remain insoluble because of the presence of crosslinks, entanglements, or crystalline regions. These crosslinked polymer networks are synthesized from a variety of hydrophilic monomers. The crosslinks they contain can be either chemical or physical, and the number and type influence many of the network properties. Because of their high water content and elastic properties, hydrogels can be used in many biological applications, such as contact lenses, bioadhesives, and controlled-release matrices.¹

The purpose of this study was to prepare hydrogels from poly(vinyl alcohol) (PVA). PVA hydrogels can be formed via both physical and chemical crosslinking. PVA can be physically crosslinked by techniques that insert crystalline regions, which act as crosslinks. Pappas et al.^{2,3} extensively studied how linear PVA can be crystallized from concentrated solutions by repeated cycles of freezing and thawing that form crystalline regions. These gels proved to be stable at room temperature for several months, but from a mechanical and thermal perspective, the physical crosslinks were

not as strong or as stable as a chemically crosslinked network.

An alternative to physical crosslinking is to use stronger covalent bonds that do not have the limitations mentioned above. These chemical hydrogels can be formed using a bifunctional compound, which reacts with hydroxylic groups of PVA. Although crosslinking is much easier with this technique, it is difficult to obtain uniformly crosslinked networks because of the imperfect mixing and diffusion of the crosslinker. So, in this study we proposed to incorporate a crosslinkable function as a pendent reactive group in the polymer. This approach has recently been used to obtain hydrogels formed from acrylate-modified poly(vinyl alcohol) macromers.⁴ Likewise, we report the synthesis of highly crosslinked materials from side chain vinyl-terminated PVA derivatives.⁵

In this study a glycidyl-modified PVA was synthesized. Although the reaction of PVA with epichlorohydrin has been previously described,⁶ it needs drastic conditions (high temperature and pressure). Thus, in this study PVA was previously reacted with phthalic anhydride to obtain half-esters. This esterification makes it easier to react epichlorohydrin with carboxylic groups.

Differential scanning calorimetry (DSC) was used to study the thermal properties and kinetic parameters involved in the crosslinking processes. Isoconversional kinetic analysis was applied to nonisothermal data to determine the dependence of activation energy on the degree of conversion. In addition, thermogravimetry (TGA) was used to test the thermal stability of polymers, and the swelling behavior of these hydrogels was studied as a function of the degree of crosslinking.

Correspondence to: V. Cádiz (cadiz@quimica.urv.es).

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EXPERIMENTAL

Materials

The degree of hydrolysis of poly(vinyl alcohol) (PVA; Fluka, Germany) was 86%–89%, and the average degree of polymerization was 300. Phthalic anhydride (Fluka) was purified by recrystallization. Benzyltrimethylammonium chloride (BTMA; Aldrich), 4-dimethylaminopyridine (DMAP; Fluka), epichlorohydrin (ECH; Fluka) and dimethylsulfoxide (DMSO; SDS, France) were used as received.

Esterification reaction

PVA (0.05M of hydroxyl group) was dissolved by stirring in DMSO (50 mL) at room temperature. Different ratios of carboxylic anhydride (OH/acyl group 1:0.35 and 1:0.2) and pyridine (py/acyl group 1.2:1) were added at room temperature and stirred for 3 days. The polymer was obtained by precipitation into aqueous HCl (0.1M). These products were purified as follows: dissolving in 0.1M NaOH and precipitation with 0.1M HCl (3 times). All polymers were dried under vacuum at room temperature to a constant weight.

Modification with epichlorohydrin

PVA-PA33 (0.01M of carboxylic group) was dissolved at reflux temperature by stirring in ECH (25 mL). The temperature was decreased to 80°C, and BTMA (0.001 mol, carboxylic group/ammonium group ratio 10:1) was added. Using ¹H- and ¹³C-NMR spectra, the acid was observed to disappear at 30 min. The glycidyl derivative (PVA-PA33-ECH) was obtained by removing most ECH under vacuum and by precipitation into diethyl ether. The product was dissolved in acetone and precipitated with water (3 times) to purify it. PVA-PA14-ECH was synthesized from PVA-PA14 using ECH/DMSO (3:1) as the solvent. All polymers were dried under vacuum at room temperature to a constant weight.

Water absorption measurements

The dynamic water absorption of the samples was measured by two gravimetric procedures. In one procedure a polymer sample of 100 mg was placed in a desiccator over P₂O₅ to establish constant weight. The sample was accurately weighed and then placed in a closed chamber containing a saturated aqueous solution of potassium nitrate that 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 until the hydrated weight was constant. Absorbency was calculated as grams of

water per gram of dry polymer. In the second procedure a polymer sample that had been weighed accurately was immersed in distilled water at room temperature and left until equilibrium was attained. Once the swelling had terminated, the surface was dried and the weight gain measured. Equilibrium was reached after an immersion time of about 24 h.

Instrumentation

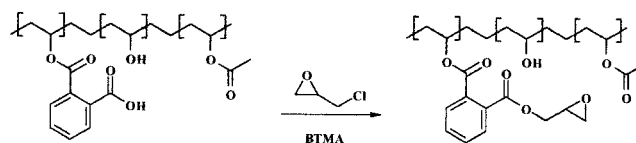
¹³C-NMR spectra were obtained using a Gemini 300 spectrometer with DMSO-d₆ as solvent. IR spectra were recorded on a MIDAC GRAMS/386 FTIR spectrometer. Elemental analyses (EA) were carried out using a Carlo Erba 1106 device.

Calorimetric studies were carried out on a Mettler DSC-30 thermal analyzer, using modified PVA samples of known weight (ca. 5 mg) in covered aluminum pans under a nitrogen atmosphere at different heating rates (5°C, 10°C, 15°C, and 20°C/min). Isoconversional kinetic analysis was carried out using the Mettler-Toledo TA 8000 kinetic software. Thermogravimetric analyses were carried out with a Perkin-Elmer TGA-7 thermal analyzer in N₂ at a heating rate of 20°C/min, using modified PVA samples of known weight (ca. 5 mg).

The equilibrium absorption of water of all the samples was measured at room temperature using an electronic microbalance (Mettler AB204) with an accuracy of ± 10⁻⁴ g. Reported values of equilibrium water uptakes were averaged over 5 measurements, and for each type of sample water absorption was replicated three times.

RESULTS AND DISCUSSION

PVA was dissolved in dimethyl sulfoxide (DMSO) in the presence of pyridine and esterified with phthalic carboxylic acid anhydride in a homogeneous medium, using different amounts of anhydride, as has been previously described.⁷ Using the ratios specified in the experimental part, phthalic derivative polymers with a modification degree of 33 phthalic units (PVA-PA33) and 14 phthalic units (PVA-PA14) per 100 total units were obtained. The degrees of modification did not coincide with the ratio of the reagents in the feed. The polymers were precipitated in water acidified with HCl to obtain free carboxylic acid derivatives. Yields were calculated by taking into account the de-



Scheme 1

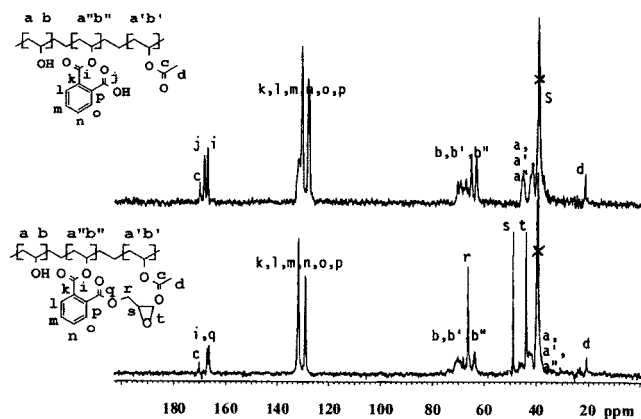


Figure 1 ^{13}C -NMR spectra of PVA-PA33 and PVA-PA33-ECH recorded in DMSO-d_6 .

gree of modification reached. The degree of substitution was calculated by elemental analysis and ^1H -NMR spectra. Both results were very similar.⁸ IR and NMR spectroscopy confirmed the structures of these polymers.

We prepared glycidyl derivatives of these polymers by reaction with a considerable excess of epichlorohydrin and using BTMA as catalyst⁹ (see Scheme 1). The derivative PVA-PA33 was synthesized with only epichlorohydrin as a solvent, whereas the PVA-PA14 needed to add DMSO to complete the dissolution. Although the vinyl alcohol-vinyl phthalate copolymers obtained still had some hydroxyl groups, they did not react with epichlorohydrin in the conditions described above because they were less reactive than carboxylic acid and needed drastic conditions (high temperature and pressure).

IR spectroscopy showed that the OH vibration corresponding to the COOH group disappeared and that oxirane group vibrations appeared at 910 and 840 cm^{-1} . The ^1H -NMR spectra recorded in DMSO-d_6 were extremely complex because the nonequivalent five protons of the glycidyl group overlapped with the signals of the main chain. The resolution of the

^{13}C -NMR was better and confirmed the structures. Figure 1 shows the spectra of PVA-PA33 and its glycidyl derivative PVA-PA33-ECH for the sake of comparison. In the latter, the three glycidyl carbon signals appear at 43, 48, and 66 ppm. In the carbonylic region, the free acid signal (168 ppm) disappears and a signal from the new ester formed appears at 166.5 ppm. This and the fact that the aromatic signals are simpler because the aromatic ring is more symmetrical seem to confirm that complete esterification has taken place.

The vinyl alcohol-vinyl glycidyl phthalate copolymers were thermally characterized by DSC and TGA, and the results are summarized in Table I, which also shows the thermal data of PVA and vinyl phthalate copolymers. As can be seen, the insertion of aromatic moieties in PVA increases the T_g values and the further insertion of the glycidyl group slightly decreases the T_g values because the side chain flexibility increases and the polarity and the possibility of hydrogen bonding decrease. The TGA data indicate that the half esters have two degradation steps, whereas the corresponding glycidyl derivatives only have the second one at higher temperatures. The first degradation in carboxylic compounds may be attributed to a decarboxylation process that is favored in aromatic carboxylic acid with an ortho substituent.¹⁰ The thermal stability of the glycidyl derivatives is greater because this decarboxylation is absent and the thermal process (up to 600°C) causes the crosslinking through the oxirane rings. Figure 2 shows the TGA curves and the first derivatives of PVA-PA14-ECH and PVA-PA33-ECH. The PVA curves are also included for the sake of comparison.

Curing reaction

The curing reaction of the oxirane-containing polymers was studied by DSC. Dynamic data showed that the curing temperature is in the range of 200°C–300°C, although the degradation begins at temperatures close to 300°C, as is shown by TGA. Therefore, crosslinked

TABLE I
Thermal Characterization of PVA-PA and PVA-PA-ECH Copolymers

	PVA	PAA-PA33	PVA-PA33-ECH	PVA-PA14	PVA-PA14-ECH
d.m. (%) ^a	—	33	33	14	14
T_g (°C) ^b	41	56	49	48	43
T_s (°C) ^c	272	201	290	198	289
$T_{10\%}$ (°C) ^c	292	228	314	239	305
T_{max} (°C) ^c	322	260/322	322	257/326	325
ΔW (%) ^c	46	24/52	23	14/37	26
dW/dt (%/min) ^c	41	9/11	23	4/10	14
$Y_{500^\circ\text{C}}$ (%) ^c	7	7	11.5	3.5	4

^a d.m. (%): vinyl phthalate or vinyl glycidyl phthalate units (per 100 total units) from NMR and EA data.

^b DSC 20°C/min.

^c TGA 20°C/min, T_s (start temperature degradation), $T_{10\%}$ (10% loss weight temperature), T_{max} (temperature of maximum rate of weight loss), W (weight loss at T_{max}), dW/dt (rate of weight loss at T_{max}), and $Y_{500^\circ\text{C}}$ (residuum a 500°C).

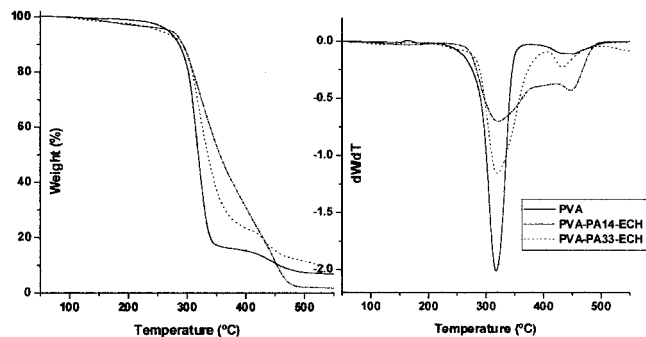


Figure 2 TGA curves of PVA and vinyl alcohol-vinyl glycidyl phthalate copolymers PVA-PA14-ECH and PVA-PA33-ECH.

polymers must be obtained at temperatures of 200°C or slightly above or by using curing agents that decrease the crosslinking temperature.

First, we studied the crosslinking of PVA-PA33-ECH and PVA-PA14-ECH with no catalyst. Isothermal curing was carried out at 200°C and at different heating times. Table II shows the T_g and ΔT_g values after curing. As can be seen, the results are similar for both polymers because although PVA-PA33-ECH can form a more crosslinked network, the PVA-PA14-ECH retains more hydroxyl groups that can interact by hydrogen bonding. Both these factors increase the T_g . Second, we studied the crosslinking of the polymers using different amounts of DMAP, a curing agent and catalyst that gives good results in the crosslinking of diglycidyl compounds.¹¹ To make the samples homogeneous, we prepared solutions of PVA-PA33-ECH in CH_2Cl_2 with 2.5, 10, 15, and 20 phr (% w/w) of DMAP and removed the solvent. Dynamic scans showed that the crosslinking exotherm shifted to lower temperatures (between 100°C and 200°C). Thus, crosslinking and degradation are separate processes (see Fig. 3). The thermograms of the samples with 2 and 5 phr of DMAP showed two exotherms, at 100°C–200°C because of catalyzed crosslinking and at 200°C–300°C because of thermal crosslinking. This latter exotherm did not appear when 10, 15, and 20 phr of DMAP were used. As these three samples gave similar results, we chose 10 phr as the suitable amount of catalyst, and isothermal experiments were made at 120°C for 10, 20, and 30 min.

TABLE II
 T_g and ΔT_g values of PVA-PA-ECH Copolymers after Curing at 200°C

Isothermal curing at 200°C (mins)	PVA-PA33-ECH	PVA-PA14-ECH
	T_g (ΔT_g)	T_g (ΔT_g)
10	98 (+49)	98 (+55)
20	101 (+52)	104 (+61)
30	112 (+63)	109 (+66)

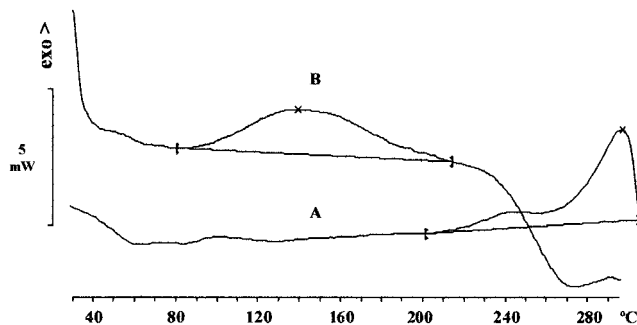


Figure 3 DSC scans at 20°C/min of (A) PVA-PA33-ECH (33 glycidyl units per 100 total units) and (B) PVA-PA33-ECH + 10 phr of DMAP.

Table III shows the results. The ΔT_g s are similar to those obtained for thermal crosslinking without DMAP. This suggests that the degrees of crosslinking are similar but at significantly lower temperatures.

Curing kinetics

The activation energy (E_a) of the reaction for curing the PVA-PA33-ECH with 10 phr of DMAP was obtained by dynamic DSC scans or isothermal experiments. In our case, we calculated the curing activation energies by dynamic method B,¹² which is based on the peak exotherm temperature varying in a predictable way with the heating rate. This allows the activation energy to be calculated with no previous knowledge of the reaction order. Dynamic method A was not used because the results obtained for different heating rates did not coincide. These deviations may be result from the E_a being calculated from a single curve and factors such as an incorrect baseline or reaction order, or an overlapping process will contribute to inaccurate results.

From the plot of $\ln \nu$ (ν = heating rate in °C/min) versus the reciprocal of the exotherm peak for a series of experiments at 5°C, 10°C, 15°C, and 20°C/min, the activation energies were obtained by applying the Ozawa¹³ [$E_a = -R \Delta \ln \nu / 1.052 \Delta (1/T_p)$] and Kissinger [$\ln(\nu/T_p^2) = \ln(AR/E_a) - E_a/RT_p$] equations.¹⁴ Kissinger's equations were applied for $n = 1$, so the activation energy values obtained are only valid for first-order reactions. The activation en-

TABLE III
 T_g and ΔT_g Values of PVA-PA33-ECH + 10 phr DMAP after Curing at 120°C

Isothermal curing at 120°C (minutes)	PVA-PA33-ECH + 10 phr DMAP	
	T_g	(ΔT_g)
10 min	98	(+49)
20 min	102	(+53)
30 min	107	(+58)

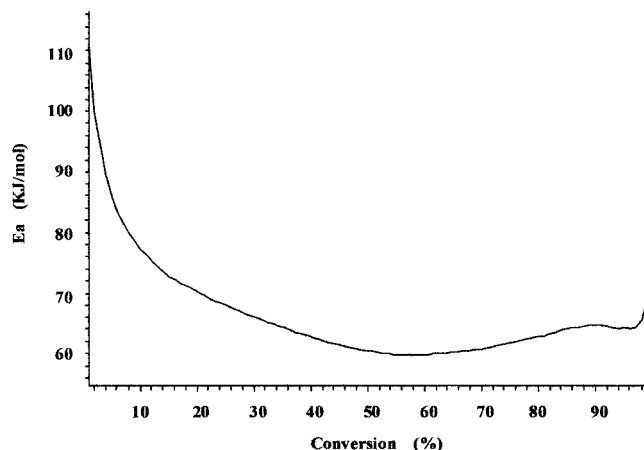


Figure 4 Isoconversional kinetic analysis. Crosslinking reaction of PVA-PA-ECH + 10 phr DMAP at 5°C, 10°C, 15°C, and 20°C/min.

ergies calculated by both methods are very similar (52 and 56 KJ/mol, respectively), so we can assume that the process has a first-order mechanism. In addition, the ASTM E698-79 based on the Kissinger equation was used. This method calculates the activation energy by an iterative process that corrects the dependence of the kinetic parameters on the temperature and includes a corrector factor D , which is tabulated in the literature.¹⁵ The value obtained (62 KJ/mol) was slightly higher than those obtained by the other two methods but comparable.

As is evident, this curing process involves several reactions, namely, initiation, propagation, termination, and chain transfer. Therefore, isoconversional kinetic analysis¹⁶ is a viable alternative in this situation. The basic idea behind this type of analysis is that the reaction rate at a constant conversion depends only on the temperature. In other words, $d \ln(d\alpha/dt)_\alpha / dT^{-1} = -(E_a)_\alpha / R$ where $(E_a)_\alpha$ is the effective activation energy at a given conversion α . For a single step process, E_a is independent of α and has the meaning of the actual activation energy. In a multistep process,

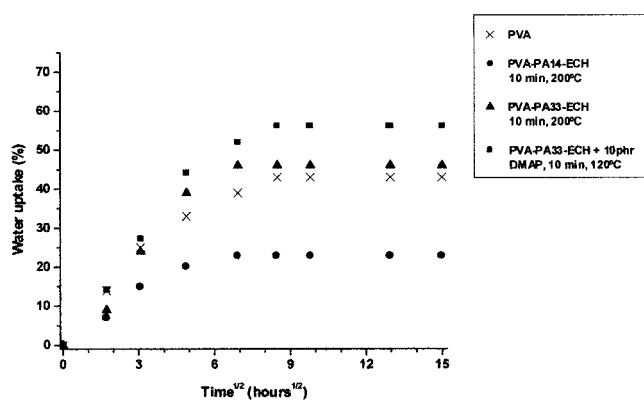


Figure 5 Water uptake against time for PVA and PVA-PA-ECH derivatives.

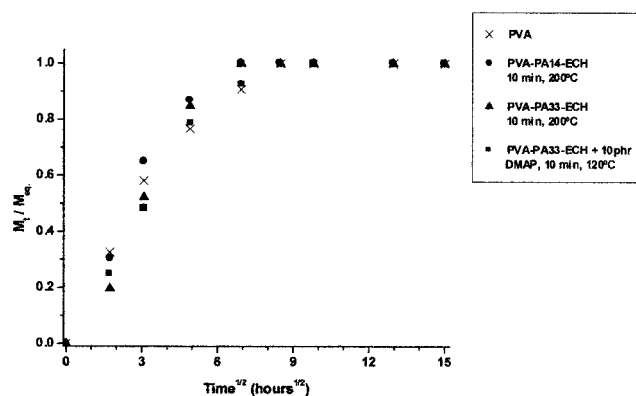


Figure 6 Water uptake against time (Fickian graph) for PVA and PVA-PA-ECH derivatives.

the effective activation energy depends on conversion, and its analysis reveals not only the complexity of the process but also identifies the kinetic scheme because the shape of E_a versus α is results from the change in the contribution of the steps to the overall reaction rate. Figure 4 shows the plot of E_a versus conversion for this polymer. As can be seen, at lower conversions, values of E_a are high. These values decrease until conversions are about 40% and can be associated with the attack of the tertiary amine on the oxirane ring. After that the E_a slightly increases because the growing chains lose their mobility. At high conversions (90%) the diffusion step becomes the rate-limiting step because of the increase in the viscosity resulting from crosslinking, and the result is that E_a increases.¹⁷

Water absorption capacity

The hydrophilic nature of the hydroxyl and carboxyl groups present in the PVA-PA-ECH hydrogels plays an important role in relation to water molecules. Thus, we used the two methods described in the experimental part, above, to study the water absorption of these compounds. When they were placed in a closed chamber containing a saturated aqueous solution of potassium nitrate (relative humidity of 93%), the results were similar for the samples crosslinked for 10, 20, and 30 min. Therefore, Figure 5 only shows the results for samples crosslinked for 10 min. PVA absorption is also shown for the sake of comparison. The T_g values, determined by thermal measurements, show that the degree of crosslinking is similar for the polymers crosslinked at 200°C or 120°C. However, as can be seen, PVA-PA14-ECH has a lesser degree of crosslinking and absorbs less than PVA, whereas PVA-PA33-ECH has a higher degree of crosslinking and absorbs more than PVA. Moreover, the polymer crosslinked at 120°C absorbs more than the one crosslinked at 200°C. This can be explained by the greater dehydration at 200°C, which decreases the number of polar hydroxylic groups. This dehydrating

TABLE IV
 Constants n for PVA and PVA-PA-ECH Derivatives

PVA	0.50
PVA-PA33-EPC + 10 phr DMAP crosslinked at 120°C	0.51
PVA-PA33-ECH crosslinked at 200°C	0.52
PVA-PA14-ECH crosslinked at 200°C	0.55

effect should be higher in PVA-PA14-ECH because the linear polymer initially had more hydroxylic groups, and this should explain the lower absorption of the least crosslinked polymer.

The water absorption of a material can be related to time by means of the following equation¹⁸: $M_t/M_{\text{equilibrium}} = kt^n$ where M_t is the relative weight gain at time t , $M_{\text{equilibrium}}$ is the relative weight gain in the equilibrium, and k and n are constants. When $n = 1/2$, the material has a Fickian diffusion. In this case, sorption curves as a function of the square root of time are linear in the initial stage, and above the linear portion absorption curves are concave to the abscissa.¹⁹ Figure 6 shows the sorption-time curves for Fickian behavior of the crosslinked polymers at 200°C and 120°C. As can be seen, they all have a linear initial stage. The constant n has been calculated using the above equation (Table IV), and in all cases the n values are very close to $1/2$, which confirms the Fickian behavior.

Finally, the absorption capacity was measured by immersing the samples in water. This process proved to be faster than the method described above, and the amount of water absorbed was also higher. So, in just a few hours, absorption values were between 55% and 95%, whereas at significantly longer times the first method led to absorption values between 25% and 55%.

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