

Effect of crosslinking on the mechanical and thermal properties of poly(vinyl alcohol)

M. Krumova, D. López, R. Benavente, C. Mijangos, J.M. Pereña*

Instituto de Ciencia y Tecnología de Polímeros, CSIC, Juan de la Cierva 3, 28006 Madrid, Spain

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Abstract

Poly(vinyl alcohol) was crosslinked with hexamethylene diisocyanate in solution. A broad range of degrees of crosslinking, from 1.7 up to 74 mol% of reacted hydroxyl groups, was achieved. The variation of the thermal and mechanical properties of PVA with the crosslinking density show an initial decrease due to the diminution of the crystallinity of the system, caused by the crosslinking. After an abrupt rise at about 20%, the properties tend to level off independently on the increase of the crosslinking. This behaviour is explained as a result of the competitive action of at least three factors during the crosslinking: (i) weakening of the existing physical network due to hydrogen bonding; (ii) formation of a chemical network; and (iii) introduction of flexible moieties. The last factor is closely connected with the specific chemical structure of the crosslinker itself. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Poly(vinyl alcohol) crosslinking; Mechanical properties; Thermal properties

1. Introduction

The chemical resistance and physical properties of poly(vinyl alcohol) (PVA) have led to its broad industrial use. However, the physical properties of PVA depend to a greater extent on the method of preparation than it is the case with other polymers [1]. The final properties are affected by the polymerisation conditions of the parent poly(vinyl acetate) as well as by the hydrolysis conditions, drying and grinding. It is difficult to assign specific physical properties to solid poly(vinyl alcohol) as this designation refers to an array of products, including copolymers of vinyl acetate–vinyl alcohol.

On the other hand, chemical crosslinking of linear polymers may provide feasible routes for the improvement of the mechanical properties and thermal stability [2,3]. Several crosslinking methods have been published for different uses, since as a rule, all multifunctional compounds capable of reacting with hydroxyl groups can be used to obtain tridimensional networks in PVA [4–6]. Crosslinked PVA find a very promising application in the preparation of biomedical materials [4] and of magnetic-field-sensitive gels [7].

As far as our knowledge, hexamethylene diisocyanate was scarcely used as a crosslinking agent in PVA.

Nevertheless, a comparison of three usual difunctional hardeners showed that only hexamethylene diisocyanate was the most suitable crosslinker [8]. Usually the crosslinking density greatly influences the properties of the final polymer. Therefore the aim of the present work is to offer an extensive study of the evolution of the mechanical and thermal properties of PVA with increasing degree of crosslinking in the broad range from about 2 to 74%, using hexamethylene diisocyanate as a hardener.

2. Experimental

2.1. Materials

PVA is a commercial product (Gohsenol NL05) with a degree of hydrolysis of 85% and a molecular weight, measured by osmometry, of 22000 g/mol. The tacticity measured by ¹H NMR was syndio = 21.0%, hetero = 53.2% and iso = 25.8%. Hexamethylene diisocyanate was purchased from Aldrich and used as received. Dimethyl sulfoxide (DMSO), *N,N*-dimethylformamide (DMF) and tetrahydrofuran (THF) (Scharlau) were purified by distillation prior to use.

2.2. Crosslinking reactions

A polymer solution was prepared by dissolving 0.81 g of

* Corresponding author.

E-mail address: perena@fresno.csic.es (J.M. Pereña).

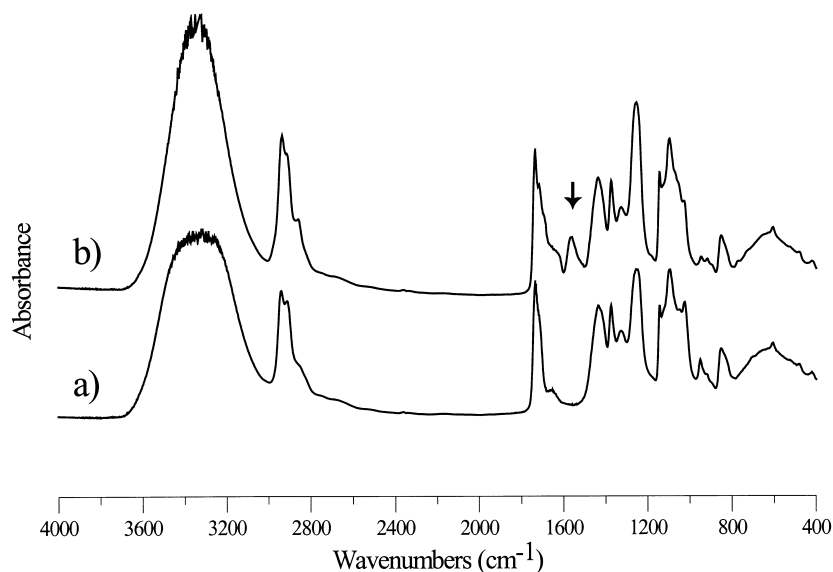


Fig. 1. IR spectra of: (a) PVA; and (b) PVA crosslinked with hexamethylene diisocyanate (degree of crosslinking 10%, expressed as mol% of reacted OH groups).

PVA (13.7 mmol of vinyl alcohol units) in 10 mL of a DMSO/DMF (1:1, v/v) mixture at 80°C. When the polymer was completely dissolved, the solution was cooled down to 0°C. A solution of hexamethylene diisocyanate of appropriate concentration was prepared at 0°C in 5 mL of the DMSO/DMF mixture. Both solutions were mixed under vigorous stirring for 5 min. When homogenisation was achieved the solution was poured into glass plates and allowed to react for 12 h at room temperature. The degree of crosslinking was varied by using different amounts of hexamethylene diisocyanate keeping the polymer concentration (5%, w/w) and the total volume of the reaction mixture constant. The films of the crosslinked PVA were purified by extraction with tetrahydrofuran in a Soxhlet apparatus for 12 h and then dried at 40°C under vacuum for 24 h.

2.3. Characterisation techniques

2.3.1. Infrared spectroscopy

The degree of crosslinking expressed as mol% of the reacted hydroxyl groups was determined by IR spectroscopy on a Nicolet 520 IR-FT spectrometer and by elemental analysis. In order to calculate conversions from the IR spectra, a calibration curve was recorded.

2.3.2. Dynamic mechanical thermal analysis

The viscoelastic behaviour of the crosslinked polymers was tested on a Polymer Laboratories DMTA MKII dynamic mechanical thermal analyser, working in tensile mode at a constant stress. The complex modulus and the loss tangent were determined at frequencies of 1, 3, 10 and 30 Hz over a temperature range of –140 to about 80°C. The

experiments were carried out in nitrogen atmosphere with a heating rate of 1.5°C/min.

Samples were prepared from the extracted crosslinked films, obtained as described above. Rectangular samples of 2.2 mm width, about 3 cm length and 150–450 μm thickness were cut.

The apparent activation energies of the relaxations were calculated according to an Arrhenius-type equation, from the maximum values of the loss tangent at the four mentioned frequencies.

2.3.3. Differential scanning calorimetry

The calorimetric measurements were carried out using a Perkin–Elmer DSC-7 calorimeter, connected to a CCA7 cooling system. DSC traces were recorded between –20°C and 220°C at a heating rate of 20°C/min. The values of the glass transition temperature T_g were taken as the temperatures of the midpoint of the increment of the specific heat capacity, ΔC_p , of the transitions, and the T_m values from the maximum of the melting peak in the second scan.

2.3.4. Microhardness

A Vickers indenter attached to a Leitz microhardness tester was used to carry out microindentation measurements at room temperature. A contact load of 0.49 N and a contact time of 25 s were employed. Microhardness values MH in MPa were derived from the residual projected area of indentation according to $MH = kP/d^2$, with d being the length of the impression diagonal, P the contact load applied, and k a factor equal to 1.854 [9]. Ten measurements for each data point were averaged.

2.3.5. Wide-angle X-ray diffraction

Wide-angle X-ray diffraction patterns were recorded in

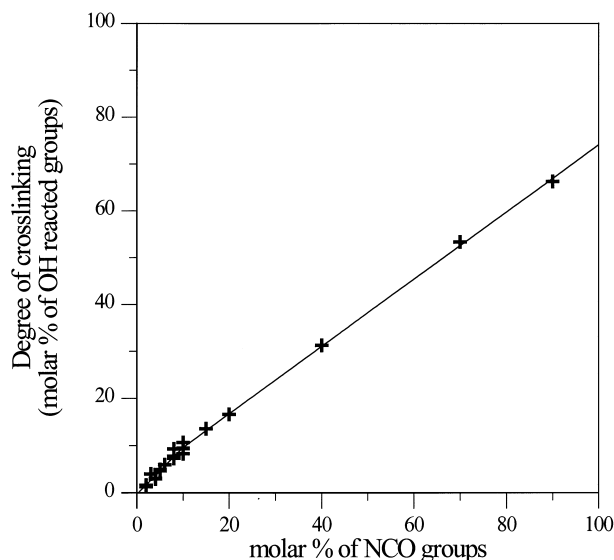


Fig. 2. Degree of crosslinking as a function of the mol% of NCO groups, with respect to hydroxyl groups in the reaction mixture.

the reflection mode at room temperature by using a Philips diffractometer with a Geiger counter, connected to a computer. Ni filtered CuK_α radiation was used. The diffraction scans were collected at 2θ between 4 and 44° , using a sampling rate of 1 Hz. The goniometer was calibrated with a standard of silicon.

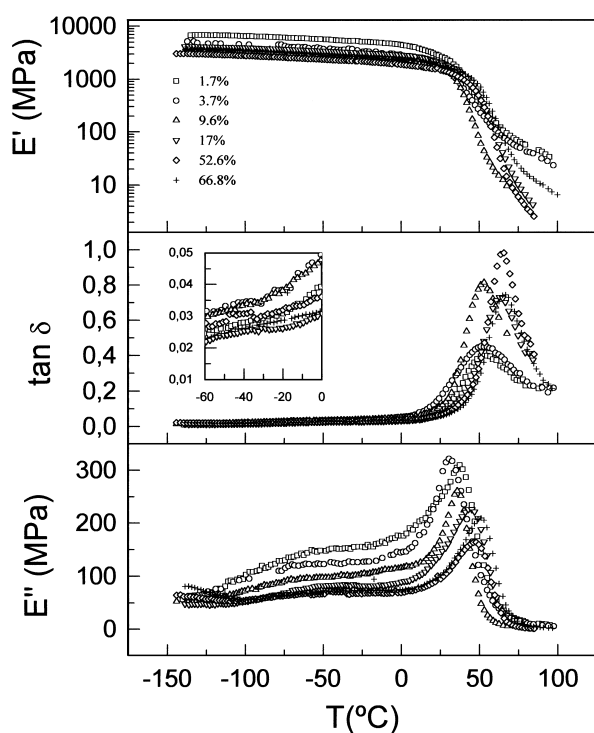


Fig. 3. Temperature dependence of the storage modulus (upper), loss tangent (middle) and loss modulus (lower) of PVA samples with different degrees of crosslinking.

3. Results and discussion

3.1. Crosslinking of PVA

The reaction of alcohols with isocyanates to form carbamates is well known and analogous reactions with PVA could be realised. Thus, crosslinking of the PVA may be achieved by reacting hydroxyl groups along the polymer chain with diisocyanates to give urethane crosslinks. The crosslinking reaction of PVA with hexamethylene diisocyanate was performed as indicated in the Section 2. The resulting materials were insoluble in common polar and apolar solvents, indicating their crosslinked nature. The presence of the urethane crosslinks in the polymer has been proven by IR measurements, where the appearance of a characteristic peak centred at 1564 cm^{-1} can be seen that corresponds to the amide II region of the carbamate [10] formed during the crosslinking reaction (see Fig. 1). Additional characteristic peaks of the carbamate group cannot be unambiguously assigned due to the overlapping by the signals of the starting material. The absence of the typical signal corresponding to the asymmetric stretch of the $\text{N}\bar{\gamma}\text{C}\bar{\gamma}\text{O}$ group, centred at 2277 cm^{-1} , indicates that both functional groups of the hexamethylene diisocyanate have reacted and that no grafting of the 6-isocyanohexyl group has occurred.

In order to calculate conversions from the IR spectra, a calibration curve was recorded. The spectra of the crosslinked PVA, whose composition had been determined by elemental analysis, were recorded and the ratio of the integrals of amide II peaks (1564 cm^{-1}) to deformation $\delta(\text{CH})$ peaks at 1376 cm^{-1} plotted as a function of the mol% of the reacted hydroxyl groups [11].

In Fig. 2 the degree of crosslinking determined from the calibration curve is shown as a function of the mol% of isocyanate groups with respect to vinyl alcohol units in the reaction mixture. It can be seen that up to a ratio NCO/OH of 1:10 the reaction is almost quantitative. For higher ratios the extent of the reaction decreases what is probably due to a reduced accessibility of the reactive groups caused by an increase of the network density. The maximum degree of conversion reached under the given conditions indicated in Section 2 was 74%.

3.2. Dynamic mechanical and thermal behaviour

The dynamic mechanical properties of PVA with 13 different degrees of crosslinking were studied. In Fig. 3 typical DMTA curves at 3 Hz of some crosslinked samples are shown, including storage modulus (E'), loss modulus (E'') and loss tangent ($\tan \delta$) as a function of temperature (T) in $^\circ\text{C}$. Two relaxations, β and α in order of increasing temperature, were found. The relaxations will be considered separately in the following.

The β relaxation has a relatively low intensity and is better observed in the loss modulus plots (lower part of Fig. 3). The broad maximum at low temperatures (from

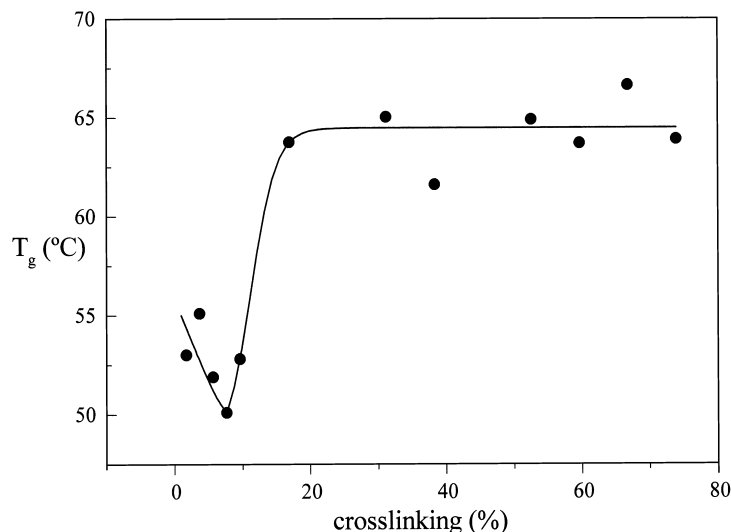


Fig. 4. Evolution of the temperature location of the α relaxation at 3 Hz (T_g) with the crosslinking.

about -100 to 0°C) is indicative of a complex relaxation produced by motions of hydroxyl groups connected to water molecules [12,13]. Other authors [14] consider the β relaxation as a typical water relaxation. In the present work the mean value of the activation energy for the β relaxation is

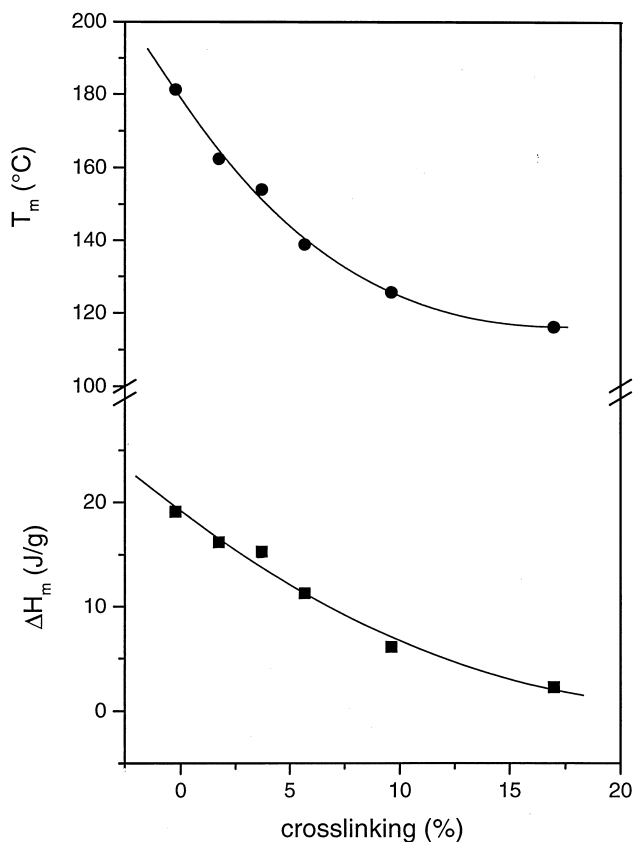


Fig. 5. Dependence of the enthalpy of fusion ΔH and of the melting temperature T_m on the degree of crosslinking.

around 120 kJ/mol, that is a high value for the water relaxation. Therefore, we can consider the β relaxation as a consequence of hydroxyl motions favoured by the water molecules.

The temperature location of the maximum of the β relaxation slightly shifts with the degree of crosslinking between -50 and -37°C and the apparent activation energy increases from about 105 to 140 kJ/mol. These variations can be explained with the slight restriction of the side chain movements due to the increasing density of the crosslinking. The intensity of the β relaxation decreases continuously up to a crosslinking of about 30% , after that it levels off.

The intense peaks in E'' and $\tan \delta$ curves corresponding to the α relaxation are accompanied by a pronounced decrease of E' at about the same temperature. Moreover, the α relaxation displays a high value of the apparent activation energy, near to 300 kJ/mol, as expected for a glass transition. These concurrent features led us to consider this relaxation as the glass transition of the studied crosslinked PVA.

The glass transition temperatures of the studied samples are lower than the usual value for poly(vinyl alcohol) as a consequence of the relatively high residual vinyl acetate content. As reported in [11], the T_g of 98 – 99% hydrolysed PVA is 85°C , whereas that of 87 – 89% hydrolysed PVA drops to 58°C . Thus, the T_g values measured in the present study for the low crosslinking densities agree well with the latter reported values [11].

The evolution of the temperature location of the α relaxation with the crosslinking is shown in Fig. 4. An initial slight decrease up to 10% of crosslinking is observed, followed by an abrupt rise at about 17% and a levelling off at a T_g value of about 65°C independently on the crosslinking density.

In order to explain these results, one has to take in account that the studied system is a very complex one. It is known that PVA is a semicrystalline polymer in which high physical interactions between the polymer chains, due

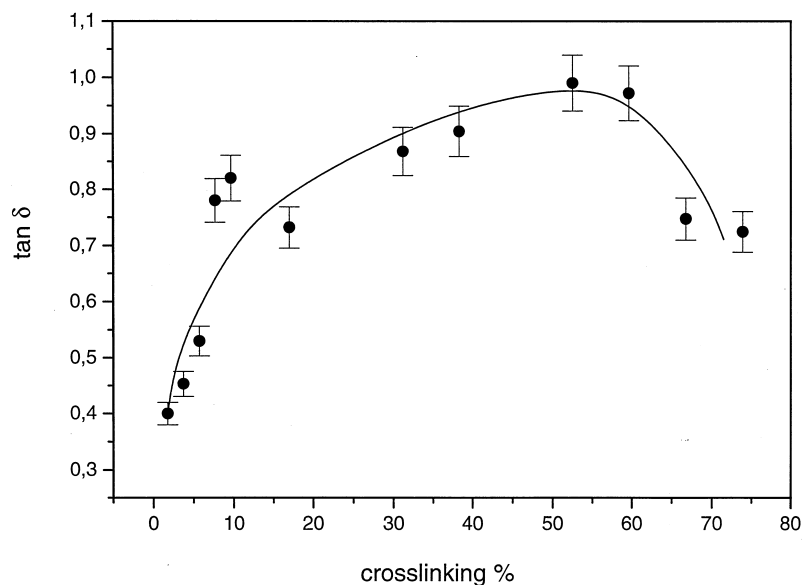


Fig. 6. Variation of the intensity ($\tan \delta$ basis) of the α relaxation with the crosslinking.

to hydrogen bonding between the hydroxyl groups exist [15]. The introduction of a crosslinking agent affects both, crystallinity and physical network, originating variations in the T_g values of the system.

Parallel DSC studies (Fig. 5) show a rapid decrease of the enthalpy of fusion ΔH and melting temperature T_m and testify to diminution of crystallinity and perfection of the crystal structure with crosslinking increase. At about 15% of crosslinking crystallinity vanishes. The diminution of the degree of crystallinity causes the slight decrease of the T_g in the first region (Fig. 4) of crosslinking densities. After that, the slope in Fig. 4 shows a characteristic rise in the T_g value caused by the crosslinking and a subsequent levelling off independently on the network density.

It is known that several factors can influence the T_g values of the crosslinked polymers: main chain rigidity, crosslinking density and the chemical structure of the hardener introduced. The PVA hydroxyl groups contribute, by hydrogen bonding, to the stiffness of the linear polymer. By introducing a crosslinking agent, the number of hydroxyl groups diminishes and hydrogen bonding interaction decreases, which produce a diminution in the stiffness. On the other hand, the crosslinking increases the rigidity and the new moieties introduced can affect T_g in a different way, depending on their structure. In our case the crosslinking agent used is hexamethylene diisocyanate, e.g. the bridges created between the polymer chains are not rigid ones, but flexible sequences of six methylene groups. The trend of the T_g variation with the crosslinking (Fig. 4) shows that beyond 20% of crosslinking the expected increase in T_g due to the formation of the chemical network is compensated by the reduction of T_g ought to the weakening of the physical network and to the plasticising effect of the introduced

flexible moieties. The maximal increase in T_g achieved with crosslinking in this study, in comparison to the linear polymer, is about 15°C.

Fig. 6 shows the variation of the intensity of the α relaxation, measured on $\tan \delta$ basis, as seen in the middle part of Fig. 3. Its gradual increase with increasing crosslinking could be related to a homogenisation of the amorphous phase with the disappearance of the crystals and the better ordering of the polymer chains in a network. Highest crosslinking densities restrict the motions and lead to diminution of the relaxation intensity.

Linear poly(vinyl alcohol) displays another dynamic mechanical relaxation at higher temperature. It has been named α' and related to motions in the crystalline phase [16]. This relaxation has not been found in the samples studied in the present work because they have a very low, if any, crystalline content, as deduced from the DSC measurements (Fig. 5).

The shape of the curves $\log E'$ vs temperature, for temperatures above the glass transition, changes according to the physical structure of the polymeric network, as can be seen in Fig. 3 (upper part). For low values of crosslinking densities (below 10%) the PVA samples display a smooth decrease of the storage Young's modulus, a behaviour similar to that of semicrystalline polymers. However, at intermediate crosslinking values, the trend of the decrease of the Young's modulus is akin to that of the amorphous polymers. At high crosslinking densities (above 60%), the increasing number of entanglements leads again to a smooth decrease that resembles the behaviour of semicrystalline polymers. Moreover, the highest values of the storage modulus, in the low temperature region, correspond to the PVA samples with low degree of crosslinking. The evolution of the E' value at 25°C, measured at 3 Hz is presented in Fig. 7.

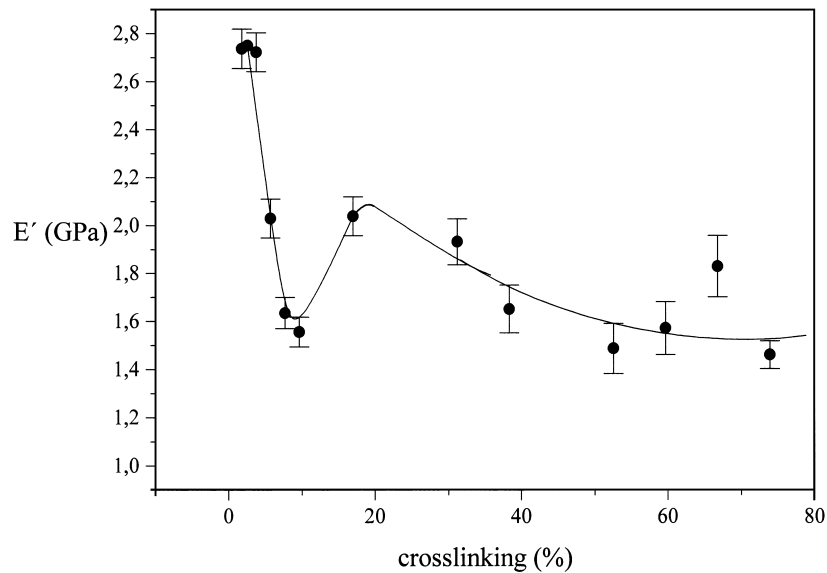


Fig. 7. Evolution of the storage modulus E' , at 25°C, with the crosslinking.

3.3. Microhardness

The dependence of microhardness, MH, at room temperature on the degree of crosslinking is illustrated in Fig. 8. A nearly linear decrease of MH up to about 9% of crosslinking is observed. This is related with the rapid decrease in the degree of crystallinity of the polymer, as was concluded from the DSC studies (Fig. 5). The sample with the lowest degree of crosslinking shows a microhardness value of 141 MPa, which is of the order of magnitude of the MH of PVA, measured in a previous study [17]. The difference is due to the higher degrees of crystallinity and of hydrolysis

of the former [17]. The minimum value of MH of approximately 70 MPa is reached at about 15% of crosslinking, with the complete disappearance of the crystallinity.

Like other characteristics described above, MH also presents a abrupt rise at about 17%, when the rigidity of the system increases due to the crosslinking. Beyond 30% of crosslinking the slope levels off without reaching the initial value of MH (at the lowest degree of crosslinking). This observation is explained with a very strong effect of crystallinity on microhardness of polymers [18] and the above described peculiarities of the studied system. Obviously, the augmentation of the

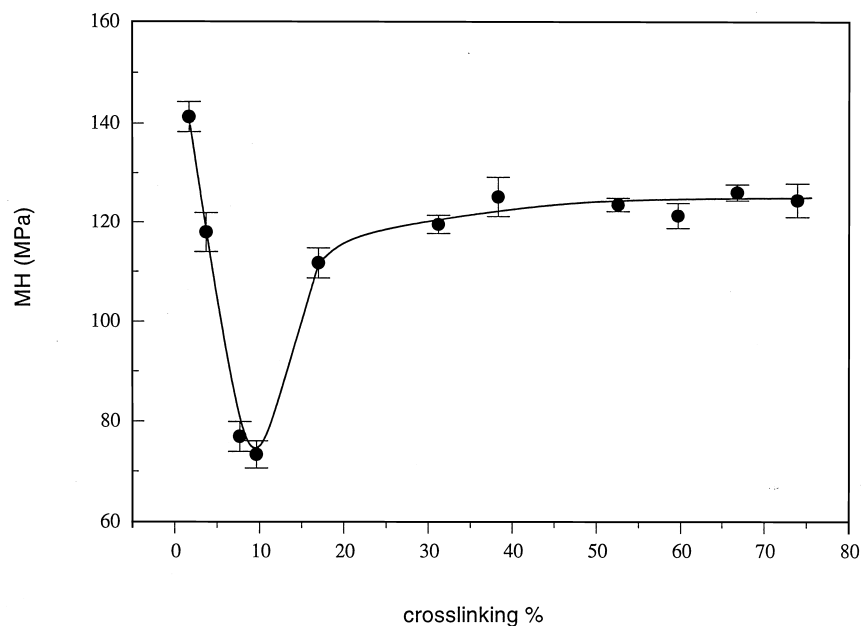


Fig. 8. Dependence of the microhardness MH at room temperature on the degree of crosslinking.

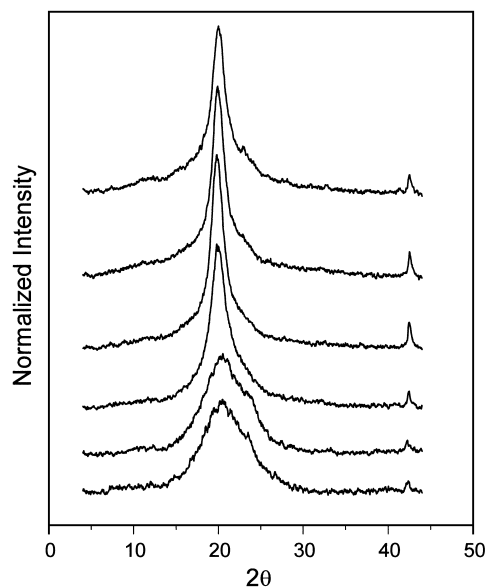


Fig. 9. The WAXS patterns of PVA for some crosslinking densities. From upper to lower, in mol%, 1.7, 3.7, 5.7, 9.6, 38.3 and 73.9, respectively.

number of flexible moieties from the crosslinking agent at higher degrees of crosslinking, prevents a further increase of the hardness of the system.

Nevertheless, no trend in decrease of the microhardness with crosslinking is detected, in contrast to the variation of the Young's modulus presented in Fig. 7. This interesting fact could be explained with different mechanisms of deformation applied in these two kinds of measurement. The results shown in Fig. 7 are obtained from a dynamic mechanical apparatus working in the tensile mode and they correspond to sinusoidal deformations of small amplitude, while the microhardness indentations have been correlated to Young's moduli only in the case of data obtained from the stress–strain tests of semicrystalline polyolefins [19].

3.4. Wide-angle X-ray diffraction

In order to relate the mechanical characteristics to the structure of the polymers, WAXS patterns were recorded and are presented in Fig. 9 for some crosslinking densities. The diffractograms do not correspond to the usual monoclinic lattice of PVA [20,21]. The position of the reflections in Fig. 9(a)–(c) is characteristic for an orthorhombic lattice. Obviously, this difference is due to the chemical composition of the studied samples. In the present study we deal in fact with a copolymer (the degree of hydrolysis of the PVA is 85%), for which an orthorhombic (pseudohexagonal) lattice is more probable. Further, the preparation conditions seem to play an important role for the formation of the crystalline structure. While in a previous study on PVA [21] the samples were crystallised from the melt, in the present case they were prepared from solution.

For crosslinking densities up to 10% no appreciable

differences in the reflections are seen (Fig. 9). Since the degree of crystallinity is relatively low and no information about the amorphous halo is available (the latter is expected to be different for each sample), no reliable conclusions about the degree of crystallinity and crystal size could be drawn.

Interesting are the WAXS patterns corresponding to the samples with the highest crosslinking densities, which are completely amorphous according to the above mentioned DSC studies. From the form of the diffractogram it can be concluded that the pseudohexagonal ordering is preserved after crosslinking even in the amorphous samples.

4. Conclusions

The detailed study of PVA with different degree of crosslinking has shown that its thermal and mechanical properties suffer an initial decrease, due to the diminution of the crystallinity of the system, caused by the increasing of the crosslinking density. After an abrupt rise at about 20% the properties do not change significantly up to the maximal achieved degree of crosslinking of nearly 74%. This behaviour is explained as a result of the competitive action of at least three factors during the crosslinking: (i) diminution of the existing physical network due to hydrogen bonding; (ii) formation of a chemical network; and (iii) introduction of flexible moieties due to the specific chemical structure of the crosslinker itself.

Acknowledgements

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