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PVC containing hydroxyl groups
II. Characterization and properties of crosslinked polymers

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Abstract

The crosslinking of poly(vinyl chloride) (PVC) modified with 4-mercaptobenzyl alcohol is studied as a function of the number of hydroxyl groups present in the polymer and the amount of crosslinking agent added. Comparison of crosslinking reaction of a hydroxylated PVC polymer synthesized in our laboratory and a commercial system shows a higher reaction rate and degree of conversion for the former. Swelling experiments of partially crosslinked polymers reveal the existence of two kinds of interpenetrated networks, chemical and physical. The appearance of the physical network is due to hydrogen bonding interactions between the remaining hydroxyl groups in the polymer chains after crosslinking. Thermogravimetric analysis and traction tests show good thermal stability of the networks obtained, and a significant improvement in the mechanical properties with respect to linear PVC. M_c values obtained from swelling experiments, mechanical tests and dynamomechanical tests are in agreement with the theoretical values. © 1999 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Chemical crosslinking of linear polymers may provide feasible routes for the improvement of polymer properties. In addition to the mechanical properties, the thermal stability is also improved in polyolefins and halogenated polymers, amongst others [1–5].

In particular, many industrial or laboratory processes, as well as commercial crosslinking agents, have been described in the literature for the crosslinking of poly(vinyl chloride) (PVC) [6–30]. Some of these have found application in the cable industry [19–21], and others are already in development [22–31]. All of these crosslinking agents lead directly, in a single step, to network formation and, as a consequence, the detailed characterization of the networks and the estimation of their dimensions are rather difficult.

In our laboratory, PVC containing hydroxyl groups by the modification of the PVC has been synthesized with a new family of thio derivatives from mercaptobenzyl alcohol. This reagent has two reactive functional groups: a mercapto group, which is randomly grafted into the polymer by substitution of the chlorine atoms, and a hydroxyl group, which reacts easily in a second step with a specific crosslinking agent [32,33]. The synthesis, characterization and properties of this hydroxylated PVC have been reported previously in this journal [33]. The modified polymer incorporating hydroxyl groups in well-defined positions can be totally or partially crosslinked, thus giving rise to networks of a well-defined number and position of crosslinks with or without free hydroxyl groups. This crosslinked polymer will have improved thermal and mechanical properties.

In this work, we report the characterization and properties of hydroxylated PVC crosslinked with diisocyanates.

2. Experimental

2.1. Crosslinking reaction

Starting from a commercial bulk polymerized PVC, the synthesis of 4-mercaptobenzyl alcohol-modified poly(vinyl chloride) (PVC-OH) was carried out according to the method described in previous work [32,33]. Solutions of PVC-OH in dry tetrahydrofuran (THF; 50 mg/ml) with different molar proportions (with respect to the number of hydroxyl groups) of 1,6-hexamethylene diisocyanate (HMDI) were prepared in 5-ml hermetically sealed glass flasks at 60°C. The homogeneous viscous solution was then placed on a glass plate and the solvent evaporated in a slow stream of dry N_2. Crosslinking of the films was carried out in a vacuum oven at 60°C over a period of 6 h.

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Purification of the networks obtained was achieved by extraction with THF (24 h) and diethyl ether (24 h) in a Soxhlet apparatus.

In this study, networks of varying crosslinking density and number of free hydroxyl groups were investigated. The latter systems were synthesized using a less than stoichometric amount of NCO groups and employing PVC-OH with different hydroxyl group contents.

2.2. Crosslinking kinetics

Crosslinking of modified PVC was followed by IR spectroscopy on a Nicolet 520 IR-FT spectrophotometer. During the crosslinking of unextracted films of 15–40 μm thickness, prepared as described above, spectra were recorded at different time intervals. The degree of conversion of the crosslinking reaction was determined using a method described previously [33,34], allowing the estimation of the concentration of reacted HMDI.

2.3. Swelling measurements

In order to determine the network dimensions of the crosslinked systems swelling experiments were performed using the following procedure. Samples with a cylindrical symmetry (diameter 1.3 cm, thickness 0.3 mm) were extracted in a Soxhlet apparatus, for 24 h in THF, and then for 12 h with diethyl ether, and finally dried for 6 h at 40°C. After determination of their dry weight (w_0), the samples were then immersed in THF at 40°C and swollen to equilibrium (48 h). The laminates were drawn from the solvent, their surfaces dried carefully and weighed (w_s) immediately. The average molecular weight between crosslinks, $\bar{M}_c$, was calculated according to the Flory–Rehner theory [35,36] using the formula:

$$\bar{M}_c = \frac{-\rho_2\left(1 -{}^{2}/_{\phi}\right)V_1V_2^{1/3}}{\ln(1 - V_2) + \chi V_2^2 + V_2}$$

$$V_2 = \frac{1}{1 + \left(\frac{\rho_2}{\rho_1}\right)\frac{w_s - w_0}{w_0}},$$

where ρ_1 and ρ_2 are the density of the solvent and the polymer, respectively, ϕ the functionality of crosslinking, V_1 the molar volume of the solvent, V_2 the volume fraction of the polymer in the swollen network, and χ the polymer–solvent interaction parameter. w_0 and w_s are the dry and swollen weights of the network, respectively. The following values were used for the evaluation: $\rho_{THF} = 0.88$ g/cm^3, $\rho_{PVC} = 1.39$ g/cm^3, $V_1 = 82.3$ cm^3/mol, $\chi = 0.21$ and $\phi = 4$.

2.4. Thermogravimetric analysis

The thermal stability of the crosslinked polymers was evaluated by thermogravimetric analysis (TGA) performed on a Perkin Elmer TGA-7, using an N_2 stream as purge gas, at heating rates of 5, 10, 15, 20 and 30°C/min in the range of 50–600°C. The initial decomposition temperatures were taken as the point of onset. The activation energies for decomposition were calculated according to the Flynn–Wall kinetic analysis model [37].

2.5. Traction tests

The stress–strain behaviour of the crosslinked PVC-OH was studied on a temperature-controlled universal Instron dynamometer. The measurements were performed at 90°C, using a 0.1 kN load cell and with a testing speed of 50 mm/min.

Samples were prepared from extracted crosslinked films, obtained as described above. Dumbbell samples of 2 mm width at the deformation zone and 100–200 μm thickness were cut. For each sample, a minimum of four samples were tested.

2.6. Dynamomechanical thermal analysis

The viscoelastic behaviour of crosslinked polymers was tested on a Polymer Laboratories DMTA MKII dynamomechanical thermal analyser. Experiments were carried out in load mode at constant stress with a reducing force device, at frequencies of 3, 5, 10 and 30 Hz, in the temperature range of 30–120°C, with a heating rate of 2°C/min.

Samples were prepared from extracted crosslinked films, obtained as described above. Rectangular samples of 2.2 mm width, 3 cm length and 100–120 μm thickness were cut.

3. Results and discussion

In a previous paper, it was shown [33] that the kinetics of crosslinking of the modified PVC with HMDI can be studied by IR spectroscopy by following the disappearance of the NCO band at 2277 cm^{-1} and the simultaneous formation of a urethane band at 1729 cm^{-1}. In the present work, it can be demonstrated that this reaction is almost quantitative and that different crosslinking densities, as well as networks with free hydroxyl groups, can be obtained according to the degree of modification of the PVC and the amount of diisocyanate employed.

The nomenclature used in this work to denominate the crosslinked polymers is based on both the degree of modification of PVC (molar percentage of hydroxyl groups) and the amount of HMDI added for crosslinking to occur (expressed as molar percentage of NCO groups). In this way, the samples are designated PVC-OH α% NCO β%, although in general we will consider 'completely crosslinked polymers' if the ratio [OH]/[NCO] = 1 and 'partially crosslinked polymers' if the ratio [OH]/[NCO] > 1.

3.1. Crosslinking reaction

In previous studies on PVC-OH crosslinking with HMDI, it was shown that, in the case of a completely crosslinked

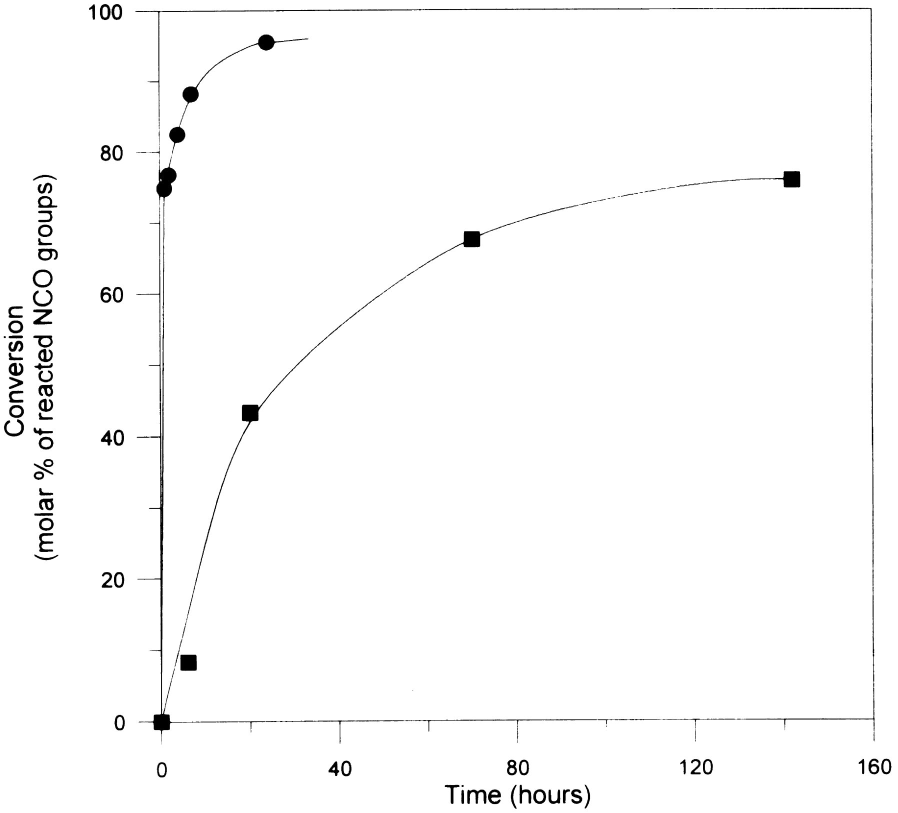

Fig. 1. Kinetics of crosslinking at 60°C and [OH]/[NCO] = 1. (●) PVC modified 6.5% with 4-mercaptobenzyl alcohol; (■) commercial (vinyl chloride–vinyl alcohol–vinyl acetate) terpolymer with 6% (molar) vinyl alcohol.

polymer, such as PVC-OH 13.2% NCO 13.2%, it is easy to reach degrees of conversion of up to 80% in 7 hours, but on extending the reaction time the conversion does not vary significantly. The degrees of conversion of PVC-OH 7.3% polymers crosslinked with 2.7, 5.0 and 7.3 mol.% of NCO at 60°C for 6 h are 100%, 98% and 94%, respectively. This means that the crosslinking reaction is practically quantitative. Only in the case of the sample with a ratio [OH]/NCO] = 1 is the degree of conversion lower than 95%. Combining these results with that observed previously, we can conclude that the crosslinking reaction is quantitative if the number of hydroxyl groups present in the polymer is greater than the number of NCO groups added. In the case of completely crosslinked polymers, the degree of conversion decreases due to a loss in the mobility of the polymer chains as the network density increases, thus reducing the accessibility to the reactive groups. This could also explain the different values of conversion reached in the samples PVC-OH 13.2% NCO 13.2% (78%) and PVC-OH 7.3% NCO 7.3% (93%).

On the other hand, we have considered it to be of interest to compare the crosslinking reaction of a commercial hydroxylated PVC with that of the PVC-OH synthesized in our laboratory. In Fig. 1, the crosslinking kinetics of both a vinyl chloride–vinyl acetate–vinyl alcohol terpolymer (with a molar content of 6% in hydroxyl groups) and PVC-OH 6.5%, with HMDI at 60°C, are shown. It can be clearly observed in this figure that the crosslinking reaction of PVC modified with 4-mercaptobenzyl alcohol has a significantly higher reaction rate and leads to larger degrees of conversion. This can be explained by the greater accessibility of the benzyl hydroxyl groups compared to vinyl hydroxyl groups: hydroxyl groups from vinyl alcohol terpolymer, directly bonded to the polymer chain, have a high steric hindrance, and the reaction is perturbed compared with that of PVC-OH, where the hydroxyl groups are separated from the chain by the mercaptobenzyl residue.

3.2. Network dimensions

In this section, the mean average molecular weight between crosslinks ($\bar{M}_c$) of the synthesized networks was studied by means of swelling measurements. In Fig. 2(a), the $\bar{M}_c$ values of networks formed from PVC 22% modification are plotted as a function of the amount of diisocyanate used for the crosslinking reaction. It can be seen that there is a strong discrepancy between the measured and the theoretical curves for low concentrations of crosslinking agent, but that quite a good agreement is observed when crosslinking is performed quantitatively. This last point is confirmed in Fig. 2(b), where the $\bar{M}_c$ values of PVC-OH crosslinked in equimolar ratios of [OH]/[NCO] are presented. In this case, the measured network dimensions agree very well the calculations. Finally, Fig. 2(c) shows the $\bar{M}_c$ values for different PVC-OHs crosslinked with a fixed amount of NCO groups (2%) as a function of the degree of modification of PVC. An increase can be observed in the deviation between the theoretical and experimental values as the degree of modification increases, i.e. with a greater number of hydroxyl groups remaining in the network.

The fact that the $\bar{M}_c$ values found in networks with free hydroxyl groups are lower than the expected mesh dimensions, and the almost independence of $\bar{M}_c$ with respect to the NCO concentration in Fig. 2(a), leads to the conclusion that a second mechanism must exist, apart from the chemical crosslinking, which links polymer chains together. It can be supposed that the presence of free hydroxyl groups in the system leads to the formation of a physical network due to hydrogen bonding interactions, which is superimposed onto the chemical network. This explanation is supported by the fact that the smaller the amount of NCO used for crosslinking, the higher the amount of free hydroxyl groups remaining in the network, and the more likely the formation of a physical network by hydrogen bonding. The existence of this type of interactions has already been shown in previous work on PVC modified with 4-mercaptobenzyl alcohol, by differential scanning calorimetry and light scattering measurements, and by the evaluation of the mechanical properties of these PVC-OH systems [33].

3.3. Thermal stability

The thermal stability of the modified and crosslinked polymers was studied by TGA. In an earlier publication [38] on the thermal degradation of PVC modified with thiol compounds, it was demonstrated that the polymer is stabilized at low degrees of modification due to the substitution of the most labile chlorine atoms, but that at higher conversions an unstabilization occurs.

In Fig. 3, the TGA thermograms of partially crosslinked and completely crosslinked PVC-OHs are compared. In the networks, the first weight loss process, which is associated with the loss of absorbed moisture and/or with the evaporation of trapped solvent, is shifted to temperatures which are about 50°C higher than in the linear polymers, where the first weight loss corresponds to the degradation of the most labile chlorine atoms.

The second weight loss process corresponds to the complete degradation of the polymeric system. In all samples, this appears in the range of 245–255°C, and a slight shift to higher temperatures is observed as crosslinking increases.

With regard to the kinetics of degradation, the application

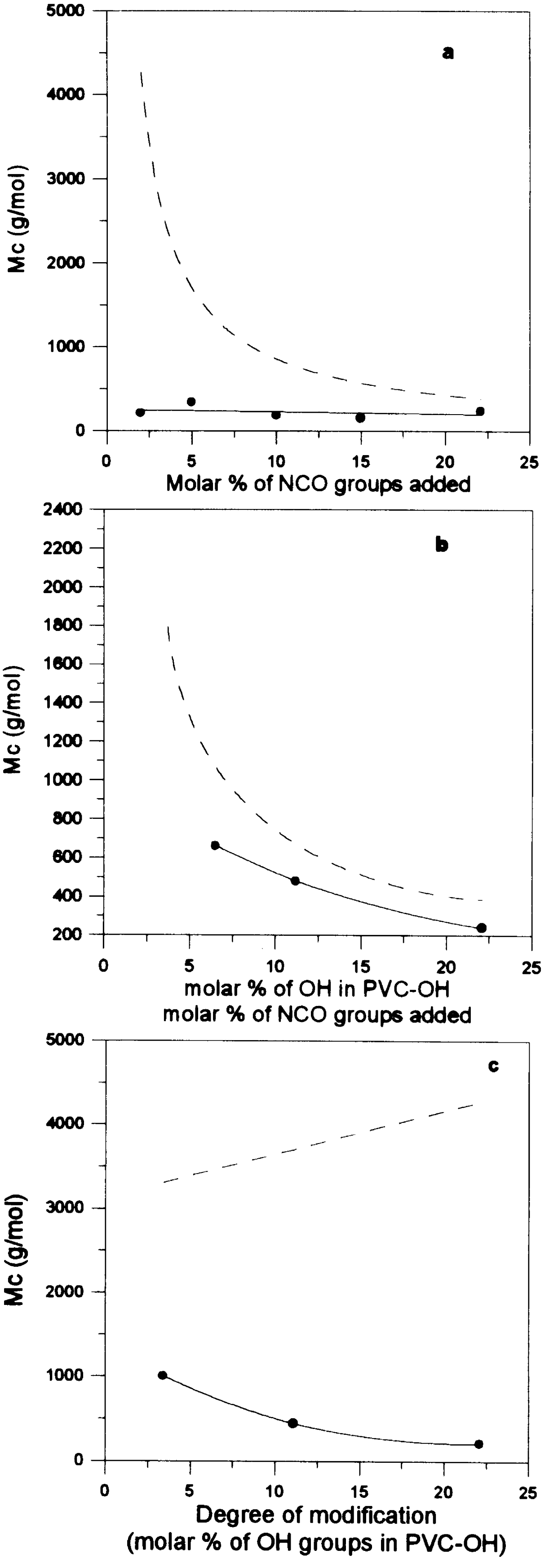

Fig. 2. Evolution of average molecular weight between crosslinks. (a) In the crosslinking of PVC-OH 22.1% with different amounts of HMDI. (b) In the crosslinking of different PVC-OHs with a ratio [OH]/[NCO] = 1. (c) In the crosslinking of different PVC-OHs with 2% (molar) NCO groups. (– – –) Theoretical calculations; (●) experimental data.

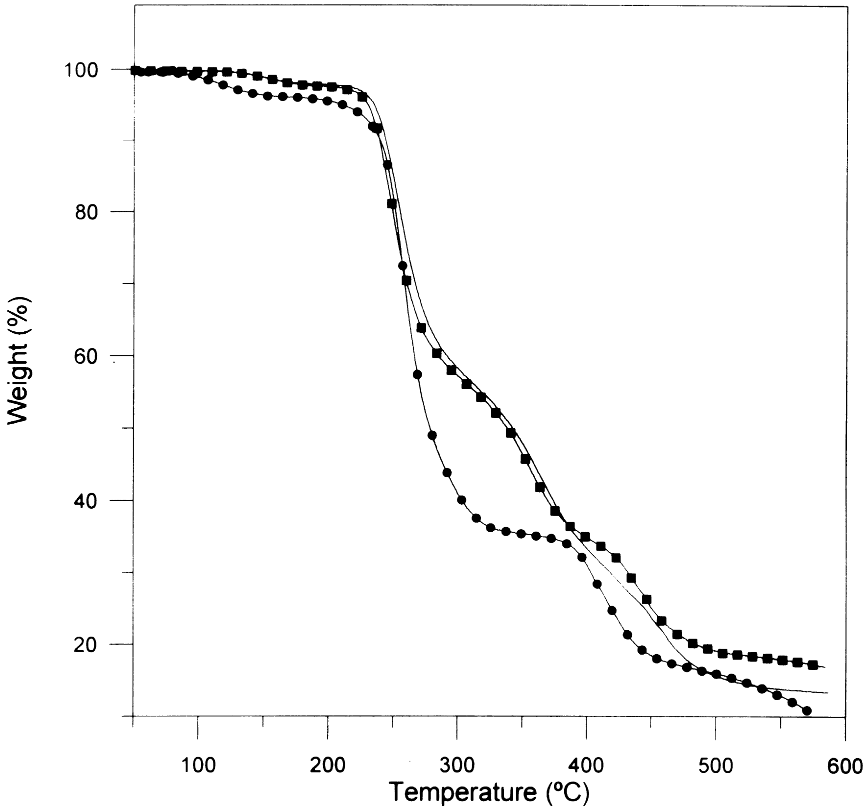

Fig. 3. Thermograms from TGA, registered at 10°C/min. (●) PVC; (■) PVC-OH 11.2% NCO 3.7%; (———) PVC-OH 11.2% NCO 11.2%.

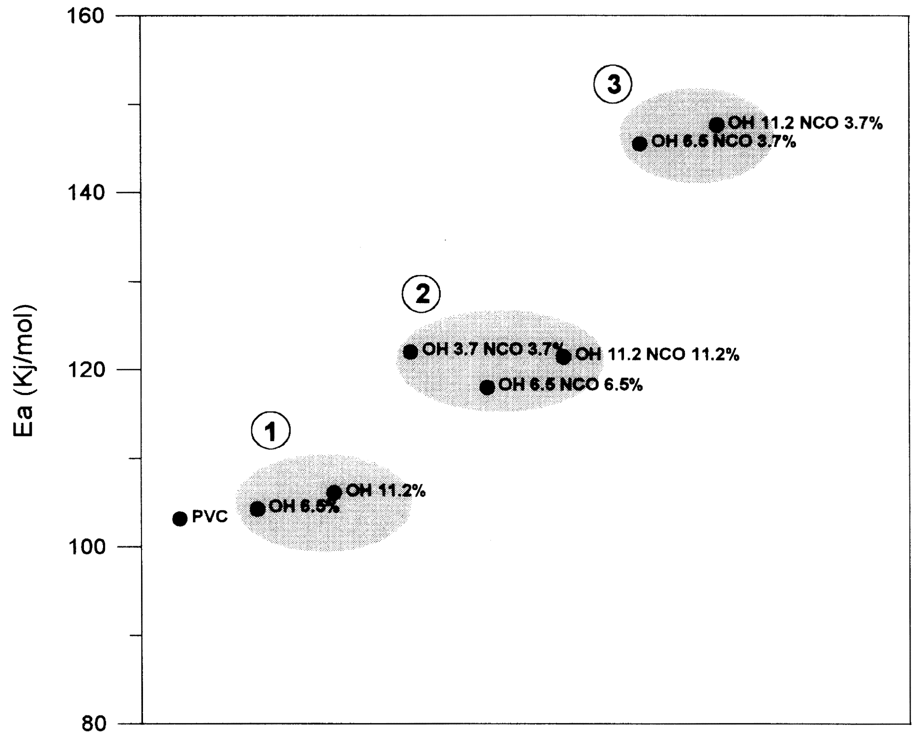

Fig. 4. Activation energies of the polymer chain degradation, determined from TGA by the Flynn–Wall kinetic model, grouped as a function of the type of polymer. (1) PVC modified with 4-mercaptobenzyl alcohol; (2) completely crosslinked PVC-OH; (3) partially crosslinked PVC-OH.

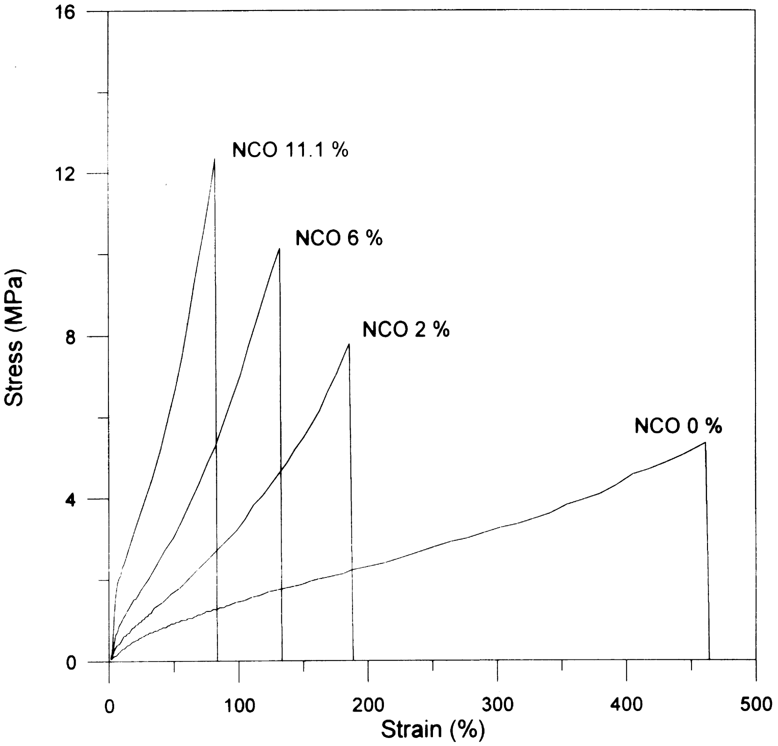

Fig. 5. Stress–strain curves of PVC-OH 11.1% crosslinked with different amounts of HMDI.

of the Flynn–Wall model to the second weight loss process allows us to obtain the activation energy (E_{ad}) for the polymer degradation. In Fig. 4, results obtained from this study are shown, where the E_{ad} values are grouped as a function of the nature of the samples: linear modified PVCs, partially crosslinked PVC-OH and completely crosslinked PVC-OH. The modified polymers have E_{ad} values similar to those of PVC, and completely crosslinked PVC-OH values are greater, but partially crosslinked PVC-OH gives the highest overall values. Although it is difficult to explain the behaviour of the latter group of samples, it is clearly demonstrated that crosslinking leads to an improvement in the thermal stability of those polymers, thus making them attractive for many applications.

3.4. Mechanical properties

Mechanical properties of modified and crosslinked PVCs were performed at 90°C on a universal dynamometer, where they were tested for tensile strength at break, Young's modulus and elongation at break. These parameters can be evaluated from the respective stress–strain curves. As an example, the stress–strain curves of PVC modified 11.1% (molar) with 4-mercaptobenzyl alcohol and crosslinked with different amounts of HMDI are plotted in Fig. 5, where the existence of an improvement in the mechanical behaviour can be observed as crosslinking increases.

In Figs. 6 and 7, Young's modulus and the deformation at break for modified PVCs with degrees of modification of 11.2% and 6.5%, respectively, are presented as a function of the amount of crosslinking agent. Young's modulus increases strongly with increasing crosslinking density and exhibits a value approximately an order of magnitude higher in the completely crosslinked state when compared to that of the linear polymer. The good agreement between the curves for PVC with different degrees of modification must be emphasized. The small differences can be explained by the variation in the number of free hydroxyl groups in the chains. On the other hand, elongation at break decreases as crosslinking increases, leading to very short elongations with respect to that of PVC.

3.5. Viscoelastic behaviour of crosslinked PVC-OH networks

The rubber elasticity theory predicts the relationship between the viscoelastic properties of a polymer network and its dimensions, which can be expressed by the following general equation:

$$\bar{M}_c = \frac{\rho RT}{G},$$

where ρ is the polymer density, G is the shear modulus, R the ideal gas constant and T the absolute temperature at which the modulus is measured.

The G values have been obtained by two different methods, the first by dynamomechanical thermal analysis (DMTA). Michel and co-workers [39] assumed that the storage modulus (G') tends to plateau at low frequencies, thus defining the equilibrium modulus from the rubber

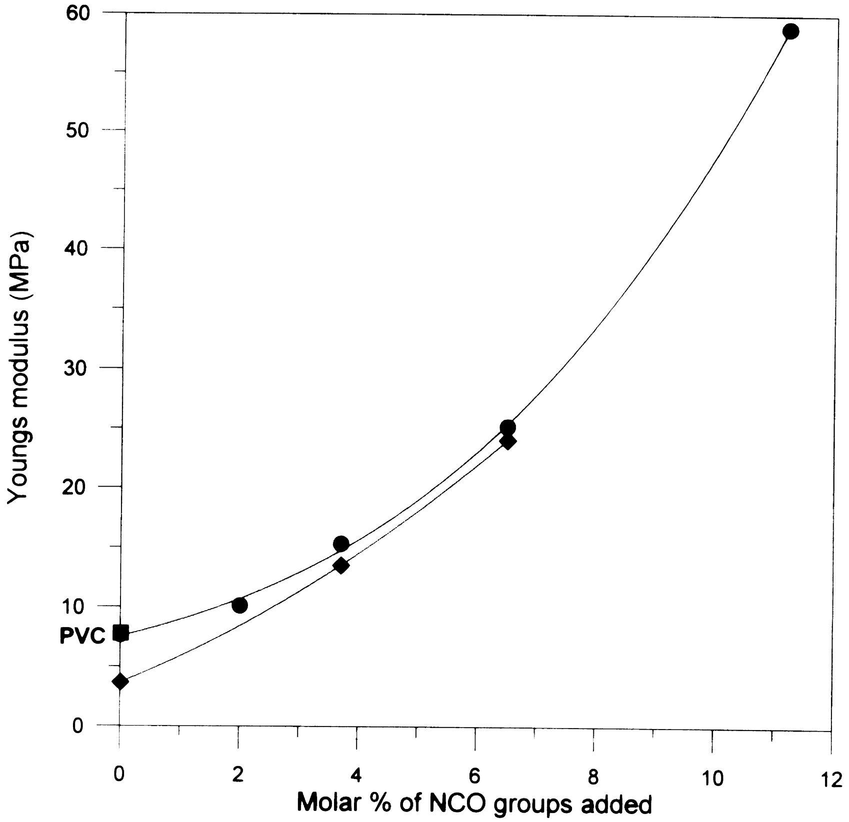

Fig. 6. Evolution of Young's modulus with the degree of crosslinking. (■) PVC; (◆) PVC-OH 6.5%; (●) PVC-OH 11.1%.

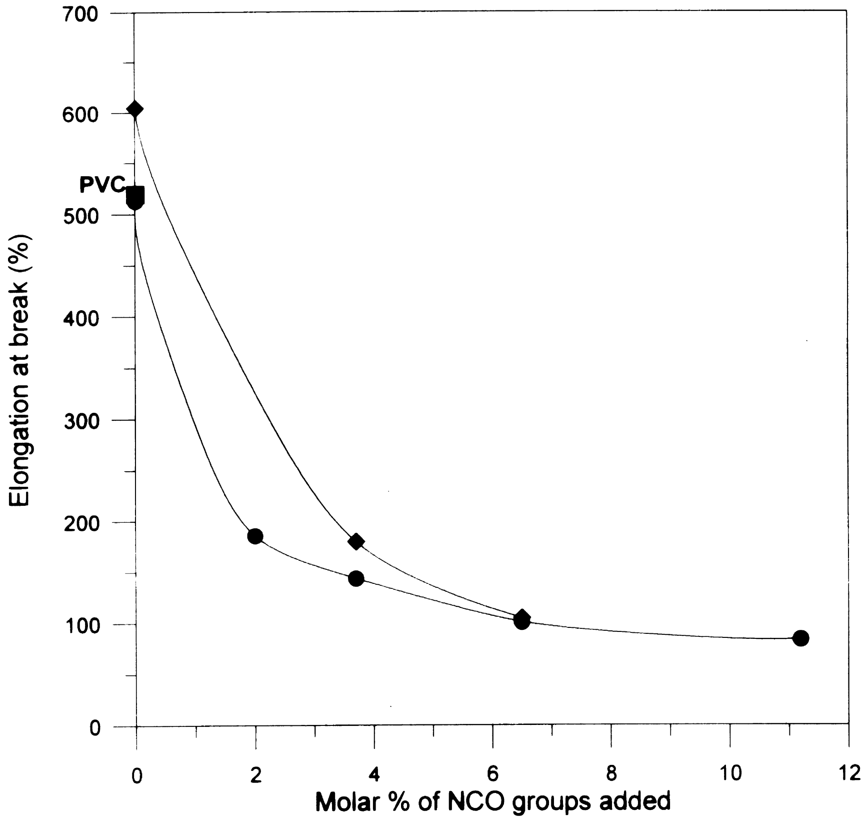

Fig. 7. Evolution of elongation at break with the degree of crosslinking. (■) PVC; (◆) PVC-OH 6.5%; (●) PVC-OH 11.1%.

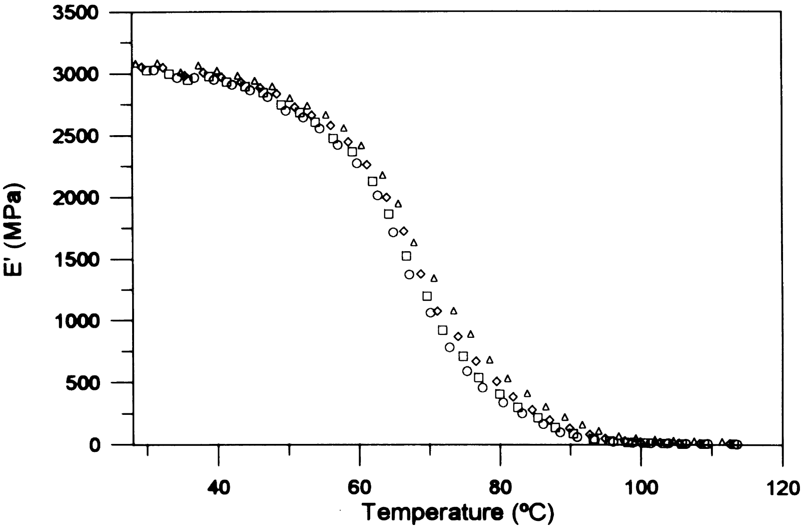

Fig. 8. Storage modulus as a function of temperature from the DMTA of a crosslinked PVC-OH (OH 24.6% NCO 24.6%) at different frequencies: (○) 3 Hz; (□) 5 Hz; (◇) 10 Hz; (△) 30 Hz.

elasticity theory. It is possible that in our case the frequencies used (3, 5, 10 and 30 Hz) may not be sufficiently low; however, at temperatures significantly higher than T_g, the G' values are almost constant, as can be seen in Fig. 8.

The second method for estimating the G values is from stress–strain curves. The modulus obtained from this type of experiment is Young's modulus, but there is a known relationship [1,40] between three types of moduli, i.e. Young's modulus (E), shear modulus (G) and bulk modulus (K), given by

$$E = \frac{9GK}{3K + G}.$$

This expression can be reduced if $T > T_g$, since $K \gg G$, and thus

$$E = 3G.$$

On that basis, $\bar{M}_c$ values were calculated from the storage modulus obtained in DMTA experiments at $T = T_g + 15$, and from the Young modulus (E) at 90°C from traction tests. These data were corrected to eliminate the contribution of the hydrogen bonding interaction (hydroxyl physical network) to the experimental E value of the crosslinked polymers, by subtraction of the E value of the corresponding linear hydroxylated polymer. The results obtained are presented in Fig. 9, and compared with those of the swelling experiments and the theoretical calculations for an ideal network.

A reasonable agreement between $\bar{M}_c$ values from swelling and traction tests is found. The agreement between experimental and theoretical values is quite good considering the non-ideal character of the real network. In this way, the global deviation of the experimental data to values lower than the theoretical ones can be explained by the existence

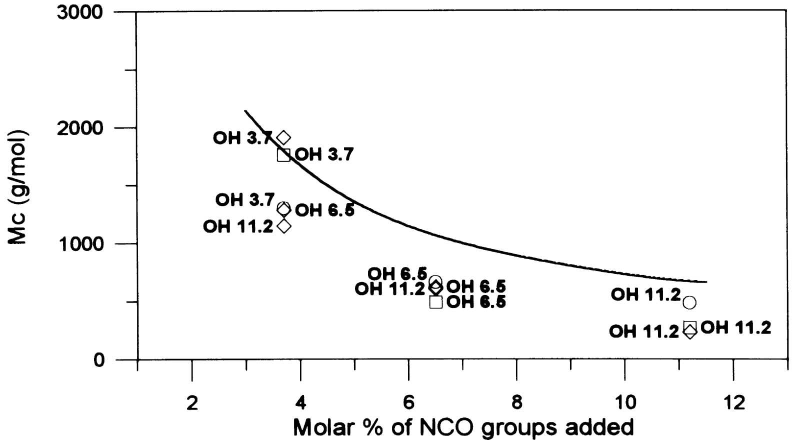

Fig. 9. Comparison of $\bar{M}_c$ values obtained by different methods as a function of the degree of crosslinking. (○) From swelling experiments; (□) from DMTA; (◇) from traction tests; (———) theoretical. The molar percentage of hydroxyl groups in PVC-OH is noted near the dots.

of physical crosslinks due to the macromolecular coil conformation in the real network, in comparison to the ordered ideal network.

4. Conclusions

The crosslinking of PVC modified with 4-mercaptobenzyl alcohol by addition of HMDI was carried out under moderate conditions and in short times, leading to a practically quantitative process. This reaction has allowed us to obtain chemical networks with different crosslinking densities and numbers of free hydroxyl groups.

In agreement with previous results on the behaviour of linear PVC-OH, the existence of a physical network due to hydrogen bonding interactions between hydroxyl groups has been found in the case of partially crosslinked polymers. The reliance of the estimated chemical network dimensions is confirmed by the agreement of the $\bar{M}_c$ values determined by different methods. The studies on the physical properties of crosslinked polymers show a good thermal stability and a huge improvement in the mechanical properties with respect to those of PVC.

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References

[1] Fischer M. Adv Polym Sci 1992;100:313.
[2] Narkis M, Tzur A, Vaxman A, Fritz HG. Polym Eng Sci 1985;25(3):853.
[3] Anderlink R, Fritz HG. Int Polym Process 1992;VII(3):212.
[4] Langley NR, Ferry JD. Macromolecules 1968;1:353.
[5] Giménez V, Mantecón A, Cádiz V. J Polym Sci, Part A: Polym Chem 1996;34:925.
[6] Mori K, Nakamura Y. J Polym Sci, Part A: Polym Chem 1978;16:1981.
[7] Mori K, Nakamura Y. J Polym Sci, Part A: Polym Chem 1978;16:2055.
[8] Mori K, Nakamura Y. Rubber Chem Tech 1984;57:34.
[9] Mori K, Nakamura Y. J Appl Polym Sci 1985;30:1049.
[10] Jandó T, Mori K. Polym J 1990;22:793.
[11] Oravec J, Oishi Y, Hirahara H, Mori K. Polym Int 1993;32:303.
[12] Klier I. Int Polym Sci Tech 1993;20:T65.
[13] Gonnu M, Michel M. Makromol Chem Macromol Symp 1989;25:219.
[14] Flores R, Perez J, Cassagnau P, Michel A, Cavaille JY. Polymer 1994;35:2800.
[15] Ducháček V, Kuta A. J Appl Polym Sci 1982;27:1549.
[16] Behal M, Ducháček V. J Appl Polym Sci 1989;37:429.
[17] Rodríguez-Fernandez O, Sánchez-Adame M. J Vinyl Tech 1991;13:184.
[18] Arias-Marín E, Ramos del Valle LF, Rodríguez-Fernandez O, Rodríguez-Velázquez J. J Vinyl Addit Tech 1995;1:217.
[19] Dufton PW. Recent developments for wire and cable. United Kingdom: Rapra Technology, 1995.
[20] Dahl R, Ryningen Å, Lundquist M, Rodgestedt M. PVC 93. The future. Technical, commercial, environmental strategy for survival. April 93, Brighton, UK, 1992.
[21] Saam JC, Thomas B. UK Patent 1485263, 1973.
[22] Hjertberg T, Dahl R, Sörvik E. J Appl Polym Sci 1989;37:1239.
[23] Hertberg T, Dahl R. J Appl Polym Sci 1991;42:107.
[24] Hearn MS, Baird JD, Nethsinghe LP, Gilbert M. Polym Commun 1990;31:194.
[25] Rodríguez-Fernández OS, Gilbert M. J Appl Polym Sci 1997;66:2111.
[26] Rodríguez-Fernández OS, Gilbert M. J Appl Polym Sci 1997;66:2121.
[27] Kelnar I, Schätz M. J Appl Polym Sci 1993;48:657.
[28] Kelnar I, Schätz M. J Appl Polym Sci 1993;48:669.
[29] Hidalgo M, González L, Mijangos C. J Appl Polym Sci 1996;61:1251.
[30] Hidalgo M, Beltrán MI, Reinecke H, Mijangos C. J Appl Polym Sci 1998;68:000.
[31] Reinecke H, Mijangos C. Polym Bull 1996;36:13.
[32] Reinecke H, Hidalgo M, Mijangos C. Macromol Rapid Commun 1996;17:15.
[33] Hidalgo M, Reinecke H, Mijangos C. Polymer 1999;40:3525.
[34] Hensema ER, Berger J. Angew Makromol Chem 1993;209:145.
[35] Flory PJ, Rehner J. J Chem Phys 1943;11:521.
[36] Flory PJ. J Chem Phys 1950;18:108.
[37] Flynn JH, Wall LA. Polym Lett 1996;4:323.
[38] Martínez G, Mijangos C, Millán J. J Macromol Sci-Chem 1982;A17(7):1129.
[39] Espinasse I, Cassagnau P, Bert M, Michel A. J Appl Polym Sci 1994;54:2083.
[40] Nielsen LE, Landel RF. In: Faulkner LL, editor. Mechanical properties of polymers and composites, 2nd ed., chap. 2. New York: Marcel Decker, 1994.