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Probing the degree of crosslinking of a cellulose based superabsorbing hydrogel through traditional and NMR techniques

F. Lenzi[a], A. Sannino[a], A. Borriello[a], F. Porro[a], D. Capitani[b], G. Mensitieri[a,*]

[a]*Department of Materials and Production Engineering, University of Naples Federico II, P.le Tecchio 80, 80125 Naples, Italy*

[b]*Institute of Chemical Methodologies, National Research Council, Research Area of Rome, via Salaria km 29.300, 00016, Monterotondo Stazione, Rome, Italy*

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Abstract

The network structure of a cellulose-based superabsorbing material has been probed by using three different techniques: ^{13}C solid state NMR, free swelling in water and uniaxial compression of water swollen samples. A good agreement between the three apporaches has been found in terms of concentration of crosslinks per unit volume.

The results have been discussed taking into account that NMR technique is able to detect only chemically effective crosslinks while free swelling and compression are sensitive to elastically effective physical and chemical crosslinks.

A depression of swelling capacity and an apparent increase of degree of crosslinking with time, promoted by ageing of the cellulosic material, has been experimentally evidenced and discussed in terms of development of intermolecular physical interactions.

Keywords: Degree of crosslinking; Cellulose; Swollen hydrogel

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1. Introduction

Superabsorbing polymeric materials have a wide range of applications, mainly in the field of personal hygiene products [1,2], which represents 80% of the hydrogels production nowadays, with more than 8000 tons demand in 1999 only on the european market. An important focus of the research in this field is material's biodegradability. Modern superabsorbents are acrylamide based products and, as such, non-biodegradable. The renewed attention of Institutions and public opinion towards environmental protection issues sensibilized some producers in the development of biodegradable superabsorbents. Potentially biodegradable cellulose based superabsorbent can be synthesized with sorption properties similar to those displayed by acrylate based products [3,4]. These materials can be obtained by chemical crosslinking of cellulose polyelectrolyte derivatives using small difunctional molecules as crosslinkers, which creates intermolecular covalent bonds among polymer molecules forming a three-dimensional hydrophilic network. Further improvement of water sorption capacity can be obtained by inducing the formation of a microporous structure [4].

Swelling properties of crosslinked hydrophilic polyelectrolites in aqueous solutions are determined by several chemical and structural factors, i.e. hydrophilicity of polymer backbone, degree of crosslinking, density and type of fixed charges, degree of ionization and amount of ionic groups and eventual presence of porosity. The relative importance of these factors depends upon the properties of aqueous solution in contact with the network, i.e. pH, ionic strength, presence of other solvents.

The free energy change associated with the swelling process is made of several contributions [5–11] that are related to polymer/solvent mixing, elastic response of the network, presence of bound and mobile ions and electrostatic interactions among fixed charges present on the polymer chains. These factors, in turn, are related to the above mentioned chemical and structural factors.

In particular, the effect of entropic elasticity of the network, which becomes of major importance at high swelling degree, is strongly dependent upon the degree of cross-linking. In fact, water sorption capacity of crosslinked polymeric networks is affected significantly by the elastically effective degree of crosslinking, which takes into

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[*] Corresponding author. Tel.: +39-817682512; fax: +39-817682404.
E-mail address: mensitie@unina.it (G. Mensitieri).

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account the effect of all segments of macromolecular chains which react elastically to their elongation promoted by network swelling. Crosslinks, which act as constraints to the movement of segment ends 'anchoring' them to the network, can be both chemical and physical: the elastically effective chemical crosslinks are all binding points among chains with the exclusion of those of them generating 'dangling ends' and 'loops'. The elastically effective physical crosslinks are, for example, chain entanglements [12] or strong intermolecular interactions. Conversely, the chemically effective crosslinks are intended as all the chemical crosslinks, both elastically effective and not.

The degree of crosslinking (d.c.) is defined as the number density of junctions joining the chains into a permanent structure. According to this definition the degree of crosslinking is given by [5]

$$\text{d.c.} = \frac{\nu}{2V} \tag{1}$$

where $\nu/2$ is the total number of chemical cross-links and V is the total volume of polymer.

In the case of a perfect network with no dangling ends, loops and entanglements, which could be obtained by joining pair of segments of linear chains through chemical cross-links, the concentration of elastically effective chain elements, $\rho_x = \nu_e/V$, corresponds to the concentration of all chemically crosslinked polymer segments (ν/V):

$$\rho_x = \frac{\nu_e}{V} = \frac{\nu}{V} = \frac{1}{\bar{v}\bar{M}_C} \tag{2}$$

where $\bar{v}$ is the specific volume of the polymer, $\bar{M}_C$ is the average molecular weight between cross-links, and ν_e/V are the moles of elastically effective chains per unit volume of network. According to the definition given above, ρ_x and $\rho_x/2$ represent, respectively, the moles of polymer segments engaged by crosslinks and the moles of crosslinks per unit volume of the network.

Generally, the determination of elastically effective crosslinking density can be performed, among other techniques, by using equilibrium swelling measurements or by performing uniaxial compression tests on swollen networks [5,13–16]. These techniques allow a straightforward determination of crosslinking density if the chemical structure is 'simple' and structural complexities (e.g. fixed ionic charges) are absent. In fact, for crosslinked polyelectrolites systems (on which superabsorbing materials are mostly based) the determination through swelling measurements can be performed only if it is possible to evaluate quantitatively the contributions arising from the presence of charges and degree of ionization in the actual experimental conditions [6–11]. A comprehensive collection of equilibrium swelling models in aqueous solutions for chemically crosslinked ionic gels is reported in Ref. [6], where the different contributions of the involved mechanisms are discussed. In turn, if the crosslinking density is determined through mechanical testing (uniaxial compression test) on equilibrium swollen gels [11–16], simplified approaches are often adopted to interpret experimental data, assuming, in general, that the interactions between charges does not affect the mechanical response and that the volume of the gel does not change during the test.

Both experimental approaches supply an overall value for the degree of crosslinking (chemical + physical crosslinking) and rely upon theoretical models for description of polymer/solvent mixing, network elastic behavior and effect of fixed charges present on polymer backbone.

The availability of an alternative experimental technique which is able to supply only the value of the chemically effective crosslinking density, could be an important aid for the characterization of crosslinked systems, both in the field of hydrophilic networks forming highly swollen hydrogels, and of thermosetting polymeric systems in general. To this aim, Solid State NMR spectroscopy repesents a non-destructive approach to gather information on the chemical structure of these amorphous, insoluble materials [17–34] independently of the knowledge of other chemical–physical and structural parameters (such as density of charges, degree of ionization and polymer/solvent interaction parameter). This approach has the advantage of not being affected by the eventual sample microporosity and that no assumptions have to be made or theoretical models have to be adopted to describe the behavior of the network. The main limit is that it accounts also for non-elastically effective chemical crosslinks (those generating loops or dangling ends) while not accounting for physical crosslinks.

In this contribution we compare the results obtained by using three different techniques, i.e. free swelling measurements, uniaxial compression and ^{13}C solid state NMR, to probe the degree of crosslinking of a cellulose based superabsorbing hydrogel synthesized by crosslinking with divinylsulphone a mixture of hydroxyethylcellulose and sodium salt of carboxymethylcellulose, in an aqueous medium.

2. Theoretical background

2.1. Determination of elastically effective degree of crosslinking from free swelling equilibrium

Swelling equilibrium of a polymer with a solvent is obtained when the chemical potentials of the solvent in the polymer phase and in the free solution are the same. This statement can be expressed in terms of osmotic swelling pressure as:

$$\Pi_{\text{MIX}} + \Pi_{\text{ELAS}} + \Pi_{\text{ION}} + \Pi_{\text{ELEC}} = 0 \tag{3}$$

This relationship is based on the assumption that the contributions are simply additive. The first term takes into account the mixing tendency of polymer and solvent. The second accounts for elastic response of the network due to the constrain imposed by the presence of chemical and physical crosslinks. The third and fourth terms, which have to be included if ionizable groups are present, are due, respectively, to differences in mobile ions concentration between gel phase and external solution and to the electrostatic interactions of charges on the polymer backbone. This last term is generally negligible in comparison to the third one in the case of highly swollen systems.

Several theories can be adopted to express mathematically the three prevailing contributions (i.e. $\Pi_{\rm MIX}$, $\Pi_{\rm ELAS}$ and $\Pi_{\rm ION}$). In the present contribution, Flory–Huggins theory [5] has been adopted for the mixing term. For the evaluation of the elastic term the hypotheses [5] of affine deformation and of Gaussian distribution of molecular chains between two crosslink points have been adopted, and the presence of solvent during crosslinking reaction has been accounted for (in fact polymer volume fraction in the starting reacting solution, $\phi_{2,\rm r}$, is smaller than 1). For the evaluation of the ionic term, it has been considered the case of an anionic polymer nework in which the ionic concentration in the external solution is negligible if compared to the ionic concentration inside the gel (ionic strength of the external solution $\cong 0$). This hypothesis is appropriate in the case at hand, in view of the moderate level of crosslinking of the network and of the circumstance that only the equilibrium of the gel with distilled water has been analysed.

A thorough treatment, reporting the analysis of a wider range of cases (e.g. non-Gaussian statistics, high ionic strength of the swelling solution) can be found in Ref. [6].

For the definition of thermodynamic equilibrium, Eq. (3) should be coupled to the expression for the equilibrium between ionic species in the gel phase and in the external solution; as first approximation, we imposed that concentrations are the same inside and outside the gel [5].

On the basis of the assumptions discussed above, the following expression for $\rho_{\rm x}$ can be derived [6,7]:

$$\rho_{\rm x} = \frac{-\dfrac{[\ln(1-\phi_2)+\phi_2+\chi\phi_2]}{v_1} + \dfrac{i\phi_2}{(z_+v_{\rm m})}}{\phi_{2,\rm r}\left\{\left(\dfrac{\phi_2}{\phi_{2,\rm r}}\right)^{1/3} - 0.5\left(\dfrac{\phi_2}{\phi_{2,\rm r}}\right)\right\}} \qquad (4)$$

where $v_{\rm m}$ is the molar volume of structural repeating unit of the network; $\rho_{\rm x}$, the moles of polymer units engaged by crossinks per cm^3 of dry network; $\phi_{2,\rm r}$, the polymer volume fraction in the reaction mixture before full swelling in distilled water (polymer volume fraction in the 'relaxed' network); v_1, the molar volume of swelling solvent; i, the fraction of polymer structural units which carry ionized couples; χ, the Flory–Huggins interaction parameter (polymer/swelling solvent); ϕ_2, the polymer volume fraction at swelling equilibrium and z_+ is the number of electronic charges carried by cations formed through dissociation of ionic groups present on polymer backbone.

In Eq. (4): $-[\ln(1-\phi_2)+\phi_2+\chi\phi_2]/v_1$ is the polymer/water mixing term. $i\phi_2/(z_+v_{\rm m})$ is the contribution related to the presence of ionized ionic couples. $\phi_{2,\rm r}\{(\phi_2/\phi_{2,\rm r})^{1/3} - 0.5(\phi_2/\phi_{2,\rm r})\}$ is the entropic elastic contribution related to the retractive tendency of macromolecular segments; it takes into account that reaction has been performed at $\phi_{2,\rm r} < 1$.

2.2. Detemination of elastically effective degree of crosslinking from uniaxial compression of swollen networks

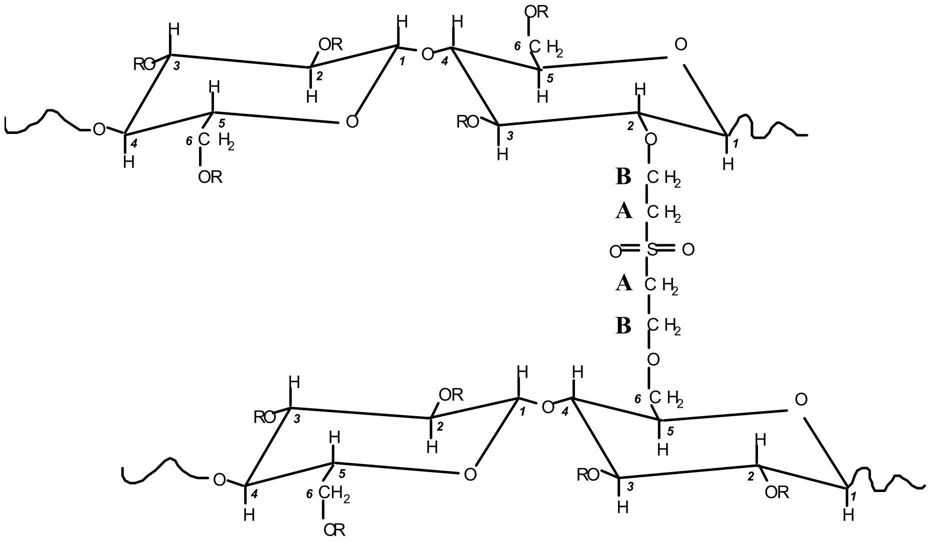
A swollen hydrogel, when submitted to a uniaxial compressive load, displays a deformational behaviour which depends upon the elastic response of deformed chains, to the interaction among fixed charges and to the free energy change associated to the release of some amount of sorbed water. By making the simplifying assumption that no volume change occurs upon compression of the swollen hydrogel, Flory [5] derived a relationship between the compressive stress and the compressive deformation for the case of a swollen croslinked polymer, based on the assumption of Gaussian statistics and of affine deformation. This expression can be easily extended to the case of $\phi_{2,\rm r} < 1$ obtaining [35]:

$$\sigma = RT\frac{\nu_{\rm e}}{V_0}\phi_{2,\rm r}^{2/3}\phi_{2,\rm s}^{1/3}\left(\alpha - \frac{1}{\alpha^2}\right) = G\left(\alpha - \frac{1}{\alpha^2}\right) \qquad (5)$$

where $\sigma = F/A_0$ is the uniaxial compressive stress (where F is the traction force and A_0 is the initial area of swollen sample cross-section), $\alpha = L/L_{\rm i}$, with L, the actual thickness of the compressed swollen sample and $L_{\rm i}$, the initial thickness of the swollen sample, R, the universal gas constant, T, the absolute temperature, $\phi_{2,\rm s}$, the polymer volume fraction in the swollen state under compression which is assumed to be equal to the value for the undeformed swollen gel, $\nu_{\rm e}/V_0$, the moles of elastically effective chains per cm^3 of dry polymer network and G is the shear modulus of the swollen network.

Although this approach is oversimplified, due to the assumption of constant volume (actually some water is squeezed out of the swollen sample as a result of compression), it is suitable to interpret gel deformation behaviour under uniaxial compression in the case of small deformations ($\alpha \longrightarrow 1$) and can be used for the evaluation of the ratio $\nu_{\rm e}/V_0$ and of $\rho_{\rm x}$.

The deviation from Gaussian statistics at large deformations can be taken into account by using a phenomenological expression to describe the behaviour of a swollen crosslinked network submitted to uniaxial extension. This expression can be derived from the expression of Mooney–Rivlin strain energy function [36] for swollen rubbers which accounts for both the deformation due to swelling and the deformation due to compression. Making the assumption of incompressibility, the following expression relating the uniaxial stress σ (referred to the cross-sectional area of undeformed swollen sample) to the extension ratio, α, can



Scheme 1. Schematic structure of CMCNa-HEC crosslinked with DVS.

be derived:

$$\sigma = 2\left(K_1 + \frac{K_2}{\alpha}\right)\left(\alpha - \frac{1}{\alpha^2}\right) \quad (6)$$

where σ has the same definition as in Eq. (5) and the values of K_1 and K_2 are proportional to the swelling ratio of the sample. According to Eq. (6), a plot of $\sigma(\alpha - 1/\alpha^2)^{-1}$ vs. $1/\alpha$ based on experimental data should be linear.

2.3. Detemination of chemically effective degree of crosslinking from solid state ^{13}C NMR measurements

^{13}C Solid State NMR analysis can be used to determine the chemically effective crosslinking degree of a polymer network. The application of this experimental procedure to the system under investigation is reported in full details in Ref. [37]. In brief, the analysis can be carried out by performing ^{13}C cross polarization magic angle spinning (CP-MAS) solid state spectra and single pulse excitation (SPE) experiments. It consists in evaluating the moles of crosslinks per polysaccharide ring by the ratio of half of the area of the resonance peak associated to methylene carbon atoms present on reacted crosslinker molecule (C atoms labeled ‘A’ in Scheme 1) to the area of resonances due to anomeric carbon atoms, C1, present on polysaccharide rings (labeled ‘1’ in Scheme 1). By using this procedure to evaluate the chemically effective degree of crosslinking, we have implicitly neglected reactions occuring between DVS and water and DVS oligomerization. The eventual occurrence of these reactions, which could cause errors in the NMR calculations, could be assessed by proper procedures of hydrolisis of crosslinked polymer and subsequent quantitative analysis of resulting fractions.

3. Experimental

3.1. Materials

Highly absorbing cellulose based hydrogels synthesized in this work have been obtained by crosslinking water solutions of carboxymethylecellulose sodium salt (referred in the following as CMCNa) and hydroxyethylcellulose (referred in the following as HEC) using divinylsulphone as crosslinking agent (referred in the following as DVS).

CMCNa (cod. 41,933-8), HEC (cod. 30,683-3) and DVS (cod.V370-0) were purchased from Aldrich Chimica s.r.l. Milano and used as received. The degree of substitution (D.S.) of CMCNa was 0.66 ± 0.03 [38], while the D.S. for HEC was about 1. Further details on starting materials are reported in Refs. [37,38].

Crosslinking reaction has been performed according to procedures reported in the literature [39]. For this study a mixture of CMCNa and HEC, with a weight ratio equal to 3/1, was first dissolved in a solution of DVS and distilled water by stirring gently at room temperature until a clear solution was obtained. The total polymer weight fraction in the solution was 2%. Two different DVS concentrations were used in order to obtain samples with two degrees of crosslinking: 0.04 and 0.133 moles of DVS per liter of solution. In the following, crosslinked samples prepared with a starting DVS concentration equal to 0.04 and 0.133 mol/l will be referred, respectively, as sample ‘L’ (low crosslinking density) and sample ‘H’ (high crosslinking density). The presence of HEC is necessary to promote quantitatively intermolecular rather than intramolecular crosslinking [39]. After the mixing stage, an aqueous solution of KOH was added as catalyst to the polymer solution until a pH 12.5 was reached. Hydrogel formation occurred in few hours at room temperature. A schematic representation of cross-linked chemical structure is reported in Scheme 1.

To remove unreacted DVS and the KOH, the partially swollen hydrogel was cut in small pieces which were then soaked in distilled water reaching equilibrium swelling under continuous stirring (washing stage). Water was used in volumes greatly exceeding that of hydrogel and was changed several times. These equilibrium swelling data, obtained both for 0.04 and 0.133 moles of DVS per liter of starting solution, have been used (see Section 4) for the determination of elastically effective crosslinking degree before desiccation took place. Typical values of free swelling right after the synthesis were around 880 and 140 g of water per gram of dry polymer, respectively, in the case of sample L and H.

After the washing stage, a dry product was obtained by desiccating hydrogel samples by phase inversion with acetone according to procedures reported in literature [40] and then kept under vacuum for some hours in order to remove residual acetone. This desiccation procedure was used since the high and connected microporosity induced by the fast water extraction procedure guarantees very high water swelling capacity, which was one of the objectives of the present research. The samples obtained with this procedure were in form of a coarse powder. A sample was considered to be desiccated when the water content was lower than 10% by weight of dry polymer. For the sake of comparison, uncrosslinked samples were also prepared (referred in the following as sample 'U'). For this purpose the starting aqueous solution of CMCNa, HEC and DVS (total polymer concentration 2% by weight, CMCNa/HEC ratio equal to 3/1 and DVS concentration equal to 0.133 mol/l) was put directly in contact with acetone and the precipitate collected. Both types of samples were then grinded under liquid nitrogen to obtain a fine powder to be used for NMR solid state analyses.

To perform reliable compressive tests, samples with the lower degree of crosslinking (0.04 moles of DVS per liter of starting solution) were also obtained in the form of thin films (around 50 μm thickness). The procedure was identical to the one reported above till the initial stage of the reaction. In fact, few seconds after the addition of catalyst and the mixing of the components, the reacting solution was poured on teflon trays to be desiccated under a mild convective air flow at 50% relative humidity. Regular films were thus obtained after a 48 h desiccation. Also in this case, samples were considered to be desiccated when the water content was lower than 10% by weight.

Wide angle X-ray scattering analysis performed on crosslinked samples indicated that the samples were totally amorphous [40].

3.2. Methods

3.2.1. Solid State NMR measurements

Finely powdered samples H, L and U were packed into 4 mm zirconia rotors and sealed with Kel-F caps. Solid state ^{13}C CP-MAS NMR spectra [41] were run on a Bruker AC-200 spectrometer, equipped with an HP amplifier for ^{1}H at 200 MHz, 120 W CW and with a pulse amplifier M3205. The spin rate was always kept at 8 KHz. The $\pi/2$ pulse width was 3.1 μs and the recycle delay was 4 s. Spectra were obtained with 1024 data points in the time domain, zero-filled and Fourier-transformed with a size of 2048 data points; 19,000 scans were performed for each experiment.

As a function of the contact time, two series of experiment were performed, with the contact time ranging from 0.02 to 7 ms.

Magic angle spinning with single pulse excitation (MAS-SPE) experiments were performed, the recycle delay was 40 s, the ^{13}C $\pi/2$ pulse width was 2.8 μs. With this experiment a single $\pi/2$ pulse is applied to excite the carbon spectrum which is recorded in the presence of MAS and dipolar decoupling (DD) [42].

Analysis of NMR resonances was performed using the deconvolution program 'GLINFIT' [43]. This program can perform the full deconvolution of overlapped lines both with Gaussian and/or Lorentzian shapes. Line widths, chemical shifts and areas along with their standard deviations were obtained. In the case reported here, the standard deviations on the obtained areas were about 10% of their nominal value.

All tests were performed at 25 °C.

3.2.2. Uniaxial compression tests

Swollen films were placed between two flat plates made of polymethylmethacrylate. Both plates and sample were immersed in a temperature controlled water jacketed container filled with distilled water to prevent drying of swollen network. The upper plate was contacted with a load cell (Burster type 8453, max load 1000 N, sensitivity 0.1 N) attached to a movable frame. The frame carrying the load cell can be moved in extremely small steps monitored by a travelling microscope (accuracy ± 2 μm). Each measuring step consisted in imposing a constant strain and in measuring the associated compressive stress. Once a constant stress value was obtained, it was taken as the equilibrium value and strain was, then, increased further. The design of the compression apparatus allows a continuous contact of the film with distilled water and the cone and cup geometry prevents the relative slipping between upper and lower plate. All tests were performed at 25 °C. For each type of sample, experiments were repeated four times and average values of stress as function of imposed deformation are reported.

3.2.3. Equilibrium free swelling tests

Equilibrium free swelling was measured by first equilibrating in distilled water small pieces of gel, right after the washing stage and then weighing samples removed from the water using a Mettler AE 100 electronic balance with a sensitivity of 10^{-5} g. Before measuring the weight, samples were quickly and gently blotted to remove liquid water from the surface and placed into sealable plastic containers of known weight. Samples were then desiccated at 50 °C under high vacuum (10^{-3} Torr) to determine the dry polymer weight. Equilibrium swelling was then expressed as ratio between grams of absorbed water and grams of dry polymer. All tests were performed at 25 °C.

3.2.4. Water vapour sorption isotherms

Water vapour sorption isotherms were determined at 25 °C by hanging the powdered sample, placed in a glass pan, to a quartz spring microbalance (Ruska Co., Tx, USA, full elongation 400 mm, max. weight 50 mg) operating in a water vapour environment at accurately controlled temperature and pressure. The spring was placed in a water jacketed chamber with service lines to a reservoir of degassed liquid water, to an accurate pressure transducer (M.K.S. Baratron 121 A, with a full scale of 100 Torr and a sensitivity of 0.01 Torr) and to a turbomolecular pump. Before each sorption run, samples were desiccated under vacuum. Water vapour was then admitted in the cell at the selected pressure. Weight increase due to water sorption was monitored by measuring the spring elongation with a travelling microscope (sensitivity of 0.01 mm) until a constant equilibrium weight was reached. Equilibrium sorption values were then reported vs water vapour activity as gram of water absorbed per gram of dry polymer. The water vapour activity at which each sorption run was performed has been evaluated as the ratio p/p_0, where p is the pressure of water vapour at which was performed the sorption run while p_0 is the water vapour pressure at the test temperature.

4. Results and discussion

In the following, we present separately the results obtained by using the three experimental approaches which will be reported as moles of effective chains per cm^3 of dry crosslinked network (ρ_x). It is worth noting that some terms used in the determination of degree of crosslinking from swelling measurements were obtained from NMR analysis, as described in the following sections. As a consequence the experimental errors in the evaluation of ρ_x from swelling measurements, is due both to the errors related to the evaluation of swelling ratio and to the errors related to the determination of some terms from NMR measurements.

Another important point of concern is that the crosslinked polysaccharide based systems under investigation are expected to slowly and progressively develop intermolecular interactions during and also after desiccation, as witnessed by a decrease of swelling capacity of the sample with the time of storage in dry conditions. As a consequence, the elastically effective degree of crosslinking (chemical + physical) increases with ageing of network, likely due to the development of intermolecular interactions, which act as additive physical crosslinks and promote a depression of swelling capacity. Also the effect of the progressive chain association on NMR measurements cannot be ruled out. For this reason the results of swelling, compression and NMR experiments used for the comparison of different techniques, refer only to samples right after their synthesis.

4.1. Degree of crosslinking from free swelling measurements

Swelling tests were performed in distilled and deionized water right after reaction and washing stage, measuring a swelling degree equal to 880 ± 50 g/g and 140 ± 10 g/g, respectively, for sample L and H. Eq. (4), was used to evaluate ρ_x from these data. To perform this calculation, some network parameters must be available: molar volume of repeating unit of the network (v_m), degree of ionization (i), Flory–Huggins interaction parameter (χ).

The value of v_m, molar volume of equivalent repeating unit of the network was evaluated from relative amounts of components as measured by NMR: (see Section 3.2.1) contents of reacted DVS equal, respectively, to 0.04 ± 0.01 and 0.33 ± 0.04 moles per mole of polysaccharide ring were found, respectively, in the case of sample L and H. These results indicate that around 9 and 21% of DVS present in the initial reacting solution was actually involved in the crosslinking reaction, respectively, for L and H sample. The resulting average molecular weights of the equivalent repeating units were 218.4 for sample L and 200 for sample H. Assuming for the dry polymer network a density equal to 1 g/cm^3, the value of v_m is numerically equal to the determined values of the average molecular weight of the equivalent repeating units. As a consequence, the values of 218.4 and 200 cm^3/mol were, respectively, assumed in the case of sample L and of sample H.

The value of i, degree of ionization, can be evaluated once the degree of substitution (DS) of CMC is determined through high field NMR experiments or by conductimetric titration. We assumed, for the interpretation of swelling in distilled water, that $i = i_{MAX}$ since all ionic groups are likely to be ionized. This assumption is supported by the fact that swelling was measured at pH ≅ 7, which is a condition promoting rather complete ionization of the carboanionic COO^- groups on the polymer backbone. Since i expresses the fraction of repeating units carrying ionized ionic couples, an equivalent repeating unit is introduced in order to calculate the degree of ionization: it is a molar average of CMCNa and HEC repeating units and DVS molecular weights as determined on the basis of NMR evaluation of their relative amounts. From the D.S. value of CMCNa (0.665 ± 0.03, see Ref. [38]) it can be easily inferred that i_{MAX} of pure CMCNa (for the case of pH > 7) is ≅ 0.665. Consequently, on the basis of the average molecular weight of the equivalent repeating unit of the

Table 1
Values of relevant terms appearing in Eq. (4) and numerical values with standard deviations of the mixing, elastic and ionic contributions for samples L and H

	Sample L	Sample H
v_m	218.4 cm^3/mol[a]	195 ± 5 cm^3/mol[a]
v_1	18 cm^3/mol	18 cm^3/mol
χ	0.98	0.98
$\phi_{2,r}$	0.0204	0.0235 ± 0.001
ϕ_2	$1.14 \times 10^{-3} \pm 0.05 \times 10^{-3}$	$7.14 \times 10^{-3} \pm 0.5 \times 10^{-3}$
$-[\ln(1-\phi_2)+\phi_2+\chi\phi_2]/v_1$	$-3.46 \times 10^{-8} \pm 0.3 \times 10^{-8}$ mol/cm^3	$-1.35 \times 10^{-6} \pm 0.2 \times 10^{-6}$ mol/cm^3
$i\phi_2/v_m$	$2.6 \times 10^{-6} \pm 0.1 \times 10^{-6}$ mol/cm^3	$1.45 \times 10^{-5} \pm 0.2 \times 10^{-5}$ mol/cm^3
$\phi_{2,r}\{(\phi_2/\phi_{2,r})^{1/3} - 0.5(\phi_2/\phi_{2,r})\}$	$7.23 \times 10^{-3} \pm 0.1 \times 10^{-3}$ mol/cm^3	$1.20 \times 10^{-2} \pm 0.05 \times 10^{-2}$ mol/cm^3

[a] Assuming density of bulk polymer = 1 g/cm^3.

crosslinked structure, values of i_{MAX} for samples L and H were calculated to be, respectively, 0.500 ± 0.020 (about 50% of repeating unit carry an ionized group) and 0.390 ± 0.020 (about 40% of repeating unit carry an ionized group).

Flory–Huggins interaction parameter has been evaluated by fitting water vapor sorption isotherm for crosslinked network at 25 °C using the model introduced by Flory [5] to evaluate the chemical potential of a solute dissolved in a crosslinked polymer, as modified to take into account that crosslinking reaction has been performed at $\phi_{2,r} < 1$:

$$\ln a_1 = \frac{\mu_1 - \mu_1^0}{RT} = \underbrace{[\ln(1-\phi_2) + \phi_2 + \chi\phi_2^2]}_{\text{`}\beta\text{'}} + \underbrace{\frac{v_1 v_e}{v_0}(\phi_2^{1/3}\phi_{2,r}^{2/3} - 0.5\phi_2)}_{\text{`}\alpha\text{'}} \tag{7}$$

where v_1 is water molar volume, a_1 is water activity, μ_1 is the chemical potential of water in the mixture, μ_1^0 is the chemical potential of pure liquid water. For equilibrium sorption with a water vapor at an activity a_1 in the range 0–0.8, α term is <0 since $\phi_{2,r} < 1$. This implies that sorbed amount for a crosslinked polymeric system should be higher than that for the same uncrosslinked polymer system. Actually the experimental results (see Fig. 1) points to the opposite, thus indicating that in this activity range the contribution of term α is much lower than contribution of β term. In other words, the change of χ due to modifications in the chemical composition of polymeric system promoted by crosslinking reaction, overwhelms the effect associated to the entropic responce of macromolecular segments which, if any, would increase, instead, sorption capacity. In fact, it can be readily seen that in the range $a = 0.2$–0.6 the numerical value of α term, in the right hand side of Eq. (6), is less than 1% of the value of β term. As a consequence data fitting has been performed in the range 0–0.6 neglecting the term α and using only term β.

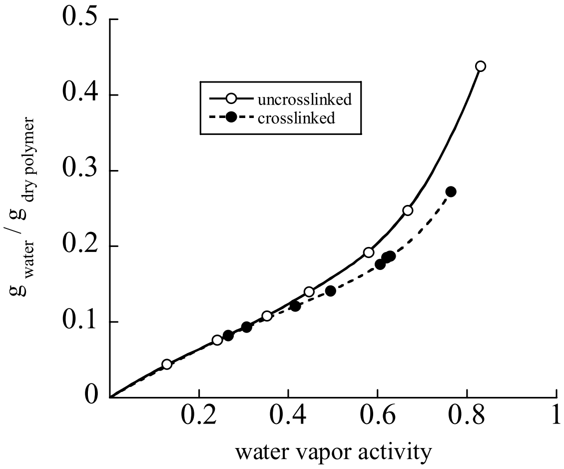


Fig. 1. Water vapour sorption isotherms at 25 °C for powdered samples U and L. Lines are drawn to guide the eye.

Water vapor sorption isotherm was evaluated for samples U and L immediately after desiccation, before the interactions related to network aging develop. The values of χ as determined by using Eq. (7) were 0.77 and 0.98, respectively, for sample U and L.

The difference of the values for χ are related to the difference in the chemical structure of sample L as compared to sample U, which is characterized by a lower hydrophilicity due to the presence of reacted DVS molecules. It is worth noting that the parameter χ is a function of polymer volume fraction expressed, in general, by a Taylor series expansion [44,45]:

$$\chi = \chi_1 + \chi_2\phi_2 + \chi_3\phi_2^2 + \cdots \tag{8}$$

where χ_1, χ_2 and χ_3 are independent of concentration. For the evaluation of mixing contribution in Eq. (4) we adopted a constant value for χ, equal to 0.98. This assumption is justified by the fact that in the case of highly swollen, fully ionized networks, the effect of changes in parameter χ on swelling behaviour is rather negligible (see for example Ref. [6]).

In Table 1 are summarized the calculated values for the relevant terms appearing in Eq. (4) along with the numerical values of the mixing, elastic and ionic contributions for both samples.

Using Eq. (4), ρ_x values were then determined obtaining $3.54 \times 10^{-4} \pm 0.25 \times 10^{-4}$ and $10.60 \times 10^{-4} \pm 2.5 \times 10^{-4}$ moles of crosslinks per cm^3 of crosslinked dry polymer, respectively, for sample L and H. $\bar{M}_C$ values, as evaluated from Eq. (2), were, respectively, equal to about 900 and 3000 g/mol, which are rather small values. For this reason, the degree of crosslinking was also evaluated by using an alternative expression for the elastic term accounting for non-Gaussian chain statistics, which is more appropriate when $\bar{M}_C$ value is small [6,46]. Since results obtained were only slightly different from those based on the hypothesis of Gaussian statistics (a value for ρ_x was obtained which was about 15% smaller), this assumption was considered adequate for the sake of comparison of ρ_x as evaluated from swelling experiments with the results of the other techniques.

It is worth of note that, as anticipated previously, equilibrium swelling properties of the investigated hydrogels in distilled water have been found to steadily decrease with the time elapsed after desiccation stage and before swelling test. This behavior is not related to a further decrease of absorbed water in the dried polymer, which has been found to remain constant, through thermogravimetric analysis. It is likely that during the time interval between desiccation and re-swelling of the films, physical interactions developed among polysaccharide chains involving electron donor–acceptor groups. These interactions imposed a further mobility constraint to macromolecules, acting as additive physical crosslinks. Since these interactions are expected to increase with time, sample aged for longer times consistently displayied a lower sorption capacity related to the increase of entropic response of the network.

4.2. Degree of crosslinking from uniaxial compression tests

The shear modulus of the swollen gel, G, to be used to determine the degree of crosslinking from uniaxial compresion tests, was evaluated in the limit of small deformations ($\alpha \cong 1$). In particular, the numerical value has been obtained from a Mooney–Rivlin plot [36] of compression data (see Fig. 2) by extrapoliting to the Y axis a linear fitting of data. This analysis was performed only on sample films L. In Fig. 3 experimental results are reported as compressive stress (σ) vs. α, along with those predicted adopting in Eq. (5) the value of G determined as discussed above. Data fitting is quite acceptable down to a value of $\alpha \cong 0.35$: for lower values, the simplified approach on which Eq. (5) is based, is inadequate.

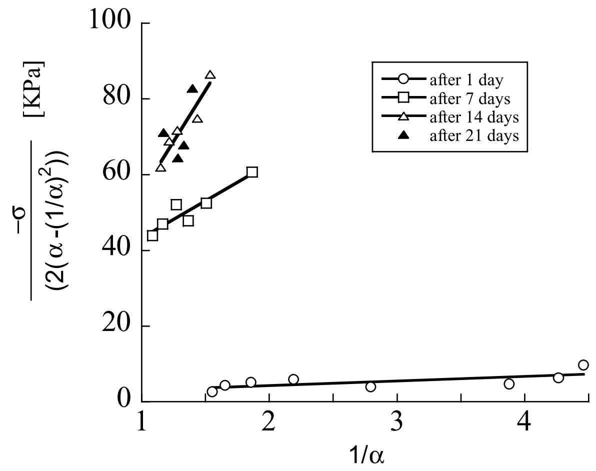


Fig. 2. Mooney-Rivlin plots for equilibrium swollen films of type L, evaluated at 25 °C: lines represent linear fittings.

The value of ρ_x obtained from these measurements for sample L was $2.4 \times 10^{-4} \pm 0.3 \times 10^{-4}$ moles of crosslinks per cm^3 of crosslinked dry polymer, which is in close agreement with the value obtained from swelling experiments.

Compressive measurements performed on aged sample, clearly show an increase of apparent degree of crosslinking with the time of aging as can be inferred from Figs. 2 and 3 (curves at 7, 14 and 21 days after desiccation). Similar trends were obtained from swelling measurements. Values of apparent crossliking degree as function of aging time, as determined from swelling and compression tests, are reported in Fig. 4. The reason for the mismatch, at long desiccation times, between the values of ρ_x as evaluated by the two techniques has not yet been elucidated.

4.3. Degree of crosslinking from NMR measurements

4.3.1. ^{13}C CP-MAS NMR spectra

In Fig. 5(a) the ^{13}C CP-MAS spectrum of a physical mixture obtained by mechanical mixing of CMC-Na and HEC powders (3/1), is shown.

At 104.0 ppm the resonance of anomeric carbons C1 of anyhydro D-glucose units unsubstituted in the C2 position is observed, while at 97.8 ppm the signal of the anomeric carbon C1(2*) of units substituted in position 2 is observed. The shoulder at 82.7 ppm is mostly due to C4.

The intense and broad resonance centred at about 75.1 ppm is mostly due to C2, C3 and C5, however also resonances due to the oxyethylene chains of substituents

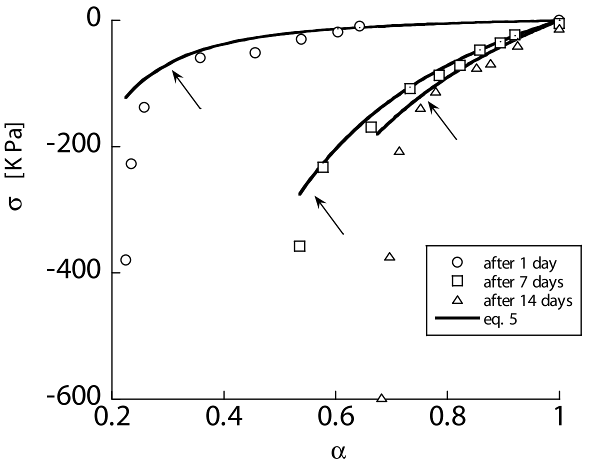


Fig. 3. Uniaxial applied compressive stress as function of α, for equilibrum swollen films of type L, measured at 25 °C. Lines represent the values predicted through Eq. (5): arrows mark the values of α at which deviations from experimental results become remarkable.

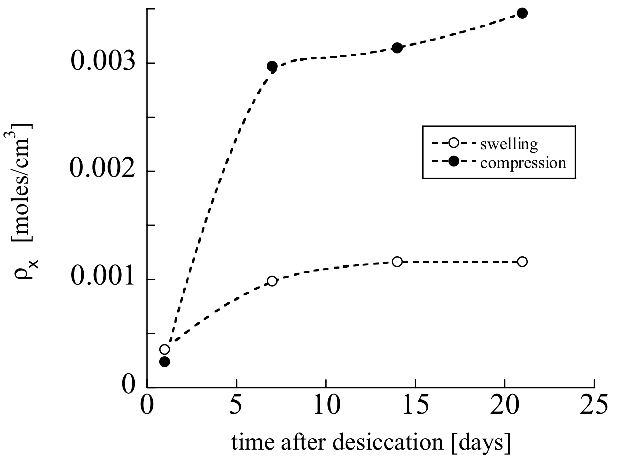


Fig. 4. Time evolution of ρ_x for films of type L, as evaluated from swelling and from uniaxial compression tests. Lines are drawn to guide the eye.

resonate in this range of frequency. At 62.7 ppm the resonance of unsubstituted C6 carbon atoms is observed.

In Fig. 5(b) and c the spectra of sample L and the spectrum of sample H are reported. The resonance at 56.0 ppm is due to methylene carbons of type A (see Scheme 1) i.e. to carbons adjacent to the sulfoxide group, while methylene carbons of type B resonate in the same crowded range of frequency of C2, C3 and C5, and cannot be resolved in a solid state spectrum. It is worth of note that the resonance at 56.0 ppm is fully absent in the spectrum of the uncrosslinked sample (see Fig. 5(a)).

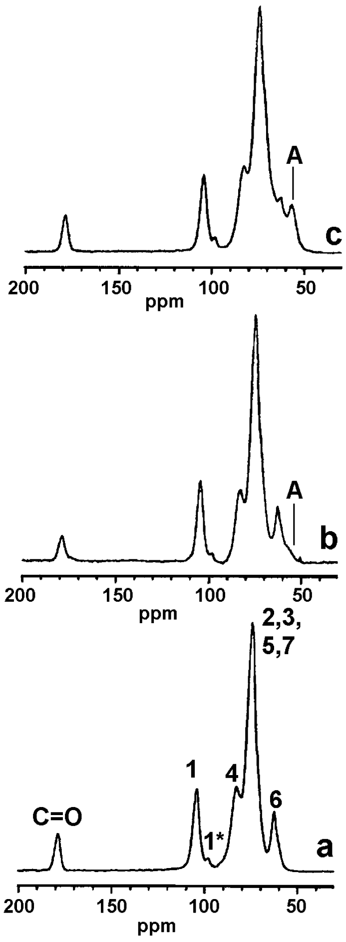


Fig. 5. ^{13}C CP-MAS NMR spectra of (a) a physical mixture of an uncrosslinked CMC-Na /HEC powder (3/1); (b) sample L with low degree of crosslink; (c) sample H with high degree of crosslink. The assignment is also reported.

4.3.2. Semi-quantitative evaluation of carbon spectra at the solid state

Since the intensity of carbon resonances depends on the cross-polarization rates, ^{13}C CP-MAS spectra are not quantitative.

The question rises when semi-quantitative information must be obtained. To this aim, the cross-polarization dynamic has to be carefully investigated [47].

The cross-polarization dynamics can be described by the equation:

$$S(t) = \frac{S_0}{\lambda}\left[1 - \exp\left(\frac{-\lambda t}{T_{\mathrm{IS}}}\right)\right]\exp\left(\frac{-t}{T_{1\rho}(^1\mathrm{H})}\right) \tag{9}$$

$$\lambda = 1 + \frac{T_{\mathrm{IS}}}{T_{1\rho}(^{13}\mathrm{C})} - \frac{T_{\mathrm{IS}}}{T_{1\rho}(^1\mathrm{H})}$$

where S_0 is the area and/or intensity of the investigated resonance at $t = 0$, $T_{1\rho}(^1\mathrm{H})$ and $T_{1\rho}(^{13}\mathrm{C})$ are the proton and the carbon spin-lattice relaxation times in the rotating frame and T_{IS} is the cross relaxation time between protons and carbons.

In homogeneous systems in which $T_{1\rho}(^1\mathrm{H})$ is single-valued, i.e. all resonances show the same $T_{1\rho}(^1\mathrm{H})$ value within the experimental error, the S_0 values are the 'true' intensities and/or areas of the resonances under investigation. Under these circumstances signals will be in the correct intensity ratio allowing a semi-quantitative analysis [48].

A different approach must be used when carbon resonances show different $T_{1\rho}(^1\mathrm{H})$ values. In such a case the MAS-SPE experiment is mandatory for obtaining a semi-quantitative analysis. However this experiment has two main drawbacks: since no cross-polarization from protons to carbons is applied, the signal/noise ratio is poor; the recycle delay (RD) between successive scans must be long enough to allow all carbon sites to relax back to equilibrium. The recycle delay strictly depends on T_1 (^{13}C) values. In many rigid glassy or crystalline polymers T_1 (^{13}C) may be very long, up to 10^2–10^4 s. Note that for a quantitative measurement: RD $> 5\, T_1$ (^{13}C). Hence in many cases this approach is unrealistic.

4.3.3. Degree of crosslinking in CMCNa/HEC/DVS networks

^{13}C CP-MAS spectra of sample H have been run as a function of the contact time t, with t ranging from 0.02 to 7 ms. The area of few selected carbon resonances has been reported against the contact time (see Fig. 6). Fitting the

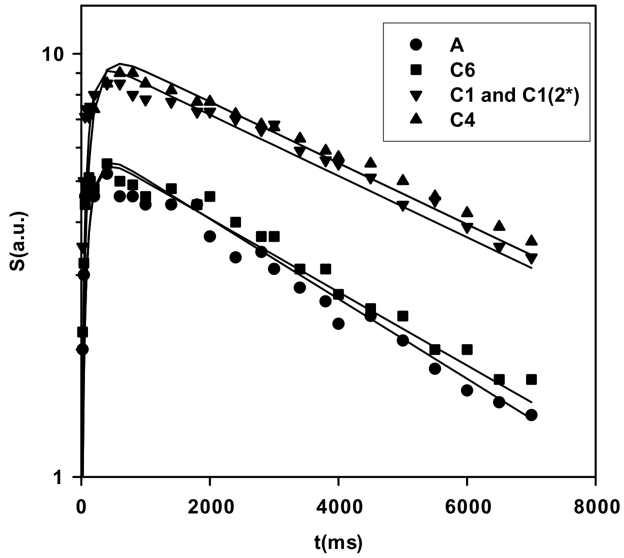


Fig. 6. Correlation between the areas of resonances of the ^{13}C CP-MAS spectrum of sample H and the contact time t. Lines through experimental points are obtained fitting the experimental data to Eq. (9).

experimental data to Eq. (9), for each resonance S_0 and $T_{1\rho}(^1H)$ values have been obtained (see Table 2).

The ratio (R) of moles of reacted DVS and moles of polysaccharide rings can be calculated from the ratio between a half of the area of the resonance due to methylene carbons of type A, S_0(A), and the area of anomeric carbons C1 and C1(2*), S_0(C1):

$$R = \frac{S_0(A)/2}{S_0(C1)} \tag{10}$$

The value of R for the case of sample H (R(H))was calculated to be 0.28 ± 0.03.

However since $T_{1\rho}(^1H)$ values of the resonances, respectively, due to C1 and A are not strictly the same within the experimental errors, see Table 2, MAS-SPE spectra were also performed.

In the case reported here, a reasonable RD value (40 s) between successive scans allowed all carbon atoms to fully relax back to equilibrium.

In Fig. 7 the ^{13}C MAS-SPE spectra of sample L (a) and H (b) are shown; note that the resonance A due to methylene carbons has been evidenced.

Chemical shifts, line widths and areas obtained from experimental spectra have been used as an input in a program performing a full spectral deconvolution. The deconvoluted spectra of sample L and H are shown in Fig. 7(c) and (d).

Table 2
S_0 and $T_{1\rho}(^1H)$ values and the standard deviations for sample H obtained fitting the experimental data to Eq. (9)

C atoms	S_0	$T_{1\rho}(^1H)$ (ms)
C1, C1(2*)	12.0 ± 1	6.0 ± 0.3
C4	12.0 ± 1	5.5 ± 0.4
C6	6.6 ± 0.5	5.0 ± 0.3
A	6.5 ± 0.5	4.6 ± 0.3

Using the areas obtained from the deconvoluted spectra, from Eq. (10) R(L) and R(H) were evluated to be, respectively, equal to 0.04 ± 0.01 and 0.33 ± 0.04 moles of reacted DVS per mol of polysaccharide ring.

The detailed procedure for the evaluation of crosslnking degree by means of ^{13}C solid state NMR is reported in a previuos paper [37].

From the value of R(L) it has been calculated that in 1 cm^3 of crosslinked polymer sample L there were, on the average, respectively, 0.0208 g of DVS and 0.9792 g of polysaccharide fraction (assuming density of the dry polymer equal to 1 g/cm^3). It follows that there were 4.40×10^{-3} moles of polysaccharide rings per cm^3 of crosslinked dry polymer and, on the average, $0.04(4.40 \times 10^{-3})$ moles of crosslinks per cm^3 of dry polymer. By using these results we obtained for the case of sample L a value for ρ_x equal to $3.50 \times 10^{-4} \pm 0.9 \times 10^{-4}$ moles/cm^3 of crosslinked dry polymer.

Similarly, in the case of sample H, in 1 cm^3 of crosslinked polymer there were, on the average, respectively, 0.149 g of DVS and 0.851 g of polysaccharide fraction (assuming again a density of the dry polymer equal to 1 g/cm^3). It follows that there were 3.83×10^{-3} moles of polysaccharide rings per cm^3 of crosslinked dry polymer and, on the average, $0.33(3.83 \times 10^{-3})$ moles of crosslinks per cm^3 of dry polymer. By using these results we obtained for the case of sample H a value for ρ_x equal to $25 \times 10^{-4} \pm 3 \times 10^{-4}$ moles/cm^3 of crosslinked dry polymer.

4.4. Comparison of the three techniques

A substantial agreement among the results obtained for

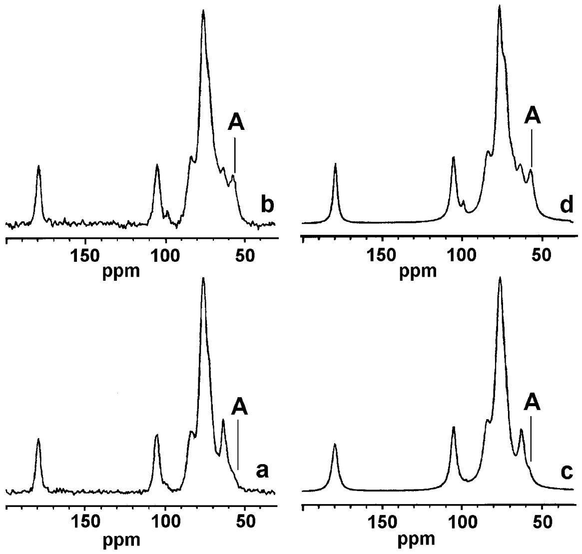


Fig. 7. ^{13}C MAS-SPE experimental spectra of sample L (a) and H (b), on the right the deconvoluted spectra (c) and (d) are shown.

Table 3
Values of ρ_x with standard deviations as evaluated through free swelling, NMR and uniaxial compression experiments on samples L and H

	Swelling	NMR	Uniaxial compression
Sample L	$3.50 \times 10^{-4} \pm 0.25 \times 10^{-4}$ mol/cm^3	$3.50 \times 10^{-4} \pm 0.9 \times 10^{-4}$ mol/cm^3	$2.4 \times 10^{-4} \pm 0.3 \times 10^{-4}$ mol/cm^3
Sample H	$10.60 \times 10^{-4} \pm 2.5 \times 10^{-4}$ mol/cm^3	$25 \times 10^{-4} \pm 3 \times 10^{-4}$ mol/cm^3	–

ρ_x through the three different techniques was observed, as summarized in Table 3.

The different approaches adopted provide different results due to peculiar assumptions proper of each procedure of evaluation as mentioned in the course of reported calculations. However, the agreement is satisfactory and some observations can be made. In fact, since NMR technique gives results quite close to those obtained from swelling and compression, it can be deduced that the contribution of physical crosslinks is negligible, at least right after occurrence of crosslinking reaction. This is likely due to the fact that the low polymer concentration at which crosslinking reaction was performed induced a rather small amount of entanglements.

As reported previously, during desiccation step following crosslinking reaction, interactions slowly develop promoting an increase of the effective physical crosslinking (entanglements + interactions) and, consistently, a marked decrease of sorption capacity (ageing effect).

5. Conclusions

A comparison of a NMR based approach, aimed to the determination of the degree of crosslinking of polymer networks, with traditional experimental procedures has been presented. It evidenced how the different experimental approaches can be used sinergistically to gather detailed information on the network structure. In fact, the methods are sensitive to different chemical and physical structural parameters of the macromolecular system.

The estimation of degree of crosslinking of a cellulose based network as performed by swelling, compression and NMR measurements, have been found to agree in the limits of the experimental accuracy of the methods, although, in the case of samples characterized by a higher degree of crosslinking, NMR measurements lead to a slight overestimation, as compared to swelling experiments. This conclusion is limited to the case of investigated degree of crosslinking, which are those of interest for the application of this material in the field of superabsorbing systems.

These results points to a substantial correspondence, for the cellulose based system considered and for the adopted crosslinking conditions, between chemically effective and elastically effective crosslinks, at least in the limits of the investigated chemical composition and of simplified theoretical models adopted to interpret data.

Aging of dry samples has been found to promote a decrease of swelling capacity, which is likely due to the development of intermolecular interactions. Evidence of this effect has also been found in the results of compression experiments performed on swollen gel.

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