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Evaluation of the Degree of Cross-Linking of Cellulose-Based Superabsorbent Hydrogels: A Comparison between Different Techniques

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Summary: Three different techniques have been applied to the evaluation of the degree of cross-linking of superabsorbent cellulose-based hydrogels obtained from water solutions of carboxymethylcellulose sodium salt (CMCNa) and hydroxyethylcellulose (HEC), chemically cross-linked with divinyl sulfone. These polyelectrolyte hydrogels are biodegradable and have the same sorption capacity as acrylate-based superabsorbents on the market. A ^{13}C solid state NMR analysis was carried out on dry samples of hydrogel to obtain the degree of cross-linking, an important parameter that affects the swelling and mechanical properties of a hydrogel. Dynamic mechanical analysis was performed during the hydrogel cross-linking using a parallel plate rheometer under oscillatory deformations in order to monitor the evolution of the hydrogel viscoelastic properties during the synthesis. The value of $|G^*|$ and the slope of the stress-deformation ratio plots from uniaxial compression tests were used to evaluate the elastically effective degree of cross-linking according to classical rubber elasticity theory. Moreover, a dynamic mechanical analysis was carried out on cross-linked hydrogels at different degrees of swelling in order to investigate the influence of the swelling on the mechanical properties and the application of rubber elasticity theory to swollen hydrogels.

Keywords: degree of cross-linking; dynamic mechanical analysis; hydrogels; NMR; swelling

Introduction

Macromolecular hydrogels are generally obtained by chemical or physical stabilization of macromolecular chains in a three dimensional polymer network, and have been widely used in many biomedical applications such as drug delivery systems,[1-3] soft tissue substitutions, contact lenses,[4] superabsorbents for personal hygiene products,[5-6] enzyme immobilization and scaffolds for cellular growth in tissue engineering or body water elimination systems.[7]

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Polyelectrolyte hydrogels, being characterized by the presence of ionic groups linked to the molecular network, are able to absorb extremely large amounts of water and are very sensitive both to environmental conditions and to the porosity of the structure.[8-9] A new class of biodegradable hydrogels has been synthesized[10] but they have a lower sorption capacity than acrylate-based superabsorbents. The efforts to increase the swelling capacity by inducing a microporous structure in a natural polymer-based hydrogel have led recently to the synthesis of biodegradable cellulose-based hydrogels.[11]

The investigation of the relationship among the mechanical properties, the degree of cross-linking and the swelling degree of this kind of hydrogel is still a matter of discussion. The degree of cross-linking is one of the most important parameters for evaluating the swelling and mechanical properties of hydrogels because of its direct influence on the entropic elasticity of the network, but there is still no well assessed method to evaluate it. Usual techniques are equilibrium swelling measurements or uniaxial compression tests on swollen networks,[12] which can determine the number of elastically effective network chains arising either from chemical or from physical cross-linking mechanisms. To simplify the interpretation of experimental data, a few hypotheses are usually adopted: no effects of the charge interactions on the mechanical response and invariance of the gel volume during the test. However, the presence of microporosity and fixed ionic charges can significantly affect the mechanical properties of the hydrogel.[13-14] Another approach to the determination of the degree of cross-linking is solid state NMR spectroscopy, which, from its insight into the chemical structure of the hydrogel, supplies the value for the chemically effective degree of cross-linking, independently of the knowledge of other chemical-physical and structural parameters.

In this work three different techniques were applied to evaluate the degree of cross-linking of superabsorbent cellulose-based hydrogels. Application of classical rubber elasticity theory to swollen hydrogels was analysed and adapted to the experimental data.

Experimental

Cellulose-based hydrogels were synthesized in a partially swollen state by cross-linking an aqueous solution of carboxymethylcellulose sodium salt (CMCNa) and hydroxyethylcellulose (HEC) in a weight ratio of 3:1, with a solution of 0.04M divinylsulphone (DVS) as a cross-linking agent, according to a procedure described in previous papers.[11,15] CMCNa and HEC are both cellulose ethers where substituent groups are respectively methylcarboxylic groups and oxyethylene chains. The degree of substitution and the relative distribution of substituents in C-2, C-3 and C-6 position in cellulose ethers may strongly affect the properties and the behaviour of these polymers.

^{13}C Solid State NMR measurements were performed 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.

Compression tests and dynamic mechanical analysis were carried out at 300 K on a parallel plate rheometer (ARES, Scientific Rheometric), with a cross-head speed of 1.2 mm/min and a frequency of 1 Hz respectively. The parallel plate surface was properly modified in order to prevent hydrogel slipping.

Results and Discussion

^{13}C Solid State NMR Spectroscopy. ^{13}C Solid State NMR measurements were carried out on dry cross-linked and uncross-linked samples with the same polymer concentration. A more detailed description both of the experimental method and the evaluation procedure for the degree of cross-linking is reported elsewhere.[15] The ^{13}C CP-MAS spectra are shown in Figure 1. The resonance at 56 ppm, observed only in the spectrum of the cross-linked samples as a small shoulder, is due to the methylene carbon atoms adjacent to the sulfoxide group, while methylene carbon atoms in other positions resonate in the same crowded range of frequency of polysaccarides (70-80) and cannot be resolved in solid state spectra. DVS oligomerization and reactions occurring between DVS and water, which could cause errors in the NMR calculations, are implicitly neglected.

The degree of cross-linking, expressed as the number of cross-links per monomer, was calculated from the ratio between one-half of the area of the resonance peak at 56 ppm (due to the carbons present on cross-linker molecules after the reaction) and the sum of the area related to resonance peaks associated with anomeric carbon atoms present on polysaccharide rings (carboxylated at 97ppm and unsubstituted at 104ppm), which was used as a reference. The resulting degree of cross-linking is 0.04 moles per mole of polysaccharide ring. As a consequence, assuming the density of the dry polymer equal to 1 gcm^{-3}, a value for the degree of cross-linking equal to 1.76×10^{-4} mol cm^{-3} is obtained.

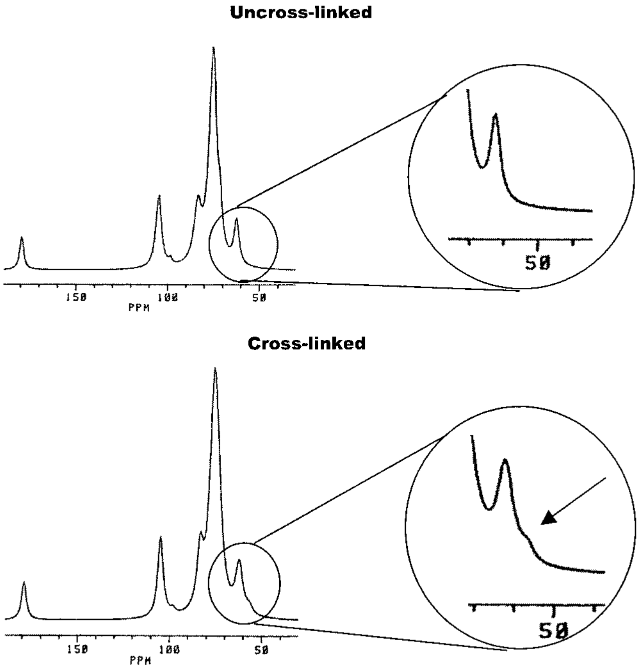

Fig. 1. ^{13}C CP-MAS spectra of uncross-linked and cross-linked hydrogel sample.

Uniaxial Compression of Swollen Networks. Assuming a constant volume during the compression of the swollen hydrogel, the Flory relationship[12] between the compressive stress σ, expressed as applied force per unit area of undeformed hydrogel, and the compressive strain λ, expressed as the ratio of deformed to undeformed length of swollen hydrogel, is the following:

$$\sigma = \nu RT\Phi^{1/3} \frac{\overline{r_0^2}}{\overline{r_F^2}} \left(\lambda - \frac{1}{\lambda^2} \right) \qquad (1)$$

where ν is the cross-linking density, i.e. the number of active network chains per unit volume, R is the gas constant, T is the absolute temperature and $\overline{r_0^2} / \overline{r_F^2}$ is called front factor, $\overline{r_F^2}$ being the mean square end-to-end distance of an equivalent free random coil and $\overline{r_0^2}$ the mean square end-to-end distance of a cross-linked random coil. The term Φ is the volume fraction of polymer in the swollen hydrogel and takes into account the swelling contribution, which is responsible for the decrease in cross-linking density and the increase in the mean square end-to-end distance. The basic assumption of Equation (1) is that the network is perfect in that all cross-links in the network are effective in giving rise to the elastic stress and there are no entanglements and chain ends. Several other relationships may be derived immediately from Equation (1). Assuming for hydrogels a Poisson ratio of 0.5 (as for rubbers), the shear modulus of an ideal rubber-like hydrogel can be written to a good approximation as:

$$\mathbf{G = \nu RT\Phi^{1/3}\frac{\overline{r_0^2}}{\overline{r_F^2}}} \qquad (2)$$

Since some water is squeezed out of the swollen sample during the compression, the assumption of constant volume during compression is not always verified. However, in the limit λ→1, this expression for G is usually used to evaluate the cross-linking density, assuming a value of unity for the front factor. The calculated value of ν is 0.47×10^{-6} mol cm^{-3}.

Dynamic Mechanical Analysis during and after Synthesis. A dynamic mechanical analysis at 1 Hz was performed on the polymer solution (CMCNa, HEC, DVS and catalyst) in order to monitor the cross-linking process during the hydrogel synthesis. As shown in Figure 2, an increase in the torque and modulus G' with the reaction time denotes an increase in the elastic response of the material due to cross-linking of the viscous polymer solution, i.e., the formation of covalent bonds in the three dimensional network. After about two hours from the beginning of the cross-linking process, a steady value of G' is followed by a further slow increase in cross-link density, leading to much higher values of the modulus at very long reaction times. DMA measurements performed on aged samples (one and two weeks after the synthesis) detected an increase in the modulus up to about 265 Pa. The distinct peak in the G'' curve can be attributed to the irreversible losses that occur during cross-linking. The value of |G*| was used to calculate the cross-link density ν according to Equation (2) by assigning a value of unity to the front factor. The value of ν obtained is 0.39×10^{-6} mol cm^{-3}.

From Table 1 it can be observed that the values calculated from uniaxial compression and DMA tests are quite similar to each other, but very different from those obtained from NMR measurements. This difference can arise considering that NMR measurements yield a degree of chemical reaction of DVS double bonds in dry samples, including also those chemical bonds that generate loops or dangling ends, which are ineffective for elastic stress. Therefore, the basic assumption of tetrafunctional cross-links, i.e. permanent tie-points between two chains, is not satisfactory because a number of network imperfections are possible, such as chain loops (intramolecular cross-linking such as CMC-CMC or HEC-HEC bonds), wasted cross-links (when a short chain is cross-linked once) or dangling ends in CMC and HEC chains. All these network imperfections contribute to decrease the elastic response of the hydrogel and, consequently, the degree of cross-linking calculated from mechanical methods. Furthermore, hydrogel microporosity, the ionic contribution related to the presence of bound and mobile ions and electrostatic interactions among fixed charges present on the polymer chains, contribute to make difficult the interpretation of mechanical experimental data obtained in swollen conditions.

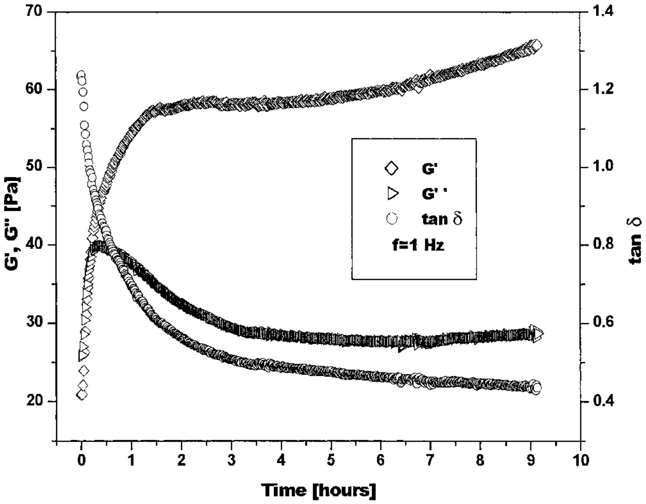

Fig. 2. Dynamic mechanical monitoring at 1Hz and 300K of the cross-linking process of the cellulose based hydrogel.

As demonstrated by Graessley,[16] the front factor can be very different from unity in its dependence on the functionality of the network, and can be altered by swelling in a different way from that predicted by rubber elasticity theory. In particular, for the case of a cross-link functionality equal to 4, a correction factor of 0.5 should be used in Equation (1). The deformational behaviour displayed by swollen hydrogels depends on all these above mentioned contributions, neglected for calculation simplicity, and also on the free energy change associated with the release of a certain amount of adsorbed water.

Table 1. Values of the degree of cross-linking calculated by different techniques.

Technique	Degree of cross-linking
	mol/cm^3
NMR spectroscopy	1.76×10^{-4}
Uniaxial compression	0.47×10^{-6}
Dynamic mechanical analysis	0.39×10^{-6}

The mechanical spectrum of the hydrogel is shown in Figure 3 for the swelling degree Φ=0.009. The slight increase of G' with the frequency denotes a weak viscoelastic behaviour of the hydrogel sample.

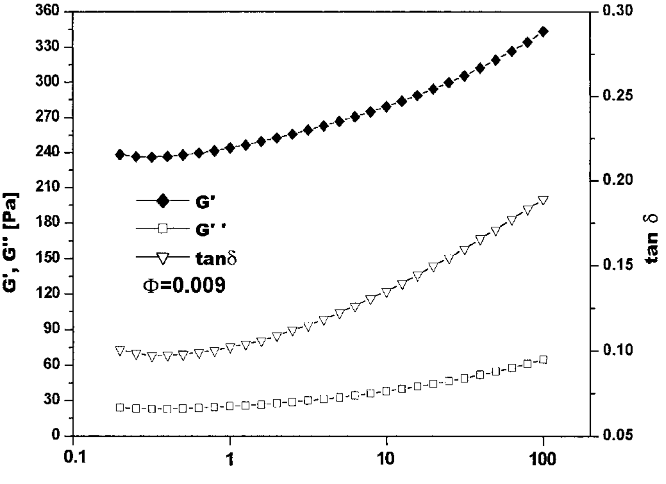

Fig. 3. Mechanical spectrum at 300K of the cellulose based hydrogel at Φ=0.009 .

To investigate the influence of swelling on the mechanical properties, a dynamic mechanical analysis was carried out on cross-linked hydrogels at different swelling degrees. The value of the complex shear modulus $|G^*|$ at 1Hz is displayed as a function of the polymer volume fraction Φ in the swollen hydrogel in Figure 4. The experimental data exhibit a dependence on Φ of the type:

$$|G^*| = \nu RT\Phi^{0.54} \tag{3}$$

This equation is an empirical expression accounting for all the deviations from rubber elasticity theory related to the effects of the swelling, mentioned above. The exponent n=0.54, which differs from the theoretical value of 0.33 predicted by Equation (1), results from regression analysis of the data of Figure 4.

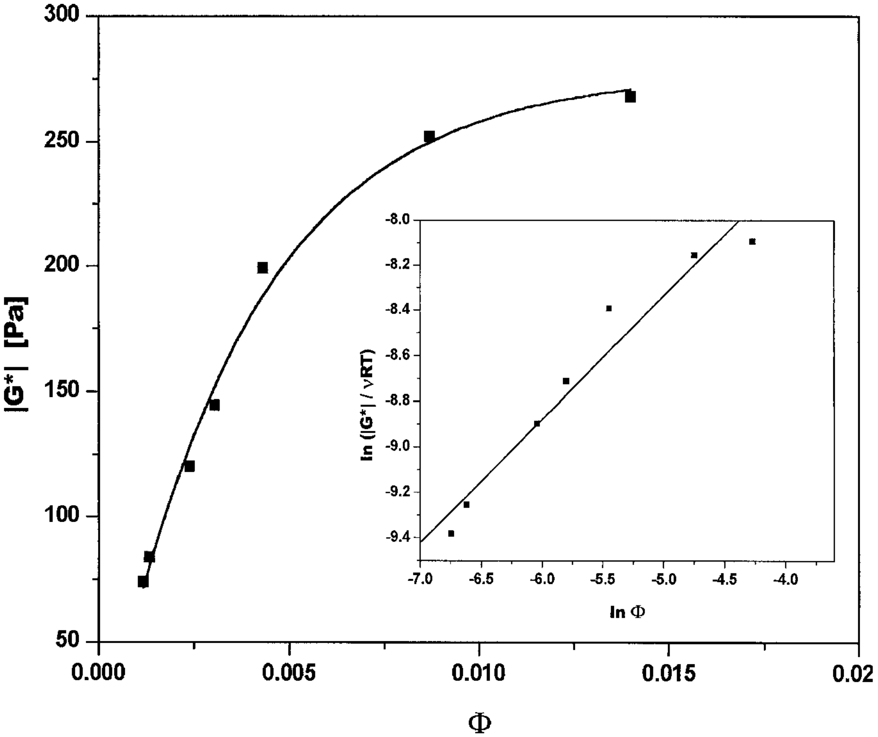

Fig. 4. Effect of the swelling on the shear modulus G* measured at 1 Hz and 300 K.

Conclusions

In this work three different techniques were used to evaluate the degree of cross-linking of a superabsorbent cellulose based hydrogel. The chemically effective degree of cross-linking, obtained from ^{13}C solid state NMR analysis, was compared with the elastically effective degree of cross-linking obtained from uniaxial compression and dynamic mechanical experiments. The difference between mechanical and chemical measurements can be explained by observing that many hypotheses in rubber elasticity theory, made to simplify the calculations, are not satisfactory in the case of polyelectrolyte swollen hydrogels because of their complex chemical structure, containing fixed ionic charges, characterized by microporosity and in presence of strong swelling. The DMA analysis, performed on hydrogel samples at different degrees of swelling, leads to a power law dependence of the shear modulus on the polymer volume fraction characterized by an exponent n=0.54, indicating a deviation from classical rubber elasticity theory (n=0.33).

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