Ultrasonic monitoring of the network formation in superabsorbent cellulose based hydrogels

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Abstract

Biodegradable hydrogels are finding increasing interest in the academic and industrial field due to their high swelling capacity and the potential for many novel applications enabled by their biodegradability. The monitoring of the hydrogel cross-linking process is a crucial step for predicting hydrogel performances in terms of degree of swelling and viscoelastic properties.

In this work, the chemical cross-linking of cellulose based hydrogels has been monitored during synthesis in water by means of ultrasonic wave propagation and low frequency dynamic mechanical analysis (DMA). The effect of the cross-linker concentration on the hydrogel acoustic behaviour has been also analysed and correlated with the different elastic response developed by the macromolecular hydrogel.

The results demonstrate the reliability of the ultrasonic wave propagation in the following network formation process of a superabsorbent hydrogel, being capable of following the limited changes in the physical properties of the reacting solution.
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1. Introduction

Hydrogels are chemically or physically cross-linked structures composed of hydrophilic homopolymers or copolymers [1]. Over the past 30 years, hydrogels have found numerous biomedical and pharmaceutical applications [1–4]. Cellulose based superabsorbent hydrogels, recently synthesized [4], are finding increasing interest in the scientific and industrial field due to their biodegradable character and the high swelling capacity [3–10]. These hydrogels are obtained by cross-linking of cellulose derivatives using difunctional molecules as cross-linkers, which covalently bind different polymer molecules in a three-dimensional hydrophilic network.

These cross-linked hydrogels exhibit a swelling behaviour in aqueous solutions strongly dependent on several chemical and structural factors (i.e. hydrophilicity of polymer backbone, degree of cross-linking, density and type of fixed charges, amount of ionic groups and eventual

presence of porosity) and by the properties of the aqueous solution in contact with the network (i.e. pH, ionic strength, presence of other solvents) [1,3,11–13]. Therefore, an in situ monitoring of the network development during the chemical stabilization process is necessary for predicting and controlling hydrogel physical properties, in particular the degree of cross-linking.

There is a general lack of techniques to monitor in situ the hydrogel formation. The photon transmission technique [14] and the electronic speckle pattern interferometry [15] are the only few examples found in the literature. Among non-optic techniques, the propagation of ultrasonic waves could be one of the most suitable for monitoring the hydrogel formation stage, due to its non-destructive character and the possibility of an on-line implementation in industrial processes.

Ultrasonic wave propagation, acting as a high frequency deformation applied to the polymeric solution, depends on the viscoelastic behaviour of the material under test, being strongly affected by transition temperatures, morphology, cross-linking density, etc. For this reason, low-intensity ultrasound has been successfully applied to detect the phase

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transformations occurring during cross-linking of thermo-setting resins [16–24] and the structural changes during water sorption in dry hydrogels [25–28]. Nevertheless, no ultrasonic studies have been so far carried out during hydrogel cross-linking starting from very dilute solutions.

In this work, the propagation of ultrasonic longitudinal waves has been applied to monitor the stabilization of aqueous solutions of cellulose polymer into superabsorbent hydrogels through chemical cross-linking. The ultrasonic results, obtained at 10 MHz, have been compared with those of dynamic mechanical analysis (DMA) carried out in the Hertz range.

2. Experimental

2.1. Sample preparation

Cellulose based hydrogels were synthesized in a partially swollen state by cross-linking water solutions of carbox-ymethylcellulose sodium salt (referred in the following as CMCNa) and hydroxyethilcellulose (referred in the following as HEC) with a weight ratio equal to 3/1. Divinyl-sulfone, referred in the following as DVS, was used as a cross-linking agent. CMCNa, HEC and DVS were purchased from Aldrich Chimica s.r.l. and used as received. According to the supplier, the degree of substitution (DS) of CMCNa is about 0.9 and the weight average molecular weight is 700 000. The molar substitution (MS) for HEC is about 1 and DS is about 1, while the weight average molecular weight is 250 000. The presence of HEC is necessary to promote quantitatively intermolecular rather than intramolecular cross-linking. Further details on starting materials are reported in a previous work [29].

Cross-linking reaction was performed according to procedures reported in the literature [4]. 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 cross-linking: 0.04 and 0.133 mol of DVS per litre of solution.

After the mixing stage, an alkaline water solution of potassium hydroxide (KOH) was added as a catalyst. Hydrogel formation occurred in a few hours (about 12–14) at room temperature in a diluted basic solution (0.02 mol/l).

2.2. Ultrasonic dynamic mechanical analysis

Ultrasonic longitudinal velocity and attenuation during cross-linking at 298 K were measured in transmission mode at the frequency of 10 MHz by means of an ultrasonic apparatus developed in the laboratory of Polymeric Materials of Lecce University. It consists of two specifically developed ultrasonic transducers, fitted into the disposable tools of a parallel plate rheometer (Ares, Rheometric Scientific) and connected with a pulser-receiver card. This latter generates a pulse train, amplifies the signal transmitted through the sample and provides an analogue/digital conversion of the signal, that, using a dedicated software, is displayed on the monitor of a PC.

After adding the catalyst, the viscous aqueous solution of CMCNa, HEC and DVS was sandwiched between the delay lines of the ultrasonic probes fitted within the rheometer oven. So, a hydrogel sample of about 2.5 mm thickness and 30 mm diameter formed at the temperature of 298 K between the transducers, operating in transmission mode. The lateral sides of the sample were sealed with silicon fluid to prevent water loss during the ultrasonic measurements, which lasted several hours.

A good acoustic coupling resulted from the aqueous nature of the hydrogel samples. The longitudinal velocity and attenuation were determined by comparison of the peak time and peak amplitude of the transmitted wave with those of a reference signal, recorded with the two transducers in contact without sample. For each kind of hydrogels, the ultrasonic measurements were replicated three times with a good repeatability of the data.

Since ultrasonic waves are mechanical waves, the acoustic properties of the cross-linking hydrogel can be used to interpret its mechanical behaviour. When the sample dimension normal to the acoustic wave is large compared with respect to the wavelength, the wave propagation is governed by the complex bulk longitudinal modulus L^*, related to the bulk (K^*) and shear (G^*) modulus as follows [30–31]:

$$L^* = K^* + 4/3\, G^* \tag{1}$$

The real and imaginary components of the complex bulk longitudinal modulus ($L^* = L' + iL''$) can be calculated from the measurement of ultrasonic longitudinal velocity and attenuation according to the following equations [30–31]:

$$L' = \frac{\rho c^2 \left[1 - \left(\frac{\alpha\lambda}{2\pi}\right)^2\right]}{\left[1 + \left(\frac{\alpha\lambda}{2\pi}\right)^2\right]^2} \quad \text{and} \quad L'' = \frac{\rho c^2 \left(\frac{\alpha\lambda}{2\pi}\right)}{\left[1 + \left(\frac{\alpha\lambda}{2\pi}\right)^2\right]^2} \tag{2}$$

where L' is the elastic or storage component of the modulus, L'' is the viscous or loss component of the modulus, c is the ultrasonic velocity, α the attenuation, ρ the material density and λ the wavelength of propagation, calculated as the ratio between ultrasonic velocity and frequency. Due to the very low polymer content in the starting solution (2% by weight), a constant value of ρ (1 g/cm^3) has been assumed.

The term $\alpha\lambda/2\pi$ remained always lower than 0.05 for the studied hydrogel, then L' and L'' can be calculated according to the following simplified equations:

$$L' = \rho c^2 \tag{3}$$

$$L'' = 2\rho c^3 \alpha/\omega \tag{4}$$

where ω is equal to $2\pi f$, being f the ultrasonic frequency (10 MHz).

2.3. Dynamic mechanical analysis

Dynamic mechanical analysis (DMA) was carried out during cross-linking at 298 K of CMCNa/HEC aqueous solutions on a parallel plate strain controlled rheometer (ARES, Rheometric Scientific). In order to prevent hydrogel slipping during measurement, plate surfaces were covered with an aramide honeycomb sheet. Immediately after adding the catalyst (KOH), the solution was poured onto the lower plate of the rheometer, after which the upper plate was positioned at a gap of 1 mm. The lateral surface of the sample was covered with a silicon fluid in order to prevent water evaporation during the experiment.

A preliminary test at fixed frequency and variable strain (strain sweep test) was performed to determine the strain amplitude values leading to a linear viscoelastic response of the sample. After this test, a sinusoidal deformation with a frequency of 1 Hz and amplitude of 5% was chosen. It must be underlined that the DMA experiments are more complex than the ultrasonic ones in terms of measurement equipment and sample preparation.

2.4. Rheological analysis

Rheological analysis was performed at 298 K on aqueous solutions of CMCNa/HEC and different concentrations of DVS cross-linker, with and without the catalyst KOH. A parallel plate rheometer (ARES, Rheometric Scientific) was used in steady state by varying the shear rate from 0.05 to $100 \, s^{-1}$.

2.5. Uniaxial compression tests

Uniaxial compression measurements were carried out at room temperature on cross-linked hydrogel samples swollen to equilibrium in distilled water. In order to remove the unreacted DVS and the KOH, the partially swollen hydrogel was soaked in distilled water reaching equilibrium swelling under continuous stirring. Water was used in volumes greatly exceeding the sorption capacity of the hydrogel and was changed several times.

The sample, in the form of a disc of 25 mm diameter and 4 mm thickness, was placed between the parallel plates of a rheometer (ARES, Rheometric Scientific). The upper plate, connected with a normal force transducer (maximum load 2000 N, sensitivity 0.01 N), was moved downward with a very low speed (0.3 mm/min), allowing to record the compressive stress and the gap between the plates (actual sample thickness).

Samples were weighed before and after the experiment to check eventual water loss, which resulted less than 1% and, consequently, with good approximation, negligible.

Assuming a constant volume during the compression of the swollen hydrogel, the Flory relationship [32] between the compressive stress σ and the compressive strain λ_{comp} is the following:

$$\sigma = RT \frac{\nu_e}{V_0} \Phi_{2,r}^{2/3} \Phi_{2,s}^{1/3} \left(\frac{L}{L_0} - \frac{1}{\left(\frac{L}{L_0}\right)^2} \right)$$

$$= G \left(\frac{L}{L_0} - \frac{1}{\left(\frac{L}{L_0}\right)^2} \right) \tag{5}$$

where $\sigma = F/A_0$ is the uniaxial compressive stress (F is the compressive force and A_0 the initial area of the swollen hydrogel), L/L_0 is the ratio of the actual thickness (L) to the initial thickness (L_0) of the swollen sample, R the universal gas constant, T the absolute temperature, $\Phi_{2,r}$ the polymer volume fraction in the reaction mixture, $\Phi_{2,s}$ the polymer volume fraction in the swollen state under compression, ν_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.

3. Results and discussion

The evolution of the ultrasonic velocity during hydrogel cross-linking at 298 K is reported in Fig. 1 for an aqueous solution of CMCNa/HEC with a 0.04 mol/l content of divinylsulfone.

At first, the addition of the catalyst promotes a rapid viscosity depression due to the further dilution of the reacting polymeric solution. As can be observed in Fig. 2, the viscosity of the reacting mixture decreases of about 60% (from 50.6 to 19.5 Pa s), whereas the cross-linker (DVS) content does not affect significantly the viscosity values, being added in less than 0.8% in volume of the reacting mixture. The viscosity decrease, arising from the addition of the catalyst, produces an abrupt decrease in the longitudinal velocity at the beginning of the ultrasonic measurement, since the speed of sound strongly depends on both the elastic properties and the density of the hydrogel.

After a few minutes of reaction, the velocity reduction, due to the addition of the catalyst, is counteracted by the growth arising from the development of the elastic properties in the hydrogel-forming network. As a result of the cross-linking process, the ultrasonic velocity grows, at first rapidly, and then, after approximately 1 h of reaction, very slowly for several hours, attesting the sluggish but continuous network development. The long reaction time, measured by ultrasonic technique, is in agreement with a former study [33] reporting a cross-linking time of about 12 h.

The discontinuous increase of the ultrasonic velocity with steps of about 10 m/s, observed in Fig. 1 after several hours of cross-linking, can be ascribed to the temporal resolution of the analogue/digital (A/D) converter of the pulser-receiver used in the ultrasonic experimental set-up associated with a change in the received waveform. Only
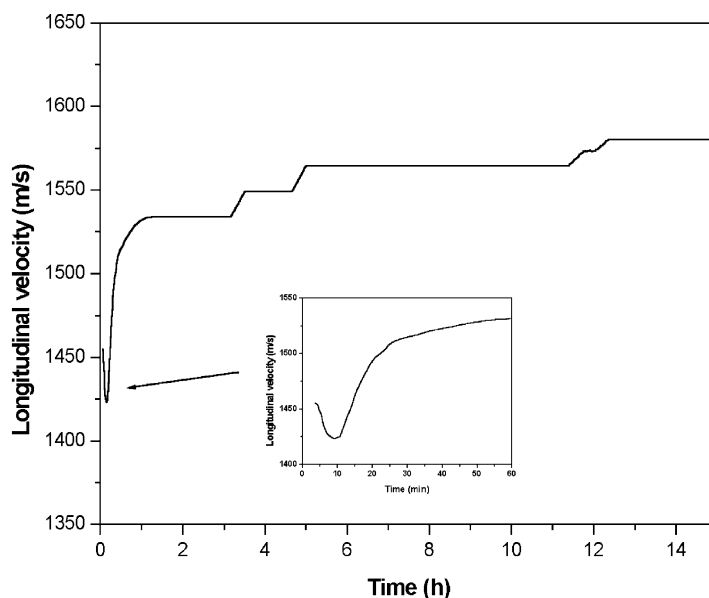
Fig. 1. Longitudinal velocity measured at 10 MHz during the cross-linking of a polymeric solution of CMCNa/HEC in water with a DVS solution 0.04 mol/l. The first hour of cross-linking is reported in the insert.

when the waveform changes in the time scale are larger than the A/D converter resolution (17 ns), they can be detected and an increase in the ultrasonic velocity is recorded. During the last part of the cross-linking process, the determination of the time of flight is affected by broader peaks with a non-well defined maximum. The slow changes in the signal waveform in the time domain are confirmed also by the analysis of the signal in the frequency domain obtained by fast Fourier transformation (FFT) analysis. As reported in Fig. 3, the appearance of new signal components at different frequencies than the resonance one (centred at about 2.75 MHz) indicates a change in the frequency response of the forming hydrogel during the cross-linking process.

The velocity approaches a plateau when the gel is nearly fully stabilized. The overall velocity increase during the long reaction time is small (about 160 m/s) if compared with the increase observed during the cross-linking of thermo-setting resins (about 1000 m/s), reported in previous works [19–24]. This difference can be ascribed to the weak elastic properties developed by the cross-linked hydrogel as a consequence of the presence of a small quantity of polymer (2% by weight) in the starting aqueous solution.

The gradual formation of the three-dimensional network was followed also by shear oscillatory measurements at low frequency by means of a parallel plate rheometer. The aim was to compare the high and low frequency dynamic mechanical analysis applied on hydrogel formation. It
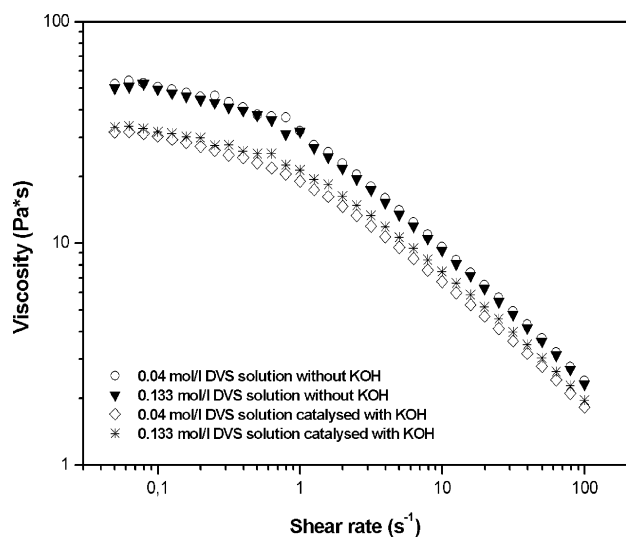

Fig. 2. Viscosity versus shear rate for aqueous solutions of CMCNa/HEC at different DVS content (0.04 and 0.133 mol/l) with and without KOH catalyst.
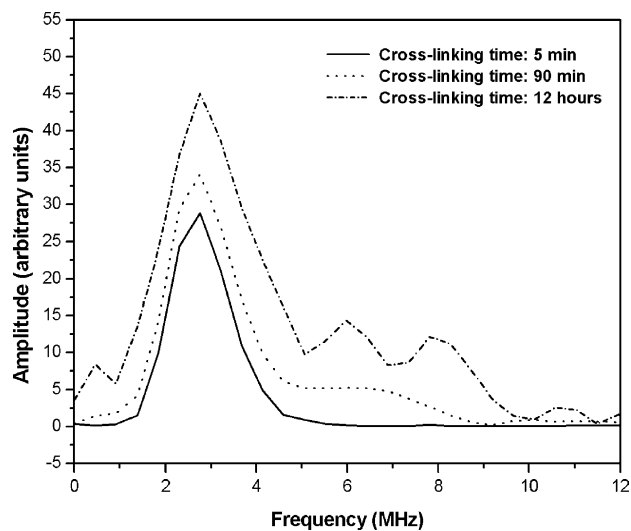

Fig. 3. FFT spectra of the acoustic signals observed during the hydrogel cross-linking at different cross-linking times.

should be kept in mind that the oscillations applied by the two techniques are different both for frequency and strain direction. In this work, the ultrasonic technique applied longitudinal waves, i.e. a series of compression and extension waves, with a 10 MHz frequency, whereas the low frequency dynamic mechanical analysis applied shear oscillatory deformations at 1 Hz.

In Fig. 4 the time evolution of G', measured at 1 Hz, and L', calculated from the velocity data shown in Fig. 1 using Eq. (3), is reported. A great difference between the magnitude orders of L' and G' values is expected if one accounts that, for a swollen cross-linked material, $G' \ll K'$ (see Eq. (1)). The reported values of L' are consistent with the value of the water bulk modulus, which is 2.2×10^9 Pa at 20 °C [34].

The effect of the cross-linker (DVS) content on the longitudinal modulus is shown in Fig. 5. It should be noted that the time is reported starting from the addition of KOH. In the first minutes of reaction, the velocity increase is quite similar for the reacting solutions with different DVS content and seems to be independent from the amount of cross-linker. Nevertheless, with increasing reaction time, the ultrasonic velocity increases slightly faster in the solution with a lower DVS content, which reaches the plateau value before the other one. This can be explained accounting for the different reactivity between the first and the second addition reaction of the DVS carbon–carbon double bonds to the cellulose molecule.

The DVS molecule presents two carbon–carbon (C=C) double bonds that can be opened and linked to the OH$^-$ groups of the cellulose molecules. The polymerization is thus characterized by a first addition of DVS carbon–carbon double bond to the cellulose chain and a second addition. Only this latter leads to a cross-linked network. It should be noted that, although the reactive sites of the cellulose chain (OH$^-$) are the same both for the first and the second
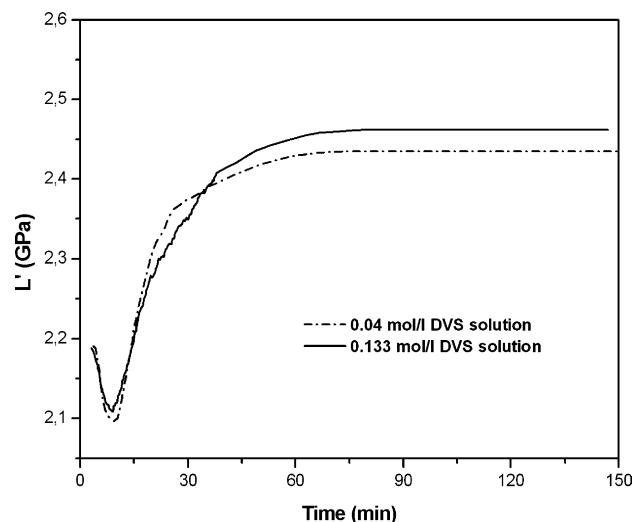
Fig. 5. Effect of DVS content on the ultrasonic longitudinal modulus measured at 10 MHz during the cross-linking at 298 K of polymeric solutions of CMCNa/HEC in water.

addition, the two reaction steps have different rate. The first C=C addition (rate constant K1 in Fig. 6) occurs between a compound of a very low molecular weight (DVS) and a side group (OH$^-$) of a polymer chain (cellulose). The second addition (rate constant K2 in Fig. 6), instead, occurs always between a cellulose OH$^-$ group and a C=C bond, but this latter now is the pendant group of a macromolecule and hence $K_1 \gg K_2$. Therefore, it may be assumed that at higher DVS concentrations, the first addition compete with the second for a longer time, reducing also the number of accessible OH$^-$ on cellulose to the cross-linking reaction. In this case, the second addition leading to cross-linking is slightly delayed and, consequently, the growth of viscoelastic properties, monitored by the ultrasonic technique, is observed later compared to the hydrogel obtained with a lower DVS concentration.

Nevertheless, once the first addition is completed and the second is in progress, a more amount of DVS originates a network with a higher cross-linking density and, consequently, improved elastic properties. The overall effect of the cross-linker amount on the final ultrasonic velocity is representative of the difference in the elastic properties developed by the two hydrogels. This result is confirmed by the uniaxial compressive behaviour, reported in Fig. 7.

The evolution with the time of the ultrasonic attenuation during cross-linking of hydrogels with different DVS content is shown in Fig. 8. The ultrasonic attenuation may be considered as the equivalent of a damping factor in a dynamic mechanical experiment [35], representing a measure of the energy loss as the wave travels through the forming network.

The curve of ultrasonic attenuation presents an asymmetric peak after an initial sudden growth, which can be related to the irreversible losses occurring during cross-linking, as can be observed also in the curing reaction of
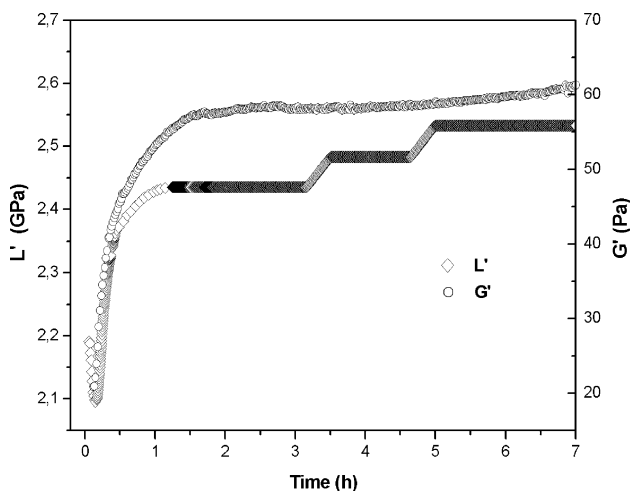

Fig. 4. Comparison between the storage longitudinal (L') and shear (G') moduli obtained during the cross-linking of a polymeric solution of CMCNa/HEC in water with a 0.04 mol/l DVS content.
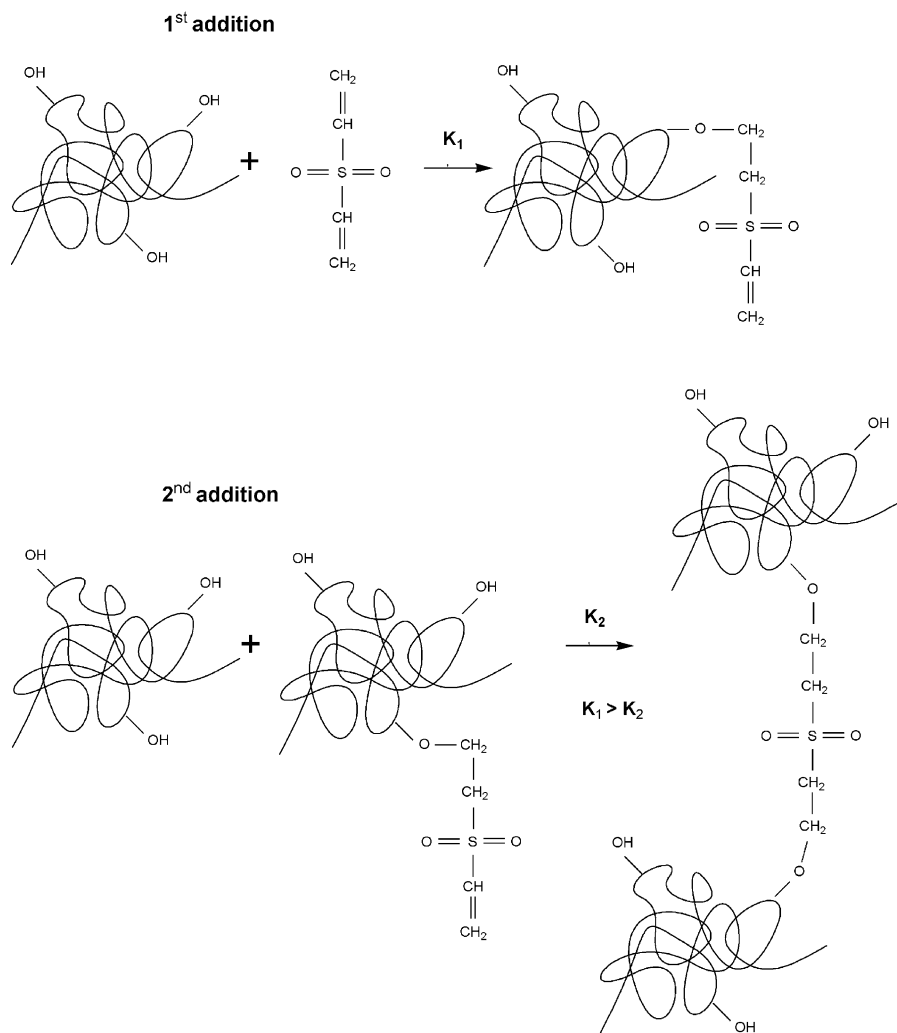
Fig. 6. The possible reaction mechanisms of the first and second addition of the DVS carbon–carbon double bonds to the cellulose chain.
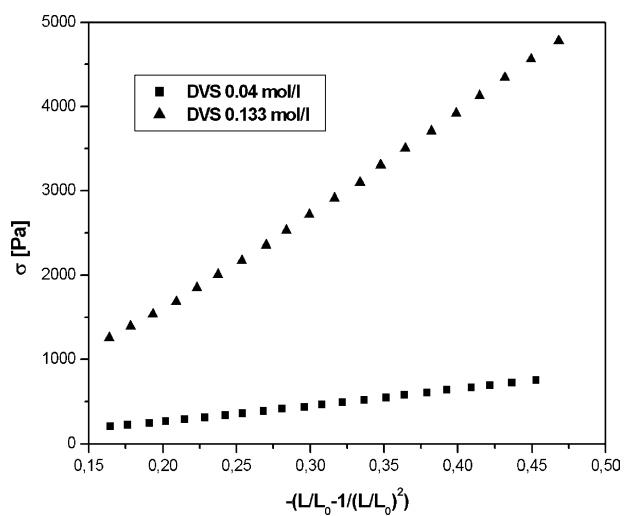

Fig. 7. Effect of DVS content on the uniaxial compressive behaviour of cross-linked cellulose hydrogels.
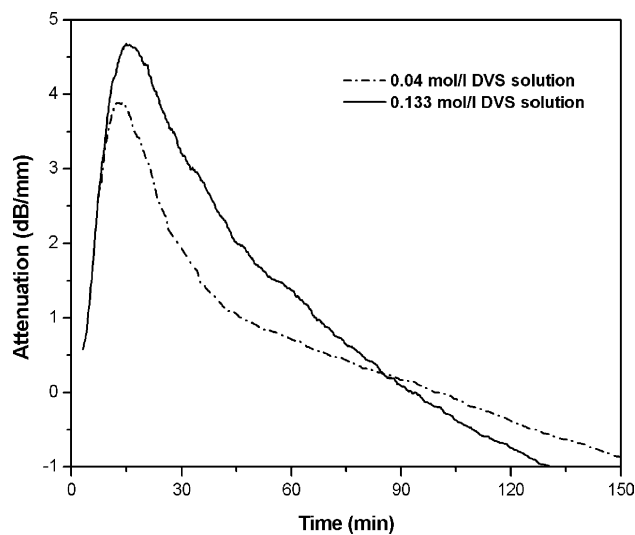

Fig. 8. Ultrasonic attenuation measured at 10 MHz during the cross-linking at 298 K of polymeric solutions of CMCNa/HEC in water with different DVS content.

thermosetting resins either at ultrasonic frequencies [16–24] either at low frequencies [35]. The maximum is followed by a slow decrease, because the dissipative losses experimented by the ultrasonic waves through a cross-linked polymer are lower than through a polymer solution. The maximum in the attenuation can be attributed to gelation, i.e. the phase transformation at which the cross-linking system transforms from a viscous liquid to a rubbery gel and the elastic shear and Young moduli present finite values.

As reported by Babayevsky and Gillham [35], which analysed the shear dynamic-mechanical properties of an epoxy resin during cure at low frequency (1 Hz), two peaks in the damping factor are expected during cure of a thermosetting resin. The first (weaker) was attributed to gelation and the second (stronger) to the transition in the glassy state (vitrification). In the case of hydrogel, only the gelation occurs during the network formation and, therefore, the attenuation peak is associated to the transformation into the rubbery state.

The effect of the DVS content on the rate of the ultrasonic velocity increase is confirmed by the trend observed in the ultrasonic attenuation (Fig. 8), where the reacting solution with a higher cross-linker content presents a delayed peak. This difference in the peak times can be explained as reported above for the differences between the rate of the velocity change. The higher peak observed at 1.33 mol/l DVS concentration can be associated, at the beginning of cross-linking process, with the development of short dangling ends arising from the reaction of a single DVS carbon–carbon double bond. On the other hand, a tight network is developed at a higher DVS content, leading to a lower attenuation (damping) at the end of the cross-linking.

The comparison between the loss longitudinal modulus L'' and the loss shear modulus G'', obtained during cross-linking at 298 K of a polymeric solution of CMCNa/HEC in water with a 0.04 mol/l DVS content, is reported in Fig. 9.
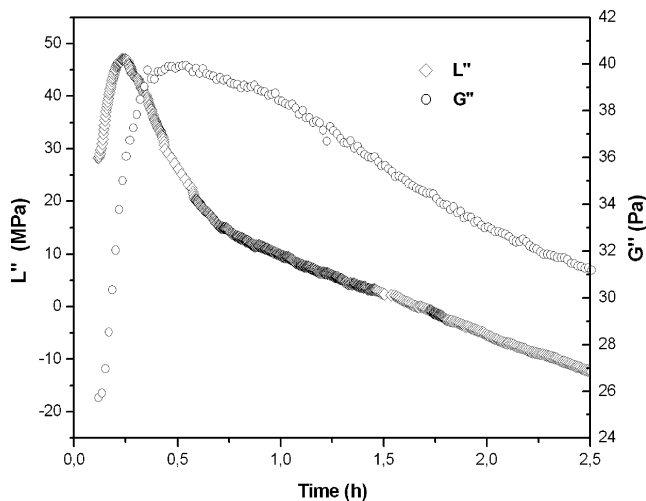

Fig. 9. Comparison between the loss longitudinal (L'') and shear (G'') moduli obtained during the cross-linking of a polymeric solution of CMCNa/HEC in water with a 0.04 M DVS content.

Since the peaks in the loss moduli correspond to a relaxation process, associated with the cross-linking, occurring in the frequency range of measurement at a fixed temperature, the peaks in L'' and G'' occur at different cross-linking times, as expected. In particular, the L'' peak is anticipated with respect to G'' peak being a high frequency dynamic mechanical response of the forming network. It should be noted that, in both low and high frequency measurements, the loss peaks are asymmetric with a slow decrease lasting several hours, due to the long time required to complete the cross-linking reaction.

4. Conclusions

The cross-linking reaction during the synthesis of a cellulose based superabsorbent hydrogel in water solution has been monitored by means of ultrasonic propagation of longitudinal waves and dynamic oscillatory shear measurements.

The increase in the ultrasonic velocity indicated the growth of elastic properties due to the development of the gel phase. The attenuation presented a bell shape indicating the occurring of irreversible losses associated with the hydrogel cross-linking.

A good agreement between the results of low and high frequency dynamic mechanical analysis has been observed although the difference in the loss peak time must be ascribed to the different magnitude order in the frequency used for both kinds of experiment.

The effect of the cross-linker concentration on the hydrogel acoustic behaviour has been also analysed and correlated with the different elastic response developed by the macromolecular gels.

The ultrasonic results presented in this work demonstrate the reliability of the ultrasonic measurements during the network formation process of a superabsorbent hydrogel. This novel technique can be a valuable tool for kinetic monitoring of hydrogel cross-linking, compared to other more complex and more expensive techniques such as solid state nuclear magnetic resonance (NMR) or Fourier transform infrared (FTIR). The non-destructive character of the deformations applied on the material and the potential implementation of the ultrasonic equipment as on-line sensors, make the ultrasonic wave propagation suitable for mechanical measurements that, so far, neither continuously nor in situ have never been performed.

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