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Preparation and Characterization of Interpenetrating Polymer Hydrogels Based on Poly(acrylic acid) and Poly(vinyl alcohol)

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Summary: Interpenetrating polymer hydrogels (IPHs) of Poly (vinyl alcohol) (PVA) and Poly (acrylic acid) (PAAc) have been prepared by a sequential method: crosslinked PAAc chains were formed in aqueous solution by crosslinking copolymerization of acrylic acid and N, N'-methylenebisacrylamide in the presence of PVA. The application of freezing-thawing cycles (F-T cycles) leads to the formation of a PVA hydrogel within the synthesized PAAc hydrogel. The swelling and the viscoelastic properties of the prepared IPHs were evaluated on the basis of the structural features obtained from solid state ^{13}C-NMR spectroscopy.

Keywords: interpenetrating hydrogels; poly (acrylic acid); poly (vinyl alcohol); solid state ^{13}C-NMR; viscoelastic properties

Introduction

Hydrogels are hydrophilic polymer networks that have a large capacity for absorbing water and that are characterized by the presence of crosslinks, crystalline and amorphous regions, entanglements, and rearrangements of hydrophobic and hydrophilic domains[1]. Polymer hydrogels have been proposed for many applications, such as the controlled delivery of medicinal drugs, artificial muscles, sensor systems, and bioseparations, because of their good biocompatibility, stimuli-responsive properties, and water permeation properties[2]. The reinforcement of a polymer hydrogel is a major problem in the expansion of its applications because a hydrogel has a poor mechanical property in water. Polymers with microphase separated morphologies, such as copolymers in which hydrophobic and hydrophilic domains alternate, seem to possess improved mechanical properties. This morphology can also be achieved with interpenetrating polymer hydrogels (IPHs).

IPHs are a combination of two or more polymers gels synthesized in juxtaposition[3]. They can also be described as polymer gels held together by permanent entanglements. The gels are held by topological bonds, essentially without covalent bonds between them. By

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definition, an IPH structure is obtained when at least one polymer gel is synthesized independently in the immediate presence of another. IPHs are an important class of materials attracting broad interest from both fundamental and applications points of view[4,5].

In the present study we report on the preparation, and on the swelling and viscoelastic properties of temperature, electrical-stimuli and pH-dependent PVA/PAAc interpenetrating hydrogels. The properties of the PVA/PAAc IPHs have been interpreted on the basis of the structural features obtained from solid state ^{13}C-NMR spectroscopy.

Experimental

Acrylic acid monomer was purchased from Aldrich and was purified under vacuum distillation to eliminate hydroquinone inhibitor. N, N′-methylenbisacrilamide (N-BAAm), used as crosslinker and potassium persulfate, used as thermal initiator were employed without further purification. Poly (vinyl alcohol), > 99% hydrolyzed, with a weight average molecular weight of 94.000 g/mol and a tacticity of syndio = 17.2%, hetero = 54.1 % and iso = 28.7%, was from Aldrich and it was used without further purification.

PVA/PAAc IPHs were prepared by a sequential method: PVA solutions (polymer concentrations ranging from 3 to 10 % (g/mL)) were prepared in hermetic Pyrex tubes by mixing the appropriate amount of polymer and water (milli-Q grade) at 100 C under conditions of vigorous stirring until the polymer was completely dissolved. Acrylic acid monomer aqueous solutions containing the thermal initiator, and the crosslinking agent were added at room temperature. The solutions were poured into glass plates, sealed with paraffin and allowed to react at 50 C for 24 hours. The obtained hydrogels were cut into specimens of cylindrical form (20 mm in diameter and 2 mm in height). Some of the specimens were tested in this state and other specimens were subjected to a freezing-thawing cycle: specimens were frozen to -32 C for 15 hours and then, were allowed to thaw at room temperature for 5 h.

Dynamic viscoelastic measurements were performed in a TA Instruments AR1000 Rheometer, using the parallel-plate shear mode to measure the storage modulus, G’, the loss modulus, G’’ and the loss tangent, tan δ. To avoid the influence of aging on the G’ modulus, the measurements for all samples were performed 2 h after the gels were prepared. The operating conditions were the following: temperature sweep between 20 and 100 C, plate diameter 20 mm, frequency 1 Hz, temperature scan 20 C/min, torque 50 μNm. The linear viscoelastic region was located with the aid of a torque sweep. All the viscoelastic measurements were performed on hydrogels swelled to equilibrium.

The cylindrical specimens of the hydrogels were immersed in distilled water and allowed to swell until equilibrium is attained at room temperature. The relative swelling ratio (Q_r) of the samples was defined by equation (1)

$$Q_r = \frac{(W_s - W_r)}{W_r} \tag{1}$$

where W_s and W_r are the weights of the swollen sample and the relaxed sample (specimen as formed, previous to the immersion in distilled water), respectively.

Solid state ^{13}C-NMR experiments were carried out using a Bruker spectrometer at 400 MHz. High resolution ^{13}C NMR was performed using magic-angle sample spinning (MAS) and high power spin decoupling. To enhance the signal to noise ratio, the cross-polarization (CP) technique was applied. Zirconia rotors were used at a spinning velocity of 4.0 KHz. The contact time for CP was 1 ms. 4000 scans were necessary to obtain an adequate signal to noise ratio. The chemical shifts of ^{13}C spectra are reported in ppm relative to TMS by taking the methine carbon of solid adamantane (29.5 ppm) as an external reference standard.

Results and discussion

Figure 1 shows the effect of PVA concentration in the relative swelling ratio of IPHs (crosslinking degree of the PAAc hydrogel 3%). As can be observed, the higher is the concentration of PVA in the IPHs, the lower is the relative swelling ratio in the IPHs subjected to one F-T cycle. In the IPHs not subjected to this treatment the relative swelling ratio decreases until a concentration of PVA of 7% (g/mL). This can be explained by the increase of intermolecular interactions and entanglements density with the increase of polymer concentration. By comparing the swelling ratio of the IPHs subjected and not subjected to one F-T cycle it can be seen that, in the first case, IPHs swell more than in the second case. This could be explained by the physical gelation of PVA within the PAAc network which increases the crosslinking density of the network.

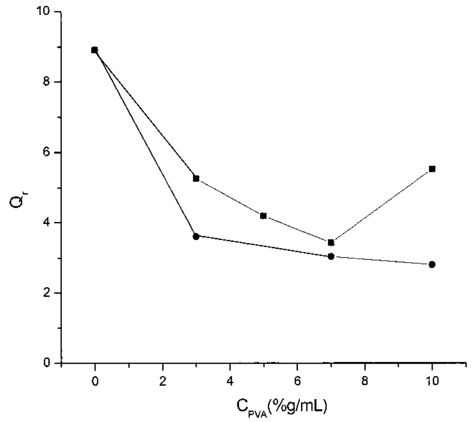

Figure 1. Relative swelling ratio as a function of PVA concentration for PAAc/PVA hydrogels subjected (•) and not subjected (▪) to a freezing-thawing cycle. PAAc crosslinking degree 3%.

Concerning the viscoelastic properties, Figure 2 depicts the storage modulus as a function of PVA concentration for IPHs with a degree of crosslinking for the PAAc hydrogel of 3%. As can be seen, the storage modulus of the IPH increases with PVA concentration. Furthermore, the IPHs subjected to one F-T cycle have higher modulus values than IPHs not subjected to this treatment. These results are in accordance with the swelling measurements.

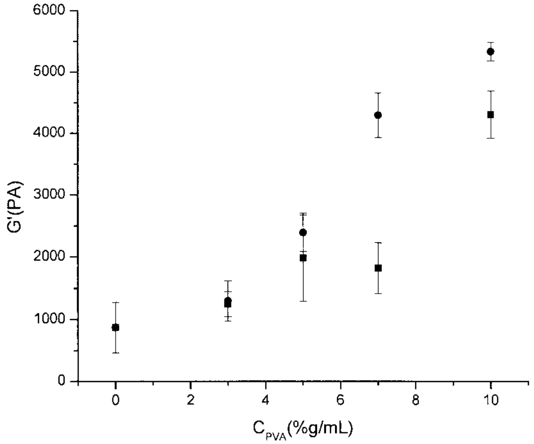

Figure 2. Storage modulus as a function of PVA concentration for PVA/PAAc hydrogels subjected (•) and not subjected (▪) to a freezing-thawing cycle. PAAc crosslinking degree 3%.

To obtain basic information on molecular interactions in the PVA/PAAc IPHs, we have performed solid state ^{13}C-NMR spectroscopy of PVA, PAAc and PVA/PAAc IPHs at room temperature. The spectra are shown in Figure 3 and the peak assignment for pure PAAc networks of crosslinking degree 3% and pure PVA films are given in table 1.

Table 1. Peak assignment for PAAc (crosslinking degree 3%) and PVA films.

Peak	Assignment	PAAc 3%	PVA 10% (g/mL)
1	(-CH_2-)	34.1	
2	(-CH-)	40.9	
3	(-CH_2-)		45.8
4	(-CHOH-)		65.0
5	(-CHOH-)		70.6
6	(-CHOH-)		76.3
7	(-CO(NH)-)	177.7	
8	(-COOH-)	181.8	

Resonance of the COOH carbon of PAAc and CHOH carbon of PVA, whose chemical shifts are very sensitive to hydrogen bond formation, consist of well resolved peaks without any overlapping for all the samples. For pure PVA, the CHOH band shows three peaks in the solid state as previously reported[6]. Terao et al[6] interpreted the chemical shifts of the CHOH resonance in terms of inter and intramolecular hydrogen bonding. They assigned peak 6 to the carbon which is linked by two hydrogen bonds to neighbor CHOH groups, peak 5 to the carbon linked by only one hydrogen bond, and peak 4 to the carbon not hydrogen bonded at all. Thus, peak 6 and 5 can be taken as indicators of inter and intramolecular hydrogen bonding of OH groups between two units of the PVA chain.

In the same way as for PVA/PAAc blends, a remarkable composition dependence of the ^{13}C-NMR spectra was observed for PVA/PAAc IPHs. Peak 6 is not observed for any of the IPHs samples. This detail indicates that the formation of two hydrogen bonds over the same hydroxyl group is restricted. This can be interpreted by the formation a PVA-PAAc complex through hydrogen bonds between the hydroxyl groups of the PVA chains and the carbonyl group of the PAAc chains. The steric hindrance introduced by the PAAc inhibits the formation of more than one hydrogen bond per monomer unit.

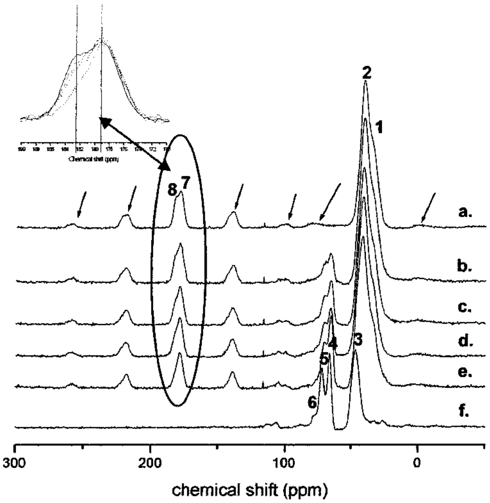

Figure 3. 13C CP/MAS spectra of dried films of: PVA (f), PAAc of crosslinking degree 3% (a) and PVA/PAAc IPHs of PVA concentration 3% (b); 5% (c); 7% (d); 10% (e) and 15% (f).

Conclusion

Interpenetrating polymer hydrogels composed of PVA and PAAc were successfully prepared by a sequential method as suggested by the viscoelastic and the swelling experiments: crosslinked PAAc chains were formed inside of a PVA solution by crosslinking copolymerization of acrylic acid and N,N′-methylenebisacrylamide. Then, the application of freezing-thawing cycles leads to the formation of a PVA hydrogel within the PAAc hydrogel[7]. Besides, solid state ^{13}C-NMR experiments has revealed the existence of hydrogen bonds between PVA and PAAc in IPHs.

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