Preparation and Characterization of Polyacrylic Acid-Poly(Vinyl Alcohol)-Based Interpenetrating Hydrogels

Rebeca Hernández, Daniel López, Carmen Mijangos

Instituto de Ciencia y Tecnología de Polímeros, C.S.I.C., Calle Juan de la Cierva 3, 28006 Madrid, Spain

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ABSTRACT: Some structural features of hydrogels from poly(acrylic acid) (PAAc) of various crosslinking degrees have been investigated through mechanical and swelling measurements. Interpenetrating polymer hydrogels (IPHs) of poly(vinyl alcohol) (PVA) and 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 freeze–thaw (F–T) cycles leads to the formation of a PVA hydrogel within the synthesized PAAc hydrogel. The swelling and viscoelastic properties of the IPHs were evaluated as a function of the content of crosslinker and the application of one F–T cycle. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 102: 5789–5794, 2006

Key words: polyacrylic acid hydrogels; viscoelastic properties; swelling properties; interpenetrating polymer hydrogels

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]

Polyacrylic acid (PAAc) hydrogels are usually prepared by free-radical crosslinking copolymerization of acrylic acid and *N,N*-methylenebisacrylamide (*N*-BAAm). Domain formation in polymer gels and resulting heterogeneities are the usual features of polymer networks produced by free radical polymerization techniques.[3] Network inhomogeneities have been studied using light-scattering techniques for various neutral or polyelectrolyte gels.[4] The results indicate the increasing extent of inhomogeneities in gels with increasing content of crosslinker.

Aqueous solutions of PVA can undergo gelation when submitted to a series of freeze–thaw (F–T) cycles. In the F–T process, crystallization of water results in the creation of interstitial domains with high polymer concentrations, where the PVA chains crystallize and hydrogen bond form. The properties of the cryogels depend on the molecular weight of the polymer, the concentration of the aqueous PVA solution, temperature and time of freezing and thawing, and the number of F–T cycles.[5,6]

PVA is well known for its processability, strength, and long-term temperature and pH stability. The characteristics that make it ideal for biomedical use are its biocompatibility, nontoxicity, minimal cell, and protein adhesion. PAAc is known to be a model hydrophilic system. Its carboxyl groups are ionized and swell considerably about the pK_a value of 4.7. As the chains are far apart above the pK_a value. PAAc is very fragile and breaks easily. To strengthen this hydrophilic system, PAAc is polymerized and crosslinked with other polymers, in particular PVA.[7]

Combinations of the two polymers can be prepared in the form of blends, copolymers, and interpenetrating polymer networks (IPNs) or interpenetrating polymer hydrogels (IPHs). IPHs are a combination of two or more polymer gels synthesized in juxtaposition.[8] 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 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.[9,10]

Gudeman and Peppas[11,12] reported on the pH-sensitive membranes from poly(vinyl alcohol) (PVA)

Correspondence to: D. López (daniel@ictp.csic.es).
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and polyacrylic acid (PAAc) interpenetrating polymer networks (IPN). In this case, the IPN was crosslinked using glutaraldehyde. Cho et al.[13,14] have prepared pH- and temperature-responsive IPN hydrogels composed of PVA and PAAc crosslinked by ultraviolet (UV) irradiation and a F–T method and investigated their swelling behavior and their potential applications as drug delivery systems.[15]

In a previous study,[16] we reported the effect of PVA concentration on the kinetics of gelation and on the molecular structure of PAAc gels. The presence of PVA chains in the reaction media during the crosslinking copolymerization of acrylic acid and *N,N′*-methylenebisacrylamide entails an increase of the gelation time. Nevertheless, the molecular structure of the resulting semi-IPH, composed of swollen clusters, is rather unaffected by the PVA concentration. The rather porous structure of this semi-IPHs put forward the possibility to form IPHs by the application of F–T cycles.

In the present work, we have prepared PVA–PAAc IPHs by a sequential method, consisting of the preparation of a PAAc hydrogel in the presence of PVA chains and subsequent gelation of the PVA chains by the application of a F–T cycle. The swelling and viscoelastic properties of the formed systems have been investigated to corroborate the formation of the interpenetrated hydrogel. In a previous step, we determined some structural parameters and properties of PAAc hydrogels synthesized through radical copolymerization.

EXPERIMENTAL SECTION

Sample preparation

Materials

The acrylic acid monomer (AAc) was purchased from Aldrich (Madrid, Spain) and was purified under vacuum distillation to eliminate the hydroquinone inhibitor. *N*-BAAm (Aldrich), used as crosslinker, and potassium persulfate (Aldrich), used as thermal initiator, were employed without further purification. PVA, > 99% hydrolyzed, with a weight average molecular weight of 94,000 g/mole and a tacticity of syndio (17.2%), hetero (54.1%), and iso (28.7%), was purchased from Aldrich and was used without further purification.

Preparation of PAAc hydrogels

The PAAc gels were prepared by crosslinking copolymerization of AAc with a small amount of *N*-BAAm in aqueous solution. The polymerization was initiated by potassium persulfate. At a constant monomer concentration of 1.25 mole/L, gels with different amounts of crosslinker were prepared (see Table I).

TABLE I
Composition of PAAc Hydrogels

Crosslinking degree (*X*) (%)	Mole *N*-BAAm	Mole $K_2S_2O_8$	Gel aspect
0.5	0.25×10^{-3}	7.5×10^{-4}	Transparent
1	0.5×10^{-3}	7.6×10^{-4}	Transparent
3	1.5×10^{-3}	7.8×10^{-4}	Transparent
4	2×10^{-3}	8.1×10^{-4}	Transparent
6	3×10^{-3}	8.4×10^{-4}	Semitransparent
8	4×10^{-3}	8.7×10^{-4}	White
10	5×10^{-3}	9×10^{-4}	White
12	6×10^{-3}	9.3×10^{-4}	White
16	8×10^{-3}	10×10^{-4}	White

The degree of crosslinking, X, is defined as the ratio of moles of crosslinking agent to moles of PAAc repeating units. The degree of crosslinking thus achieved ranged within 0.5–15%. Aqueous solutions of the appropriate amount of reactants were poured into Petri dishes and allowed to react at 50°C for 24 h. When gelation was achieved, cylindrically shaped specimens of 20-mm diameter and ~ 2-mm height were cut.

Preparation of PVA–PAAc interpenetrating hydrogels

PVA–PAAc IPHs were prepared by a sequential method: PVA solutions (polymer concentrations within the range of 3–10% (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. Aqueous solutions of acrylic acid monomer 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 h. The composition of the gels is shown in Table II.

The obtained hydrogels were cut into specimen of cylindrical form (20-mm diameter and 2-mm height). One-half of the specimens were tested in this state and the other half were subjected to a F–T cycle: specimens were frozen to −32°C for 15 h and were then allowed to thaw at room temperature for 5 h.

Methods

Swelling measurements

The cylindrical samples were immersed in deionized water (pure gels) and were kept there until equilibrium is attained at room temperature. The relative degree of swelling was determined by weighting the specimen at different times until constant weight is

TABLE II
Composition of PVA–PAAc Hydrogels

Sample	mole AAc	mole *N*-BAAm	mole $K_2S_2O_8$	mole PVA	$mole_{PVA}/mole_{PAAc}$	C_{PAAc} (mole/L)	C_{PVA} (mole/L)
PVA3PAAc3	0.05	0.0016	8×10^{-4}	0.027	0.5/1	1.25	0.6
PVA5PAAc3	0.05	0.0016	8×10^{-4}	0.045	0.9/1	1.25	1.1
PVA7PAAc3	0.05	0.0016	8×10^{-4}	0.063	1.2/1	1.25	1.5
PVA10PAAc3	0.05	0.0016	8×10^{-4}	0.09	1.8/1	1.25	2.25
PVA3PAAc6	0.05	0.0029	8.4×10^{-4}	0.027	0.5/1	1.25	0.6
PVA5PAAc6	0.05	0.0029	8.4×10^{-4}	0.045	0.9/1	1.25	1.1
PVA7PAAc6	0.05	0.0029	8.4×10^{-4}	0.063	1.2/1	1.25	1.5
PVA10PAAc6	0.05	0.0029	8.4×10^{-4}	0.09	1.8/1	1.25	2.25

obtained. The absolute degree of swelling at equilibrium was determined by thermogravimetric analysis performed in a Perkin-Elmer TGA apparatus. Pieces of the gel swollen to equilibrium were introduced in the TGA oven and maintained at 100°C until water was completely removed. The measurement of sample weight before and after water evaporation allows determination of the degree of swelling. The average molecular weight between adjacent crosslinks, M_c, for PAAc hydrogels was calculated using the Peppas–Merrill equation, which is a modified Flory–Rehner equation for highly swollen gels that are polymerized in solution:[17]

$$\frac{1}{M_C} = \frac{2}{M_n} - \frac{\left(\frac{v}{V_1}\right)\left[Ln(1-v_2) + v_2 + \chi v_2^2\right]}{v_{2c}\left[\left(\frac{v_2}{v_{2c}}\right)^{1/3} - \frac{1}{2}\left(\frac{v_2}{v_{2c}}\right)\right]} \quad (1)$$

In this equation, M_n is the number average molecular weight in the absence of any crosslinking; v the specific volume of the polymer; V_1 the molar volume of the solvent; v_2 the equilibrium polymer volume fraction; v_{2c} the polymer volume fraction after crosslinking but before swelling; and χ_1 is the polymer solvent interaction parameter (0.5 for the system PAAc–water).[18]

It should be noted that the factor (1–2 M_c/M_n) is the correction for network imperfections resulting from chain ends; the value of this factor is one for perfect networks and it is also approximated to one for crosslinking polymerizations.[17]

Rheological measurements

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, and torque 50 μNm. The linear viscoelastic region was located with the aid of a torque sweep. All the viscoelastic measurements were performed on hydrogels swollen to equilibrium.

The molecular weight between crosslinks can also be estimated by means of viscoelastic measurements. The theory of polymer networks predicts the shear modulus G for polymer gels obtained by solution crosslinking copolymerization to be[19]

$$G = \left(1 - \frac{2}{f}\right)\frac{RTCv_2^{1/3}v_{2c}^{-1/3}}{M_c} \quad (2)$$

where f is the functionality of the crosslinks ($f = 4$ for tetrafunctional networks), R is the gas constant, T is the temperature, and C is the monomer concentration [in grams per square meter (g/m^3)] The use of the front factor (1–2/f) is appropriate for dilute systems such as gels (Phantom Networks). For more concentrated Affine networks of functionality 4, the front factor becomes 1.

RESULTS AND DISCUSSION

PAAc hydrogels

It is already established that the opacity in gels is due to the spinodal decomposition of the polymer network concentration into smaller domains with two different densities: a dilute one and a dense one. These concentration fluctuations can scatter light and reduce the transmission of visible light through the gel. In the case of PAAc gels, we have obtained an increase in the opacity of the gels with the increase of *N*-BAAm obtaining white gels for crosslinking degrees higher than 6%. To study the network structures produced under the polymerization conditions used, the equilibrium swelling ratio and the mechanical modulus of the gels were measured, and the results were used in conjunction with different theories to calculate the average molecular weight between crosslinks.

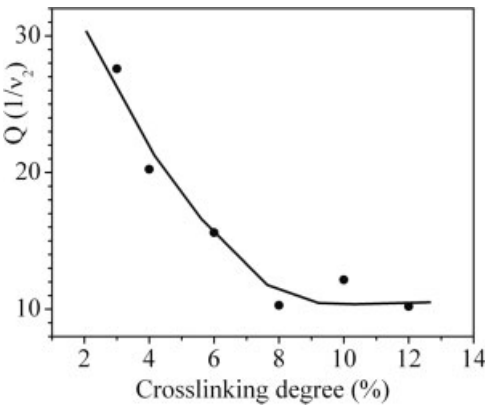

Figure 1 Swelling degree as a function of crosslinking degree for PAAc gels.

Figure 1 depicts the equilibrium swelling degree as a function of degree of crosslinking for PAAc gels. As can be seen, the values of the degree of swelling in the equilibrium decrease as the degree of crosslinking increases up to a value of 8%. For values of crosslinking degree higher than 8% the swelling degree remains constant. In Figure 2(a), the evolution of the storage modulus with temperature for PAAc gels of different degrees of crosslinking is depicted. Two conclusions can be drawn from Figure 2(a): (1) the storage modulus increases linearly with temperature, a behavior characteristic of chemical gels whose elasticity is of entropic origin;[20] and (2) the storage modulus increases with the degree of crosslinking of the gels. Figure 2(b) shows the variation of the equilibrium modulus with the degree of crosslinking for PAAc hydrogels in swelling equilibrium. As can be seen, the shear modulus increases with the degree of crosslinking according to viscoelastic theories.

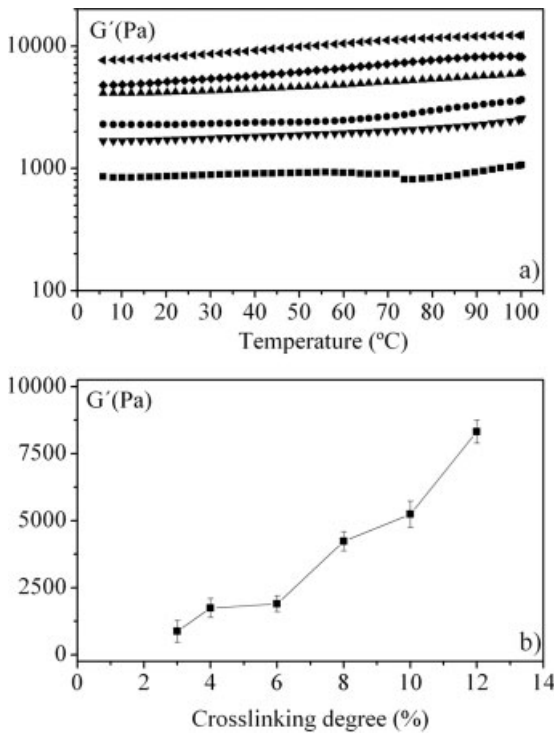

Figure 2 (a) Storage modulus as a function of temperature for PAAc gels of crosslinking degree: 3 (■); 4 (▼); 6 (●); 8 (▲); 10 (◆); 12 (◀). (b) Equilibrium storage modulus as a function of crosslinking degree for PAAc gels at T = 25°C.

M_c values were calculated using eqs. (1) and (2), and the results are shown in Figure 3, where a theoretical $M_{c,t}$ value was calculated according to eq. (3) and compared with the experimental results:

$$M_{c,t} = \frac{M_r}{2X} \tag{3}$$

where M_r is the molecular weight of AAc and X is the ratio mole of bis/mole of AAc.

As expected, M_c decreases with the crosslinking. In addition, M_c values are two orders of magnitude higher than those expected from the stoichiometry, indicating high sol fractions and network imperfections (formation of cycles) that are inherent in radical crosslinking copolymerizations.[21] The value of the cyclization parameter (k_{cyc}) can be calculated using eq. (4):[22]

$$K_{cyc} = 1 - \frac{M_r}{2XM_c} \tag{4}$$

where M_r is the acrylic acid monomer molecular weight (M_r = 72 g/mol), and M_c is the experimental average molecular weight between crosslinks (e.g., *Mc* values obtained from rheological measurements have been used). The results are summarized in Table III. Only 2–6% of *N*-BAAm used in the feed

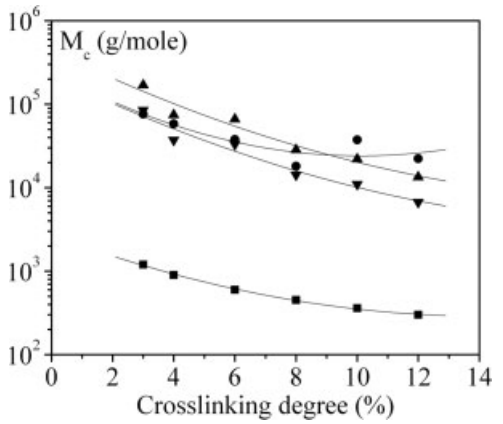

Figure 3 Average molecular weight between crosslinks as a function of crosslinking degree for PAAc gels: ■, theoretical; ●, swelling measurements; ▼, rheological measurements (phantom model); and ▲, rheological measurements.

TABLE III
Cyclization Parameter (K_{cyc}) for PAAc Hydrogels

X (mole$_{N\text{-}BAam}$/mole $_{Aac}$)	Mc (g/mole)	k_{cyc}
0.04	45,000	0.98
0.06	20,000	0.97
0.08	6,400	0.93
0.12	5,000	0.94

forms effective crosslinks in the final hydrogels. These values are comparable to those found in the bibliography[23] for polyacrylamide hydrogels. Thus, we can conclude that because of the high extent of cyclization reactions, the highly intramolecularly crosslinked microgel particles act as junction points. Increasing the content of crosslinker only increases the compactness of these junctions without changing the distance between the microgels.

In a previous study[16], we demonstrated that the molecular structure of the PAAc hydrogels is rather unaffected by the presence of PVA chains. This fact, together with a rather porous structure of these hydrogels put forward the possibility to form interpenetrating PAAc-PVA hydrogels through physical gelation of the PVA chains by application of a F–T cycle.

PVA–PAAc hydrogels

Figure 4 shows the effect of PVA concentration in the equilibrium swelling ratio of PVA–PAAc hydrogels of two different crosslinking degrees for PAAc (3% and 6%). Figure 4 presents two kinds of samples: those that have been subjected (IPHs) and those that have not been subjected (semi-IPHs) to F–T cycles.

Comparing the equilibrium swelling ratio of the hydrogels subjected and not subjected to one F–T cycle, one can see that semi-IPHs swell more strongly than IPHs. This result can be explained by the physical gelation of PVA within the PAAc hydrogel. The gelation of PVA increases the crosslinking density of the network, thus reducing the equilibrium swelling ratio. Taking into account the PVA concentration, there is a decrease of the swelling ratio up to a concentration of PVA of 5% (g/mL). Above this concentration, an increase of the swelling ratio occurs, which could be attributed to the segregation of PVA from the PAAc network due to phase separation. The phenomenon of surface segregation can be detected by FTIR-ATR spectroscopy. In Figure 5 the FTIR-ATR spectra of the upper (polymer–air interface) and lower (polymer–glass interface) surfaces of dried IPHs samples are represented.

The comparison of the band intensity at 1093 cm^{-1} (characteristic of PVA) with the intensity of the band at 1718 cm^{-1} (characteristic of PAAc) shows that the polymer–air surface is enriched in PVA, while the polymer–glass surface is enriched in PAAc. Therefore, most probably, PVA that it is not interpenetrated with PAAc is eliminated in the process of swelling and the heterogeneity of the PAAc hydrogel prevents in some way the homogeneous distribution of the PVA chains inside the gel.

Concerning the viscoelastic properties, Figure 6(b) 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 6(a) depicts the storage modulus as a function of PVA concentration for IPHs with a degree of

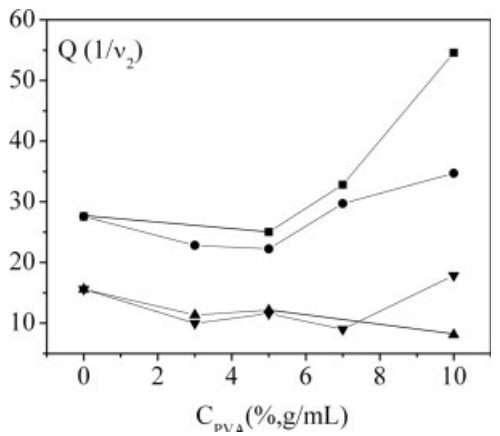

Figure 4 Equilibrium swelling ratio as a function of PVA concentration for PAAc hydrogels: ●, PVAPAAc3 subjected to FT cycle; ■, PVAPAAc3 not subjected to FT cycle; ▲, PVAPAAc6 subjected to FT cycle; ▼, PVAPAAc6 not subjected to FT.

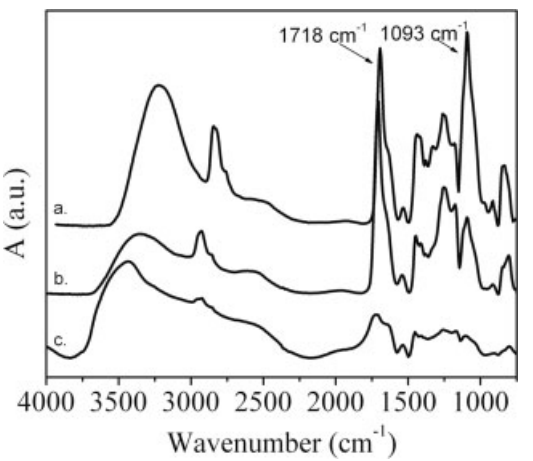

Figure 5 FTIRATR spectra of the surface polymer air (a), surface polymer glass (b), and FTIR spectrum of the PVA5-PAAc6 (c).

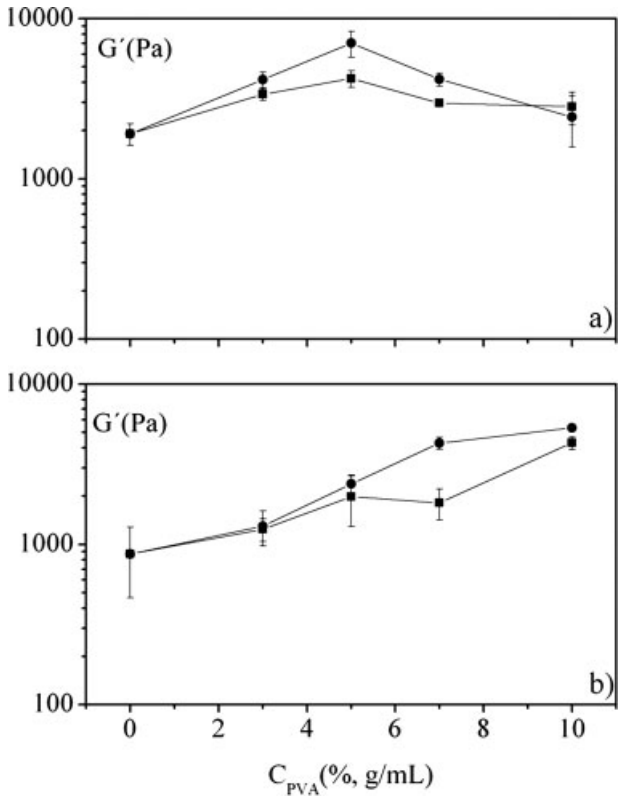

Figure 6 Storage modulus as a function of PVA concentration for hydrogels subjected (●) and not subjected (■) to a freeze–thaw cycle. (a) PVAPAAc6; (b) PVAPAAc3.

crosslinking for the PAAc hydrogel of 6%. As can be seen, they have a higher storage modulus than the corresponding IPHs with a crosslinking degree of 3% and this is in accordance with the swelling measurements. Furthermore, the storage modulus of the IPH increases with PVA concentration until a concentration of PVA of 5% (g/mL) above this concentration the storage modulus decreases for IPHs subjected to one F–T cycle and not subjected to it. This is probably due to the inhomogeneity of the sample that has a higher concentration of PVA at the surface as already shown by FTIR-ATR spectroscopy. The presence of a higher amount of segregated PVA at the surface of the samples makes the correct determination of the storage modulus of the samples impossible. Instead an ''artificial'' storage modulus is measured.

CONCLUSIONS

PAAc hydrogels obtained by crosslinking copolymerization of acrylic acid and *N*-BAAm show a heterogeneous porous structure composed of swollen clusters. The swelling and the viscoelastic measurements show that only 2–6% of the crosslinker molecules used in the hydrogel preparation are involved in the formation of effective crosslinks.

IPHs composed of PVA and PAAc were prepared successfully by a sequential method. The application of one F–T cycle to the PVA–PAAc semi-IPHs leads to the formation of IPHs, as suggested by the viscoelastic and the swelling experiments. The degree of swelling and the mechanical properties of the PVA–PAAc IPHs depend on the PVA concentration and on the degree of crosslinking of PAAc. As the degree of crosslinking of PAAc and/or the concentration of PVA increases, the degree of swelling decreases and the mechanical properties of the IPHs improve with respect to the hydrogels from pure PAAc. For large PVA concentrations and/or a high PAAc degree of crosslinking, macrophase separation occurs and the properties of the IPHs obtained worsen with respect to the pure hydrogels.

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