Organic–Inorganic Interpenetrating Polymer Networks and Hybrid Polymer Materials Prepared by Frontal Polymerization

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ABSTRACT: Novel polyacrylamide-based hydrogels containing 3-(trimethoxysilyl)propyl methacrylate and/or tetraethoxy silane were synthesized by means of frontal polymerization, using ammonium persulfate as initiator, N,N'-methylene bisacrylamide as crosslinking agent and dimethyl sulfoxide as solvent. The obtained samples were treated at pH of 2 or 5 to induce the sol–gel reaction and evaluate their swelling behavior in the conditions. The occurrence of this reaction was assessed by solid-state NMR. Moreover, the thermal properties of the dry materials were studied by differential scanning calorimetry and thermal gravimetric analysis, and their water-contact angles were measured. It was found that the amount of Si affects the extent of swelling and the hydrophilicity of the resulting materials. © 2013 Wiley Periodicals, Inc. J. Polym. Sci., Part A: Polym. Chem. 2013, 51, 4618–4625

KEYWORDS: acrylic polymers; frontal polymerization; hydrogels; interpenetrating networks (IPN); radical polymerization

INTRODUCTION Hydrogels are polymeric materials that swell in water and maintain a distinct three-dimensional structure.[1] The existence of hydrogels dates back from 1960s when Wichterle and Lim[2] proposed the use of hydrophilic networks of poly(2-hydroxyethyl methacrylate) in soft contact lenses. Since then, hydrogels have been used for many pharmaceutical[3] and biomedical applications.[4] For example, Lim and Sum[5] in 1980 established the application of calcium alginate microcapsules for cell encapsulation. In addition, hydrogels have been applied in diagnostics,[6] tissue engineering,[7] drug delivery,[8–10] and chemical sensors.[11]

Some hydrogels have been defined "smart"[12] or "stimuli responsive" because of their ability to receive process or transmit a stimulus (pH, temperature, light, ionic strength, the presence of chelating species, electric and magnetic fields, etc.) and to respond by producing an effect. For example, some of them undergo fast, reversible changes in microstructure from a hydrophilic to a hydrophobic state. This change is reversible, and thus allowing the system to return to its initial state when the stimulus is removed.

Hybrid hydrogels are referred to systems that possess components from different classes of molecules, for example, organic polymers and inorganic moieties, covalently interconnected.[13]

Interpenetrating polymer networks (IPNs) are a class of polymer blend that can be defined as a combination of two polymers in a network form in which one is synthesized or crosslinked in the presence of the other. The main characteristics of an IPN are as follows: (a) the creep and flow are suppressed and (b) an IPN swells, but does not dissolve in any solvent. Moreover, IPNs possess enhanced physical properties as compared to the normal polymer blends of their components. There are two different classifications of IPNs: (a) by chemistry and (b) by structure.[14–16]

By chemistry, the most known IPNs are (1) simultaneous interpenetrating networks and (2) sequential IPNs. In the first class, polymerizing two different monomers and the crosslinking agent in only one step forms the IPN. As for the sequential IPNs, a network is initially formed by polymerizing a mixture of monomer, crosslinking agent, and initiator

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(or catalyst), which is then swollen with the second combination of monomer and crosslinking agent.

The classification by structure of IPNs is as follows: (1) homo-IPNs: these are a special type of IPNs, where the two polymers used in the network are the same; (2) full-IPNs: in this case, the IPN comprises two networks that are ideally juxtaposed. This generates many entanglements and interactions between the networks; (3) semi- or pseudo-IPNs: in the IPN, one of the components has a linear instead of a network structure; (4) thermoplastic-IPNs: in the structure of the IPNs, at least one component is usually a block copolymer. Moreover, these IPNs are moldable, can be extruded and recycled; and (5) latex-IPNs: the most important feature of these IPNs is that the morphology depends on how the IPN components are polymerized. Normally, these IPNs are formed by emulsion polymerization.

Frontal polymerization (FP) is a process in which a monomer converts into a polymer by means of a localized reaction zone that propagates owing to interaction between the production of heat by chemical reaction and its dispersion by thermal conduction.[17] The result is the formation of a polymerization front able to self-sustain and propagate along the whole reactor. If compared with the classical polymerization techniques, FP has many advantages: shorter reaction time, low-energy consumption, easy and simple protocols, and affords obtaining materials that often have better properties than those obtained by classic polymerization.

FP was first developed in 1972 by Chechilo and Enikolopyan[18,19] with the synthesis of poly(methyl methacrylate). FP was further studied by Pojman,[20–32] Chen,[33–38] and by our group.[39–52]

We also applied FP to the obtainment of stimuli-responsive hydrogels poly(N,N-dimethylacrylamide),[53] poly(acrylamide-co−3-sulfopropyl acrylate),[54] poly(N-isopropylacrylamide-co−3-sulfopropyl acrylate),[55] P(N-isopropyl acrylamide-co-N-vinylcaprolactam),[56] and poly(2-hydroxyethylacrylate-co-acrylic acid).[57] Recently, we have proposed FP as a new method for the synthesis of graphene-containing polymer nanocomposites of poly(tetraethylene glycol diacrylate),[58] polyurethanes,[59] and poly(bisphenol A glycerolate dimethacrylate-co-tetraethylene glycol diacrylate);[60] in addition, stimuli-responsive polymer hydrogels based on PNIPAAm and poly(N-vinylcaprolactam) and containing graphene or partially exfoliated graphite or nanocrystalline cellulose have been successfully prepared by FP, as well.[61–64]

In this article, we report on the application of FP to the preparation of full IPN hybrid hydrogels. They were prepared starting from acrylamide (AAm) with the addition of 3-(trimethoxysilyl)propyl methacrylate (3-TMeOSi) and/or tetraethoxy silane (TEtOSi) as sol–gel reactants and N,N′-methylene bis-acrylamide (BIS) as the crosslinker agent. The swelling behavior, water-contact angle (WCA), differential scanning calorimetry (DSC), thermal gravimetric analysis (TGA), and nuclear magnetic resonance (NMR) were used for sample characterization.

EXPERIMENTAL

Materials
AAm (99%, FW = 71.8, mp = 84–86 °C), TEtOSi (FW = 208.33, d = 0.933 g/mL), 3-TMeOSi (FW = 248.35, d = 1.045 g/mL), BIS (FW = 154.17, mp = 300 °C) ammonium persulfate (AmPS, FW = 228.20), and dimethyl sulfoxide (DMSO, FW = 78.13, bp = 189 °C, d = 1.101 g/mL) were purchased from Sigma-Aldrich and used as received.

Hydrogel Synthesis
Hydrogels were prepared using different molar fractions of AAm, TEtOSi, and 3-TMeOSi, from the AAm homopolymer to copolymers containing up to 1.72 mol % of TEtOSi and 6.88 mol % of 3-TMeOSi, keeping constant the amounts of crosslinker (BIS, 0.25 mol % referred to the amount of AAm), initiator (0.5 mol% referred to the amount of AAm), and DMSO (2.5 mL).

A common glass test tube (i.d. = 1.5 cm, length = 16 cm) was filled with the appropriate amounts of AAm, TEtOSi, 3-TMeOSi, BIS, and DMSO. The mixture was sonicated with an ultrasonic bath at 25 °C until the mixture became homogeneous. Then, AmPS was added.

A thermocouple junction was located at about 1.5 cm from the bottom of the tube and connected to a digital thermometer to monitor the temperature. FP started by heating the external wall of the tube at the upper surface of the monomer mixture with the tip of a soldering iron. The position of the front, visible through the glass wall of the test tube, was measured as a function of time. Front temperature measurements were performed by using a K-type thermocouple connected to a digital thermometer, Delta Ohm 9416, employed for temperature reading and recording (sample rate = 1 Hz). The front velocity, V_f (± 0.5 cm/min), and the front temperature, T_{max} (± 15 °C) were measured for all samples. Once the FP was achieved, all samples were washed with distilled water to remove DMSO.

Characterization
The swelling ratio (SR%) of hybrid hydrogels was measured at various time intervals using the following equation:

$$SR\% = \frac{W_s - W_d}{W_d}$$

where W_d and W_s are the hydrogel masses in the dried and in the swollen state, respectively.

DSC thermal characterization was performed by means of a Q100 Waters TA Instruments calorimeter, using TA Universal Analysis 2000 software. Two heating ramps from −80 to 300 °C, employing a heating rate of 10 °C/min, were carried out on dry samples. The first scan was carried out to remove traces of residual solvent and determine monomer conversion by calculating the residual polymerization heat. The second was recorded to determine the glass transition temperatures (T_g).

The thermo-oxidative stability of the hydrogels was evaluated by TGA in air (gas flow, 60 mL/min), from 50 to

TABLE 1 Experimental Data for the FP of AAm/TEtOSi Hydrogels Prepared in This Study

Sample Code	TEtOSi (mol %)	BIS (mol %)	V_f (cm/min)	T_{max} (°C)	T_g (°C)
A1	0	0.25	3.8	220	226
B1	0.35	0.25	4.0	202	243
C1	0.70	0.25	4.4	192	246
D1	1.72	0.25	4.8	209	252
E1	3.50	0.25	5.9	221	255

800 °C with a heating rate of 10 °C/min. A TAQ500 analyzer was used, placing the samples (ca. 10 mg) in open alumina pans.

The morphological characterization of polymer hydrogels was carried out using a SEM JEOL 7600. Before the analysis, samples were lyophilized, fractured in liquid nitrogen, and the fractured surface was coated with gold.

WCAs were determined by a Dataphysics OCA 5, 10 instrument on the above samples previously treated at both pH 2 and 5, and desiccated before the measurement.

High-resolution NMR spectra were collected using a Varian UNITY INOVA Spectrometer with a 9.39 T wide-bore Oxford magnet. The ground samples were analyzed by ^{29}Si Cross-Polarization Magic Angle Spinning (CP/MAS) by packing each sample into a 7-mm ZrO$_2$ rotor at a spinning rate of 5 KHz. The ^{29}Si CP/MAS experiments were run with a contact time of 1 ms, recycle time of 2 s, 90° pulse lengths, a 100-kHz bandwidth, and 2000 scans in each experiment. ^{29}Si chemical shifts were referenced to that of tetramethylsilane.

RESULTS AND DISCUSSION

FP of AAm and TEtOSi: Obtainment of Composite Materials

In this series of experiments, samples composed of polyacrylamide (PAAm) and TEtOSi were prepared. This latter compound was chosen in that it is able to undergo sol–gel reaction in acidic conditions.[65,66] It should be noticed that, after the latter condensation reaction, a composite material is obtained, which is constituted of an organic polymer matrix and crosslinked silica as inorganic filler, not directly linked to each other. Moreover, after sol–gel reaction as both AAm and TEtOSi give rise to crosslinked structures, the resulting materials can be classified as organic–inorganic IPNs.

The effect of the concentration of TEtOSi (which was allowed to range from 0 to 3.50 mol %) on the main FP parameters (i.e., V_f and T_{max}) was studied by keeping constant the amounts of BIS (0.25 mol %) and AmPS (0.5 mol %) as the radical initiator. As summarized in Table 1, V_f increases with TEtOSi concentration from 3.8 to 5.9 cm/min. However, as the samples containing 0 and 3.50 mol % TEtOSi underwent

evident degradation owing to the excessive front temperature (ca. 220 °C), the following research was focused on the hydrogels having 0.35, 0.70, and 1.72 mol % of TEtOSi, only.

Frontal Copolymerization of AAm and 3-TMeOSi in the Presence of TEtOSi: Obtainment of Hybrid Composite Materials

These materials contain a constant amount of AAm, which was copolymerized with 3-TMeOSi in the presence of TEtOSi. The concentration of these two latter compounds was allowed to vary by taking into account that the subsequent sol–gel condensation reaction may involve from one to four Si linkages of TEtOSi. For such a reason, the molar ratio between TEtOSi and 3-TMeOSi was varied from 1 to 4.

In Table 2, the results from three different sets of hybrid copolymers are presented. In the first series (B1–B5), containing 0.35 mol % of TEtOSi, the molar fraction of the comonomer 3-TMeOSi was varied from 0 to 1.40 mol %. In these samples, V_f ranged from 3.5 to 5.4 cm/min. In the same interval of concentrations, T_{max} ranges from 202 to 225 °C.

The second series (C1–C5) collects polymers containing 0.70 mol % of TEtOSi and 3-TMeOSi in concentration from 0 to 2.80 mol %. V_f increases from 4.4 to 5.8 cm/min and T_{max} values range from 192 to 211 °C. However, although front velocity increases monotonically with 3-TMeOSi, T_{max} drops down in correspondence of its highest concentration (182 °C; 2.80 mol %).

In the third series (D1–D5), data of samples containing 1.72 mol % of TEtOSi and 3-TMeOSi ranging from 0 to 6.88 mol % are grouped. V_f and T_{max} were found to vary from 3.0 to 5.7 cm/min and from 208 to 225 °C, respectively, without

TABLE 2 Experimental Data Obtained for the FP of AAm, TEtOSi, and 3-TMeOSi.

Sample Code	TEtOSi (mol %)	[3TMeOSi]/[TEtOSi] (mol %)	V_f (cm/min)	T_{max} (°C)	T_g (°C)
B1	0.35	0	4.0	202	243
B2	0.35	1	5.4	216	245
B3	0.35	2	4.2	215	243
B4	0.35	3	4.1	210	247
B5	0.35	4	3.5	225	242
C1	0.70	0	4.4	192	246
C2	0.70	1	4.9	208	265
C3	0.70	2	5.3	209	256
C4	0.70	3	5.6	211	237
C5	0.70	4	5.8	182	257
D1	1.72	0	4.8	209	252
D2	1.72	1	3.0	208	275
D3	1.72	2	4.2	225	264
D4	1.72	3	5.7	211	272
D5	1.72	4	3.7	208	283
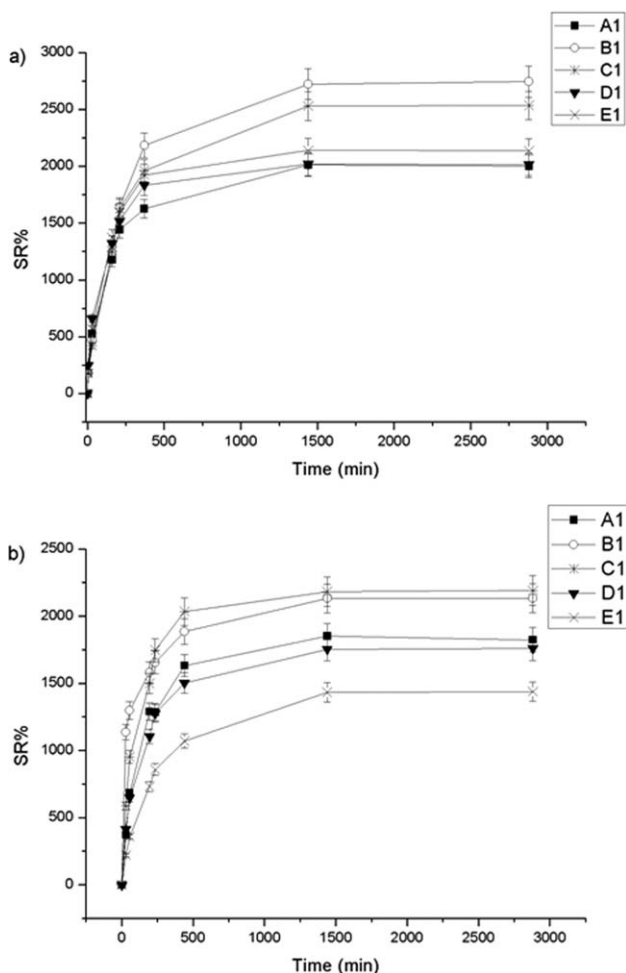
FIGURE 1 SR% as a function of time for the samples swollen at pH 5 (a) and pH 2 (b).

any apparent relationship with the ratio between TEtOSi and 3-TMeOSi.

Characterization

All samples were allowed to swell at pH of 2 or 5 and the swelling behavior of the resulting hydrogels was studied. To achieve the conversion of organosilane to Si—OH groups, by sol–gel reaction, the above acidic conditions were used.

In Figure 1, the SR% of the hydrogels made of AAm and TEtOSi as a function of time is reported for the first 2880 min (48 h). The equilibrium swelling for both pH values has been achieved approximately after 24 h. As it can be seen, after reaching the equilibrium, SR% was always comprised between about 2000 and 2700% (pH 5, Fig. 1(a)) or between about 1400 and 2200% (pH 2, Fig. 1(b)). This difference may be imputable to the larger conversion of the silane groups when stronger acidic conditions are used,[65,66] and they result in a more compact crosslinked structure.

Furthermore, in both series, the increasing of the TEtOSi content results in an initial increase of SR(%), which is then

followed by a decrease down to values that are even lower than that of the neat polymer hydrogel.

When TEtOSi is dispersed in the 3-TMeOSi/AAm copolymer instead of poly(AAm), SR% changes. Figure 2 shows the resulting trend as a function of the 3-TMeOSi concentration. TEtOSi was kept constant and equal to 0.35 mol % [Fig. 2(a)] or 0.70 mol% [Fig. 2(b)]; moreover, data refer to samples swollen at pH of 2 and 5. As expected, because of the sol–gel crosslinking, in all cases the SR decreases as the amount of 3-TMeOSi increases. However, similar to the aforementioned description, since at pH 2 the efficiency of such a reaction is higher,[65,66] samples allowed swelling in stronger acidic conditions swell less than the others.

The clear confirmation of these results was obtained from the ^{29}Si CP/MAS NMR experiments. The pertinent results of the samples swollen at pHs of 2 and 5 are shown in Figure 3.

Either spectra show three partially overlapping signals in the region between −40 and −70 ppm related to the silane organic moieties incorporated as a part of the silica wall
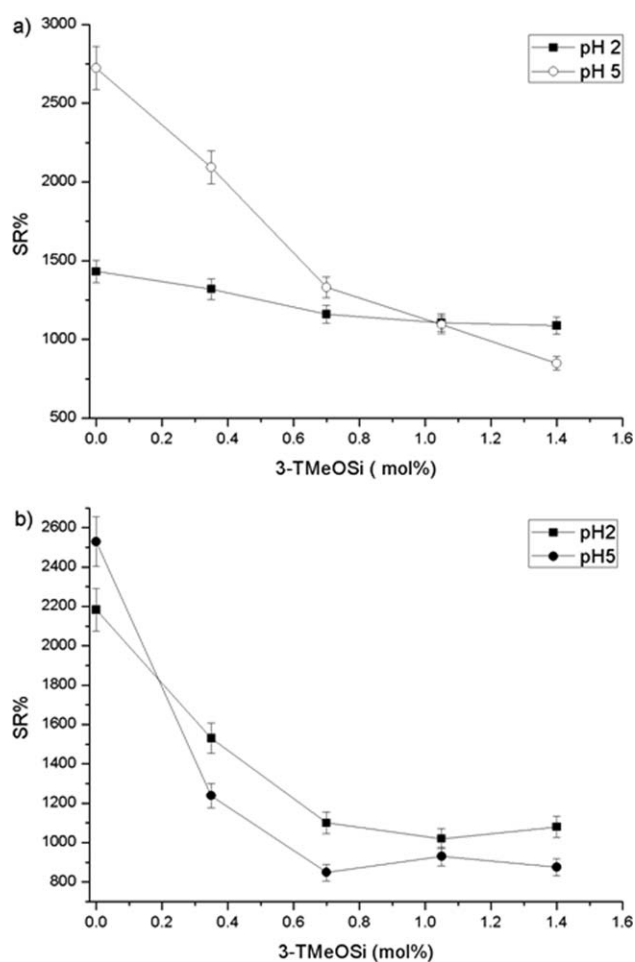
FIGURE 2 SR% as a function of the molar amount of 3-TMeOSi for the samples swollen at pH of 2 or 5. (a) [TEtOSi] = 0.35 mol %, (b) [TEtOSi] = 0.70 mol %. Data are taken at equilibrium conditions after 48 h.
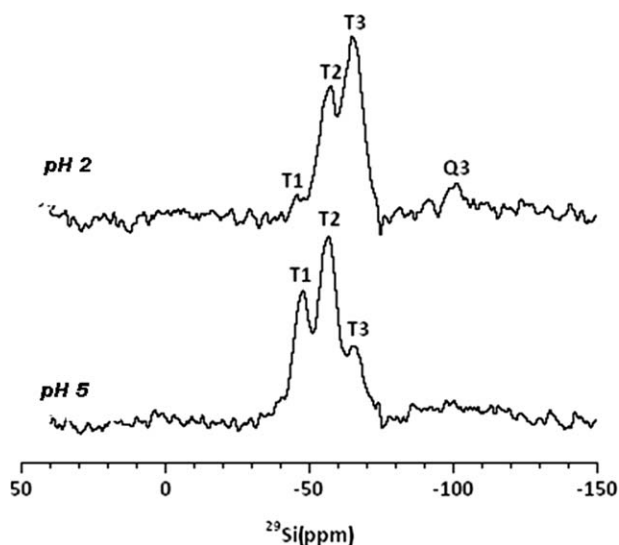
FIGURE 3 ^{29}Si CP/MAS NMR spectra for the samples D5 swollen at pHs of 2 and 5.

structure. According to the literature, they are assigned to T1 [SiC(OH)$_2$(OSi)] (−46 ppm), T2[SiC(OH)(OSi)$_2$] (−56 ppm), and T3 [SiC(OSi)$_3$] (−66 ppm) groups.[67,68]

In particular, the spectrum of the sample swollen at pH 2 shows an intense signal attributed to T3 (−66 ppm), a smaller signal attributed to T2 (−56 ppm), and a very small signal attributed to T1 (−46 ppm). This indicates a higher degree of condensation and crosslinking and means that most of silicon atoms do not have any free hydroxyl group. This spectrum shows also a signal at −101 ppm, ascribed to a Q3-type crosslinker moiety [Si(OSi)$_3$(OH),], indicating the presence of a small fraction of silica that is not involved in the bond with adjacent tetrahedral units.[69]

The sample swollen at pH 5 shows T1 (−36 ppm) and T2 signals (−56 ppm) that are more intense than the T3 one (−66 ppm). The presence of a higher concentration of free hydroxyl groups, resulting from T1 and T2 units, indicates a lower degree of condensation and crosslinking compared to the sample swollen at pH 2.

Furthermore, the thermal properties of the obtained polymer samples were evaluated by DSC and TGA. Conversion was determined by DSC, by using the following equation:

$$C\% = \left(1 - \frac{\Delta H_\mathrm{r}}{\Delta H_\mathrm{t}}\right) \times 100$$

where ΔH_r (residual) is the peak area obtained for the residual polymerization occurred during the first thermal scan, and ΔH_t (total) is the area under the curve when the polymerization was carried out in the DSC instrument. Conversion was always comprised between 90 and 95%.

As far as the T_g values are concerned (Tables 1 and 2), these were in the range of 226–283 °C, depending on the concentrations of TEtOSi and 3-TMeOSi. In particular, as expected,

poly(AAm) is characterized by the lowest T_g value, located at 226 °C (sample A1). Indeed, the addition of TEtOSi results in its significant increase to 243 °C for the sample containing 0.35 mol % of this filler; further addition gradually increases T_g up to the value of 255 °C for the sample containing 3.50 mol % of TEtOSi (Sample E1).

The glass transition temperature of the hybrid samples is also strongly affected by the presence of Si; in fact, as a general trend, the higher the content is the higher the T_g is. Moreover, a significant effect is owing to the crosslinking extent; indeed, as it can be seen by comparing samples containing different amounts of TEtOSi, the larger the amount is the higher the T_g is. For example, by comparing samples having [3-TMeOSi]/[TEtOSi] = 4 it goes from 242 °C when TEtOSi is equal to 0.35 mol % (Sample B5) to 283 °C when TEtOSi is 1.72 mol % (Sample D5).

As far as the thermo-oxidative stability of the hydrogel is considered, TGA analyses in air were performed. Table 3 summarizes the obtained values, referring to T_{10} (i.e., the temperature, at which the sample loses 10% mass) residue. It is noteworthy that the samples that did not undergo any acidic treatment, which is necessary to induce the sol–gel synthesis, exhibited a thermal stability that was even lower than that of the neat polymer matrix.

At variance, all samples treated at pH of 2 or 5 are characterized by a T_{10} higher than that of neat sample; namely,

TABLE 3 TGA data of the Obtained Samples

Sample Code	% [Si] (w/w)	T_onset (°C)
A1	0	183
B1	0.133	149
C1	0.263	130
D1	0.634	152
B5	0.638	163
C5	1.212	155
D5	2.587	197
B1[a]	0.133	196
C1[a]	0.263	203
D1[a]	0.634	192
B5[a]	0.638	221
C5[a]	1.212	245
D5[a]	2.587	222
B1[b]	0.133	198
C1[b]	0.263	233
D1[b]	0.634	217
B5[b]	0.638	196
C5[b]	1.212	232
D5[b]	2.587	219

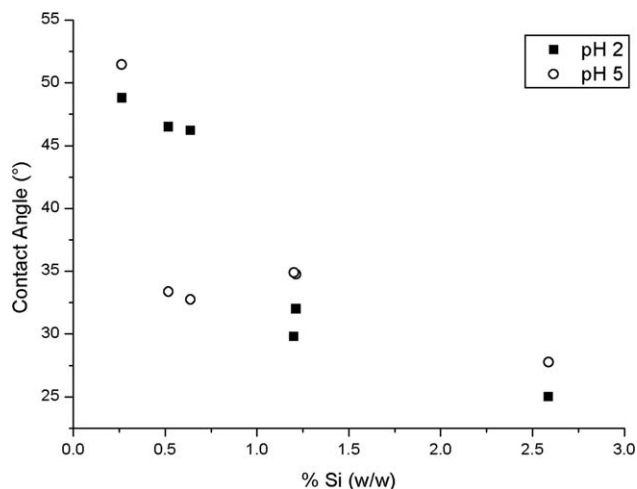[a] Sample swollen at pH 2.
[b] Sample swollen at pH 5.
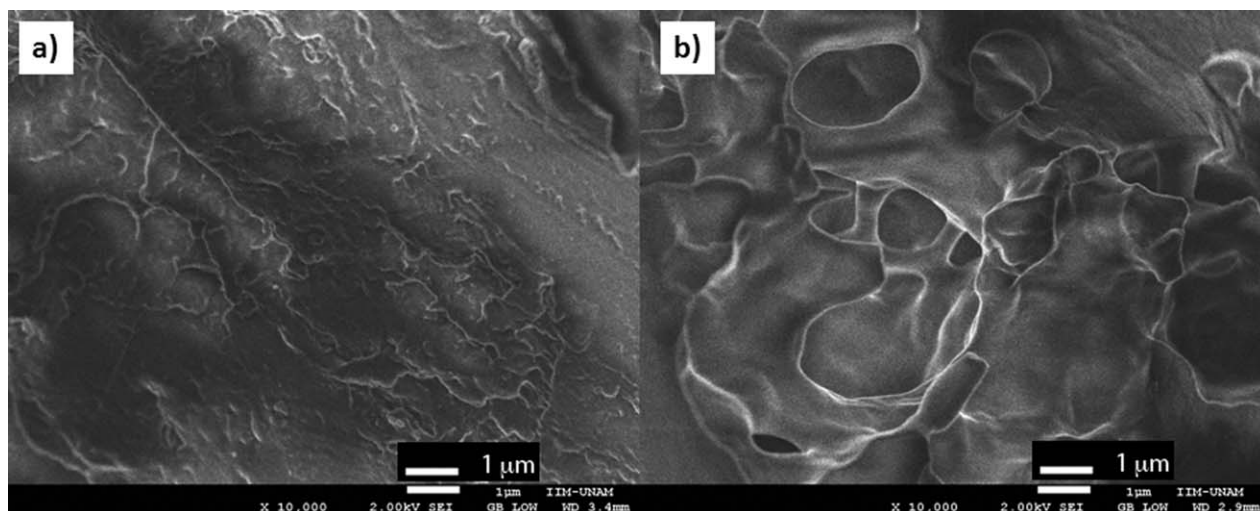
FIGURE 4 SEM images at pH 5 of (a) cross-sectional PAAm–TEtOSi hydrogel (Sample E1) and (b) cross-sectional PAAm–TEtOSi–3TMeOSi hybrid composite (Sample D5), having the highest Si content.

from 196 to 245 °C, even if the corresponding trend is not well defined.

This is a further confirmation that the sol–gel reaction is promoted during the swelling process.

The morphological structures of the PAAm/TEtOSi composite hydrogel and the hybrid composite hydrogel containing 3-TMeOSi were investigated by SEM. The analyses were carried out on samples treated at pH of 2 or 5, but micrographs did not show any significant difference among them. Therefore, it can be concluded that pH does not influence the hydrogel structure, at least at this level. This is also confirmed by the image shown in Figure 4, which is a comparison between the cross-sectional SEM images of the composite (Sample E1, Fig. 4(a)) and the hybrid hydrogel (Sample D5, Fig. 4(b)).

Finally, WCA data as a function of the total Si amount are shown in Figure 5. It is evident that, if the Si percentage in

the hydrogels is increased, for both the series of samples swollen in solutions of pH 2 or 5, the contact angle diminishes, thus accounting for an increased hydrophilicity.

It is also noteworthy that WCA values of the samples swollen at pH 2 are slightly lower than those swollen at pH 5, and thus confirming that stronger acidic conditions result in a larger hydrolysis extent.[65,66]

CONCLUSIONS

In this study, hybrid and composite IPN hydrogels of polyacrylamide were successfully synthesized through the FP technique.

In the composite hydrogel, the increasing of the TEtOSi content results in an initial increase of SR% in water, which is then followed by a decrease down to values that are even lower than that of the neat polymer hydrogel.

At variance, in the hybrid system the SR% decreases as the amount of 3-TMeOSi increases.

In both systems, it was found that, when the swelling experiments were carried out at pH 2, the SR% was less than that of the value found at pH 5. This finding is owing to a larger conversion of the silane groups when stronger acidic conditions are used,[65,66] which results in a more compact cross-linked structure. This statement was also confirmed by ^{29}Si CP/MAS NMR experiments, which evidenced the different extent of the sol–gel reaction.

Finally, by contact angle characterization, it was found that an increment of Si into hydrogel structure increases the hydrophilicity of the materials.

FIGURE 5 WCA for hybrid hydrogels having different amounts of silica and swollen at pH 2 (■) and pH 5 (○).

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