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Polyacrylamide hydrogels and semi-interpenetrating networks (IPNs) with poly(N-isopropylacrylamide): Mechanical properties by measure of compressive elastic modulus

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Semi-IPN hydrogels (based on cross-linked polyacrylamide having poly(N-isopropylacrylamide) (PN1PAAm) inside) were synthesized and their properties, such as swelling ratio and compressive elastic moduli, were studied at several temperatures. Equilibrium swelling ratios of semi-IPN markedly decreased due to the presence of less hydrophilic PNIPAAm chains. The semi-IPN presented greater elastic modulus when compared to the cross-linked PAAm hydrogel. The effect was explained as being an additional contribution of the PNIPAAm chains, which collapsed around the PAAm networks, to the elastic modulus. It was pointed out that the PAAm networks support the collapsed chains. According to the results presented in this work, semi-IPN hydrogels present better mechanical properties than the PAAm hydrogel, mainly when the PNIPAAm chains are in a collapsed state.

Introduction

The collapse of temperature-sensitive-hydrogels is a phase transition at which the gel volume changes dramatically in a narrow range of temperature [1]. This interesting characteristic may be used in a variety of applications. For instance, in controled drug delivery [2], molecular separation processes [3], tissue culture substrates [4]. However, a serious limitation of poly(N-isopropylacrylamide) (PNIPAAm) hydrogels in many applications is the low mechanical strength of such gels in a highly swollen state. In a previous work [5, 6] we synthesized semi-IPNs of cross-linked polyacrylamide (PAAm) having PNIPAAm inside. The semi-IPNs presented qualitatively good mechanical properties even in swollen state. In addition, the absence of large shrinkage in the semi-IPN hydrogels was observed at temperatures above the LCST of PNIPAAm. The results suggested that the PAAm network mechanically supports the collapsed PNIPAAm chains. A more detailed discussion is published elsewhere [7].

To confirm those achievements, the elastic modulus of the cross-linked PAAm gels having different amount of PNIPAAm inside was measured at several temperatures and, for the sake of comparison, same properties of pure PAAm hydrogels were also measured.

Materials and methods

PNIPAAm homopolymer was prepared by redox polymerization as already published [5–7]. Briefly, a solution was prepared by dissolving N-isopropylacrylamide and sodium persulfate in distilled water. This solution was previously nitrogen purged for at least 30 min to completely remove the oxygen. After, tetramethylenediamine (TEMED) was added and the flask was closed. The polymerization was carried out at ambient temperature for 24 h. Polyacrylamide homopolymer gels were prepared by photo-initiated polymerization. Acrylamide (AAm) and N,N′-methylene-bis-acrylamide (MBAAm), as cross-linking agent, were added to distilled water. To obtain semi-IPN, PNIPAAm aqueous solution, of desired concentration, was added instead of water. After nitrogen bubbling for 20 min, the solution was poured on a glass test tube of 1.2 cm diameter and 12 cm height. The tube, filled with the solution, was closed and exposed to γ-radiation from ^{60}Co at a dose rate of 216 kGy h^{-1}.

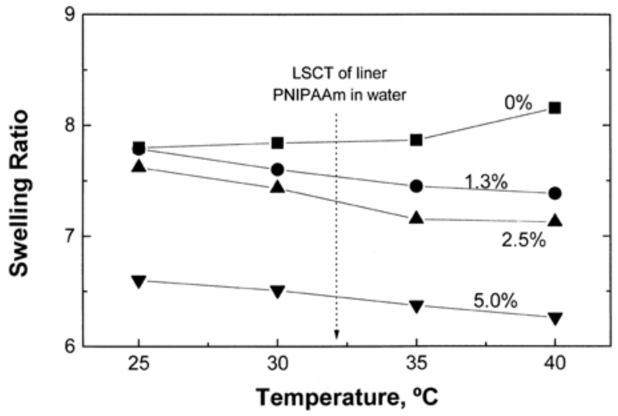

Figure 1 Swelling ratio as a function of temperature at several PNIPAAm content.

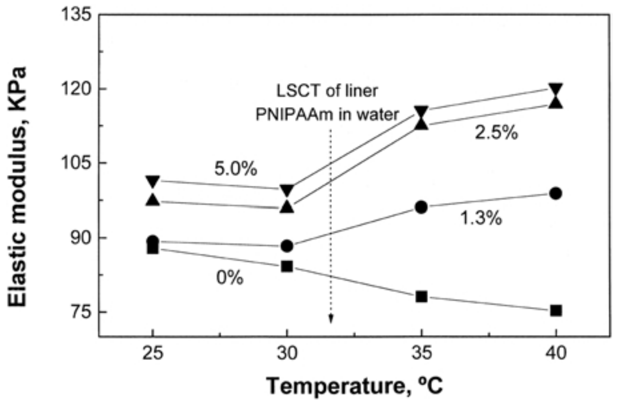

Figure 2 Compressing elastic modulus of hydrogels as a function temperature obtained for PAAm hydrogel and semi-IPNs.

After 50 min exposition, the test tube was carefully broken and the gel, in its cylindrical form, was recovered. Four kinds of hydrogels were prepared, having 0, 1.3, 2.5 and 5.0 PNIPAAm wt %. The cylindrical gels were cut in pieces of 1.0 cm height. Before the compressive experiments, the gels were maintained in water for one week at a desired temperature to remove unreacted monomers and allowing the gel to achieve swelling equilibrium. Uniaxial compression experiments were performed on the cut PAAm and semi-IPN hydrogels using a tensile testing machine, at temperatures of 25, 30, 35 and 40 °C. After adjusting the experimental parameters, each compressive experiment was done in less than one minute to avoid loss of water during the measurement. The elastic modulus, E, was determined from the slope of linear dependence of equation

$$\sigma = f/S_o = E\ (\lambda - \lambda^{-2}) \qquad (1)$$

where σ is the applied stress in Pa $\cdot$ m^{-2}, f is the value of measured force, S_o is the cross-section of the undeformed swollen specimen, and λ is the relative deformation of the specimen. Cylindrical gels, in same dimensions of those used in the compressive experiments, were swollen to equilibrium in water at temperatures of 25, 30, 35 and 40 °C. The swelling ratios were determined as being the ratio of the swollen gel weight to the dry gel weight. The apparent cross-linking density, ν_e, were determined using the equation [8]

$$\sigma = RT(\phi_{p,o}/\phi_p)^{2/3}\ \phi_p \nu_e\ (\lambda - \lambda^{-2}) \qquad (2)$$

where $\phi_{p,o}$ and ϕ_p are the polymer volume fractions in the relaxed state (gel just after polymerization) and in the swollen state, respectively.

Results and discussion

Fig. 1 shows the dependence of swelling ratio to the temperature for PNIPAAm content of 0, 1.3, 2.5 and 5.0 wt %. It could be observed that the presence of less hydrophilic PNIPA inside of hydrogel decreases the swelling ratio but no large shrinking was observed as the temperature is increased.

In Fig. 2, the dependence of elastic modulus to the temperature for PNIPAAm content of 0, 1.3, 2.5 and 5.0 wt % is presented. The E values of PAAm hydrogels decrease from 88 kPa, at 25 °C, to 75 kPa, at 40 °C. On the other hand, the E values of semi-IPN hydrogels increase as the PNIPAAm content is raised as well as the temperature. For instance, at 25 °C, the value of E to the hydrogel having 5 wt % of PNIPAAm is 101 kPa (15% higher than PAAm). At 40 °C, this hydrogel presents E equal to 120 kPa, which represents 36% more than PAAm at 40 °C and 16% more than the value of the respective hydrogel at 25 °C. The presence of PNIPAAm chains on the network increases the polymer volume fraction of the swollen gel. At 25 °C, the effect induces the formation of physical entanglements, increasing the apparent cross-linking density and then, increasing the compressive elastic modulus.

To highlight the effect of PNIPAAm chains on semi-IPN hydrogels at different temperatures, relative change in the elastic modulus was calculated taking the elastic modulus of PAAm hydrogel as reference. In this way, the G_{SI}/G_{PA} ratio was determined at several temperatures, being G_{SI} and G_{PA}, respectively, the calculated elastic modulus of PAAm and semi-IPN hydrogels. The dependence of the G_{SI}/G_{PA} ratio to the temperature for PNIPAAm content of 0, 1.3, 2.5 and 5.0 wt % in weight is presented in Fig. 3. It could be observed that an increment of the amount of PNIPAAm causes an increase in the elastic modulus. The effect is more important at temperatures above the LCST. Above 32 °C, the LCST of PNIPAAm in water [1–3, 5–8], the values of compressive elastic modulus of semi-IPN hydrogels are higher.

The effect was explained as an additional contribution

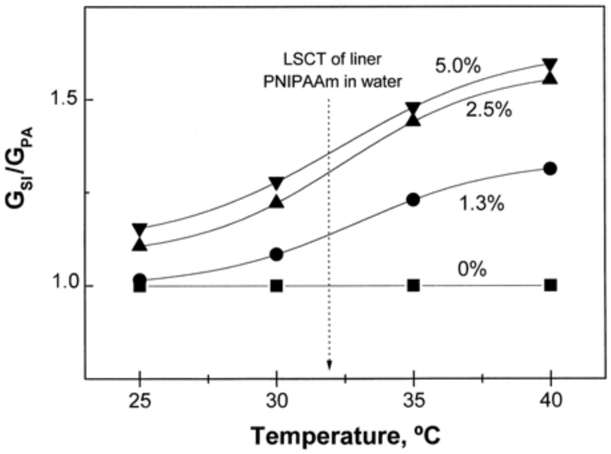

Figure 3 Dependence of G_{SI}/G_{PA} as a function of temperature at several PNIPAAm.

of the PNIPAAm chains collapsed around the PAAm networks to the elastic modulus. By swelling ratio measurements, it was verified that the collapse of PNIPAAm chains is not accompanied by a large shrinkage of the gel. It was pointed out that the PAAm networks support the collapsed chains.

Conclusions

According to the results presented in this work it could be concluded that the semi-IPN hydrogels present better mechanical properties than the PAAm hydrogel mainly when the PNIPAAm chains are in the collapsed state. This effect changes the pore size of hydrogel and confirms the build model used for explaining the sharp increases the permeability to Orange II at temperatures above LCST of such semi-IPNs and also their already published potential uses in drug delivery systems.

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References

1. T. TANAKA and D. J. FILLMORE, *J. Chem. Phys.* **70** (1979) 1214.
2. C. WU, *Polymer* **39** (1998) 4609.
3. R. F. S. FREITAS and L. CUSSLER, *Separ. Sci. and Tech.* **22** (1987) 911.
4. H. VON RECUM, T. OKANO and W. KIM, *J. Control. Release* **55** (1998) 121.
5. E. C. MUNIZ and G. GEUSKENS, Proceedings of the 15th European Society of Biomateriais Conference (Arcachon, September 1999).
6. E.C. MUNIZ and G. GEUSKENS, *J. Membrane Sci.* **172** (2000) 287.
7. E. C. MUNIZ and G. GEUSKENS, *Macromolecules* **34** (2001) 4480.
8. A. GUTOWSKA, Y. H. BAE, H. JACOBS, J. FEIJEN and S. W. KIM, *Macromolecules* **27** (1994) 4167.

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