IPN hydrogels based on PNIPAAm and PVA-Ma networks: characterization through measure of LCST, swelling ratio and mechanical properties

Adriana Cristina Wenceslau, Adley Forti Rubira and Edvani Curti Muniz[*]

Grupo de Materiais Poliméricos e Compósitos, Departamento de Química, Universidade Estadual de Maringá, Av. Colombo, 5790, 87020-970, Maringá, Paraná, Brazil. *Author for correspondence. E-mail: ecmuniz@uem.br; curtimuniz@gmail.com

ABSTRACT. IPN hydrogels based on chemically modified poly(vinyl alcohol) (or PVA-Ma), with different degrees of substitution (DS), and poly(*N*-isopropylacrylamide) (or PNIPAAm) were obtained and characterized through measures of LCST, swelling ratio and mechanical properties. Linear PVA-Ma with several DS were obtained through the chemical reaction of PVA with glycidyl methacrylate (GMA). The DS of various PVA-Ma were determined through ^{1}H NMR spectroscopy. Two steps were used for preparation the PVA-Ma/PNIPAAm membrane hydrogels. In the first step the PVA-Ma hydrogels (using PVA-Ma with different DS) were prepared by reaction of double bonds on PVA-Ma, using the persulfate/TEMED system. Using a photoreaction pathway in the second step, PNIPAAm network was prepared within the parent PVA-Ma network at different PVA-Ma/NIPAAm ratios. The studies show that degree of swelling ratio (SR) of PVA-Ma/PNIPAAm IPN hydrogels is dependent of temperature. The LCST for each IPN-hydrogel was determined by measuring the intensity of light transmitted through the hydrogel. The LCST of the IPN hydrogels ranged from 34.6 to 38.1ºC. The elastic modules of swollen IPN hydrogels increased from 25 to 35ºC but decreased by further warming to 45ºC. The LCST, swelling ratio and mechanical properties of PVA-Ma/PNIPAAm IPN hydrogels can be tailored by tuning the PVA-Ma/NIPAAm ratio.

Keywords: smart IPN hydrogels, PNIPAAm, PVA-Ma, tuning the LCST, temperature sensibility.

Hidrogéis IPN baseados em redes de PNIPAAm e PVA-Ma: caracterização através de medidas da LCST, da razão de intumescimento e de propriedades mecânicas

RESUMO. Foram obtidos hidrogéis IPN baseados em rede de poliálcool vinílico quimicamente modificado com metacrilato de glicidila (PVA-Ma), com diferentes graus de substituição (DS), entrelaçada com rede de poli(N-isopropilacrilamida) (PNIPAAm). PVA-Ma linear, com diferentes DS, foi obtido por reação de PVA com metacrilato de glicidila (GMA). O valor de DS de cada PVA-Ma foi determinado por meio de espectroscopia ^{1}H NMR. Foram utilizadas duas etapas para a preparação de membranas dos hidrogéis IPN. Na primeira etapa foram obtidos hidrogéis de PVA-Ma (usando PVA-Ma com diferentes DS) pela reação das duplas ligações do PVA-Ma. Na segunda etapa, por meio de uma foto-reação, foram obtidas redes de PNIPAAm entrelaçadas com redes de PVA-Ma, para diferentes razões PVA-Ma/NIPAAm. Os hidrogéis IPN foram caracterizados por medidas de LCST, razão de intumescimento e medida de modulo elástico. O valor da LCST para cada hidrogel IPN foi determinado por intensidade de luz transmitida através do hidrogel intumescido. Os estudos mostram que a razão de intumescimento dos hidrogéis IPN de PVA-Ma/PNIPAAm depende da temperatura. A LCST variou de 34,6 a 38,1ºC. O modulo elástico dos hidrogéis IPN intumescidos aumentou com a temperatura de 25 a 35ºC, mas decresceu com posterior aumento da temperatura, de 35 para 45ºC.

Palavras-chave: hidrogéis IPN inteligentes, PNIPAAm, PVA-Ma, ajuste da LCST, sensibilidade a temperatura.

Introduction

Hydrogel is a hydrophilic polymeric network that is able for absorbing large amounts of water, or biological fluids, without breaking its tridimensional (3D) structure (DÍEZ-PEÑA et al., 2002; PEPPAS; KLIER, 1991). Two or more interpenetrated polymer networks constitute IPN-typed hydrogels.

Such type of material can be prepared in one or more steps (BAJPAI et al., 2008). In the case of two-stepped IPN hydrogel, the network prepared in a first step is, after dried, re-swelled in a solution containing monomers and a suitable cross-linking agent that will, after further reaction(s), constitute the second network (BAJPAI et al., 2008; DE MOURA et al., 2006). When

necessary, such methodology can be repeated for obtaining subsequent interpenetrated networks (BAJPAI et al., 2008; EECKMAN et al., 2001; DE MOURA et al., 2006; SNOWDEN et al., 1996; ZHANG et al., 2004). The entanglements of polymer chains form networks that allow the improvement of properties, mainly the mechanical ones, relative to the not interpenetrated matrix (BAJPAI et al., 2008; PADMANABH et al., 2006). It is possible, for instance, to obtain IPN hydrogels that present, at same time, sensibility to temperature and pH when a network of thermal-sensitive polymer is entrapped in a network of pH-sensitive hydrogel (DÍEZ-PEÑA et al., 2002; PEPPAS et al., 2000).

The targets of this work are to prepare and characterize IPN hydrogels based on chemically modified poly(vinyl alcohol) and poly(*N*-isopropylacrylamide) obtained in a two-stepped methodology. Chemically modified PVA (or PVA-Ma) through reaction with glycidyl methacrylate, at different degrees of substitution (DS), was used for the IPN hydrogels preparation. The DS of various PVA-Ma were determined through ^{1}H NMR spectroscopy. The IPN hydrogels were evaluated through measures of swelling ratio at different temperatures using a pH 7-buffer as swelling medium. Other properties such as LCST of swollen hydrogel and compression elastic modulus were also investigated. A discussion evolving the structure-properties of so-obtained materials is made in this paper, based on achieved results.

Material and methods

Materials

Poly(vinyl alcohol) (PVA) 88 mol-% hydrolyzed, $M_W = 22,000$ (CAS 9002895), DMSO-d_6, 99.96 D atom-% (Lot 16902); N,N,N',N'-Tetraethylmethylenediamine (TEMED) 99%-purity (CAS 110-18-9), and N-isopropylacrylamide (NIPAAm), 99% purity (CAS 412781000), were supplied by Acros Organics (USA). Dimethyl sulfoxide (DMSO), CAS 9008-97-3, was acquired from Nuclear, Brazil. Glycidyl methacrylate (GMA), 97%-purity (CAS 106-91-2) was acquired from Sigma. N,N-Methylenebisacrylamide (MBAAm), 99.5%-purity (CAS 15516024) was supplied by Invitrogen. Ethanol P.A. was purchased from Synth (Brazil). All these chemicals were used as received.

Methods

i) Reaction of PVA with GMA

PVA was dissolved in DMSO by stirring at ~70°C obtaining a 10 wt-% solution. GMA was poured into aliquots of this solution to obtain the following final molar ratios [−OH(PVA)/GMA]: 1/0.025, 1/0.050, 1/0.075 and 1/0.10 (see Table 1). In all cases, TEMED was used as catalyst in conc. 1.0 mol-% relative to the PVA hydroxyl groups. The system was stirred for 6 hours under N_2 bubbling at 62°C. Afterwards, the modified polymer (hereafter labeled as PVA-Ma) was precipitated using ethanol as non-solvent. All PVA-Ma samples were dried at 40°C in an oven and stored in the dark at -5°C.

Table 1. Molar ratios [-OH(PVA)/GMA] used for reaction of PVA with GMA, the respective degree of substitution (DS) and the yield (%) obtained from ^{1}H NMR spectra.

[OH(PVA)/GMA]	1/0.025	1/0.050	1/0.075	1/0.100
DS % (mol-%r)	2.2	4.7	7.5	9.7
Yield %	88	94	100	97

ii) Characterization of PVA-Ma through ^{1}H NMR

The equipment Varian Mercury Plus BB 300 MHz spectrometer operating at 300.058 MHz was used for acquire the ^{1}H NMR spectra. Before analysis, a solution with approximately 30 mg of PVA-Ma dissolved in 0.7 mL of DMSO-d_6 was prepared. The signal of the solvent was used as internal reference (2.49 ppm). The degree of substitution (DS) was calculated for each PVA-Ma through the ^{1}H NMR spectrum according to method published elsewhere (CRISPIM et al., 2006a). Briefly, the ratio between the averaged area due to the vinyl hydrogens from methacryloyl groups, which appeared at δ 5.6 and 6.0 ppm, to the sum of areas due to vinyl hydrogens and to hydroxyl hydrogens of PVA was considered, as stated by the equation (CRISPIM et al., 2006a):

$$DS = \left[\frac{\left(\dfrac{A(H') + A(H'')}{2} \right)}{\left(\dfrac{A(H') + A(H'')}{2} \right) + A(OH)} \times 100 \right] \quad (1)$$

where:

$A(H')$ and $A(H'')$ are the areas due to two vinyl hydrogens from the methacryloyl groups and $A(OH)$ is the area due to the hydroxyl hydrogens present in the ^{1}H NMR spectrum.

iii) Synthesis of hydrogels

Two-stepped methodology was used for IPN hydrogels preparation. In the first step, hydrogel-membranes of PVA-Ma were obtained. The dried hydrogel membranes obtained in first step were used to form the PNIPAAm network entrapped the PVA-Ma network in the second step.

First step: preparation of PVA-Ma hydrogel matrices

A solution (50 mL) of each PVA-Ma (10 wt-%) was prepared. In this solution, TEMED 0.57 mol L^{-1} (0.2 mL) was dropped and the resultant solution was deoxygenated by N$_2$ bubbling for 15 min., under stirring. In sequence, sodium persulfate (Na$_2$S$_2$O$_8$) 0.2 g mL^{-1} (0.25 mL) was poured keeping the strong stirring. Each PVA-Ma/TEMED/Na$_2$S$_2$O$_8$ solution was transferred to between two glass plaques (3 x 3 cm) separated by a rubber gasket spacer (3 mm thickness) and left to react. Using this procedure, hydrogel membranes of PVA-Ma with different DS were prepared. The as-formed PVA-Ma hydrogel membranes were dipped in distilled water for one week at room conditions for removing unreacted moieties. The water was renewed every 12h. After, the hydrogel membranes were dried at room temperature. The kinetic of swelling for different PVA-Ma membranes were done to determine the time needed for reaching the equilibrium. In all cases, the reactant system was kept closed for further 24h to complete the cross-linking process.

Second step: synthesis of PNIPAAm network within PVA-Ma membranes

Membrane of dried PVA-Ma hydrogel, of known weight, was immersed in 50 mL of aqueous containing desired amounts of NIPAAm (monomer), MBAAm (cross-linker) and 0.1 g of KIO$_4$ (as photo-initiator). The amounts of chemicals used in each formulation are described in Table 2. After swelled up to equilibrium, each soft- and swollen-membrane was gently handled and transferred to between two glass plaques separated by a rubber gasket spacer (3 mm thickness). The system was exposed for 1h to an Hg lamp (low-pressure, 100 W) inside a closed camera initially at 25°C. The plaques containing the reactants were kept, one at time, at distance of ca. 15 cm from the light source. During the polymerization reaction, the temperature inside the camera raised up to ca. 50°C due to heat emitted by the lamp. After 1h of exposure each gel became completely opalescent indicating the formation of PNIPAAm network within the PVA-Ma network, as shown in photos of Figure 1, as an example.

The as-formed IPN hydrogels, hereafter labeled as IPN-1, IPN-2, IPN-3… IPN-8, were dipped in distilled water for one week at room conditions for removing unreacted moieties. The water was renewed every 12h. After be dried at room temperature, the IPN hydrogels were weighted for determination of yield for the polymerization/cross-linking of PNIPAAm (second step). The IPN hydrogels were also characterized at different temperatures, through swelling on pH 7-buffers, elastic modulus through compression tests, and measures of LCST.

Table 2. Different amounts of chemicals used in the first step and in the second step for the IPN hydrogel preparation.

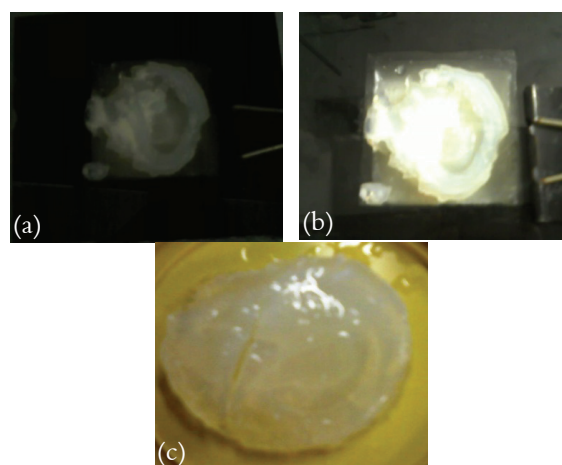| DS of PVA (%)	Mass of PVA-Ma (g)	Mass of NIPAAm (g)	Mass ratio PVA-Ma/ NIPAAm	Mass of MBAAm (g)	Label
2.2	0.2946	0.1830	1.6	0.0610	IPN-1
4.7	0.2250	0.1125	2.0	0.0375	IPN-2
7.5	0.2397	0.0959	2.5	0.0320	IPN-3
9.7	1.6648	0.5549	3.0	0.1849	IPN-4
2.2	0.3045	0.1523	2.0	0.0507	IPN-5
4.7	0.3967	0.1984	2.0	0.0661	IPN-6
7.5	0.3445	0.1723	2.0	0.0574	IPN-7
9.7	0.2998	0.1500	2.0	0.0500	IPN-8

Figure 1. Photos of hydrogel during three different times: a) hydrogel between two plaques of transparent glass before exposition to UV light; b) hydrogel during exposition to UV light; c) opalescent IPN hydrogel after be removed from plaques.

iv) Determination of LCST of PVA-Ma/PNIPAAm IPN hydrogels

Curve of relative intensity of light transmitted through swollen hydrogel as a function of temperature was built for each PVA-Ma/PNIPAAm IPN hydrogel aiming determination of LCST. For this, a piece of hydrogel membrane swelled up to equilibrium at 25°C was immersed in 20 mL of distilled water, also at 25°C, contained in a transparent glass-cell. The system was kept inside a black-camera for avoiding spurious light. Circulating water batch controlled the temperature of glass-cell. A photodiode (EG&G Optoelectronics, Model HUV200B) was used for measuring the light intensity coming from a 1 mW He-Ne laser

(λ = 632.8 nm) and traveling perpendicularly to the glass-cell. Light intensity as a function of temperature was registered in 25 to 50ºC range in a heating mode. Before each measure, the hydrogel was maintained at a desired temperature for 1h.

v) Swelling ratio IPN hydrogels at different temperatures

Aiming to verify the sensibility of IPN hydrogels to the temperature, the swelling ratios (SR) of PVA-Ma/PNIPAAm IPN hydrogels were evaluated at 25, 35 and 45ºC on pH 7-buffer with ionic strength of 0.1 mol L^{-1}. For this, dried samples of IPN hydrogels were dipped in the buffer solution and maintained at desired temperature for, at least, 48h. After removing the excess of liquid in the gel-surface using absorbent-tissue paper, the swollen sample was weighed and dried at room temperature until constant weight. The swelling ratio was measured using the equation (2)

$$SR = \frac{W_s}{W_d} \tag{2}$$

where:

W_s is the weight of swollen hydrogel and W_d is the weight of dried hydrogel. All SR data were obtained as average of triplicate (n = 3).

vi) Determination of elastic modulus (E) through compression tests

For each sample, the elastic modulus (E) was determined through compression tests performed in a Texturometer (Stable Micro System, Model TA.TXT2, UK). The apparatus was equipped with a loading cell of 5 N and with a cylindrical probe with 12.7 mm diameter. The experimental parameters were adjusted for a maximum deformation equal to 10% and (probe depth of 3 mm) at a test speed of 1 mm s^{-1}. The probe moved down in all compression tests that were performed at desired temperature (25, 35 or 45ºC). Data generated by the equipment were the force necessary for a given compression, which were subsequently converted to compressive stress (σ) versus relative strain (λ). The values of σ and the elastic modulus, E, were obtained through the following equation (DE MOURA et al., 2009):

$$\sigma = \frac{F}{A} = E(\lambda - \lambda^{-2}) \tag{3}$$

being A the probe sectional area (126.7 mm^2). Thus, the value of E for each sample was determined from the slope of the straight line obtained according to

the equation 3, σ against (λ - λ^{-2}). In all cases, the relative strain (λ) was calculated from the equation (4):

$$\lambda = \frac{\Delta L}{L_0} \tag{4}$$

where:

ΔL is the deformation of the sample and L_0 is initial sample length. The compression tests were done at 25, 35 and 45ºC, in triplicates (n = 3).

Results and discussion

i) Degree of substitution of PVA-Ma

The functionalization of poly(vinyl alcohol) by addition of methacryloyl groups from GMA was optimized in a previous work done in our lab through response surface methodology (CRISPIM et al., 2006a and b) in which the inputs temperature and reaction time were evolved. So, the optimized conditions (62ºC and 6 h) were also used in this work. Figure 2 shows the ^{1}H NMR spectra for the PVA-Ma with different DS.
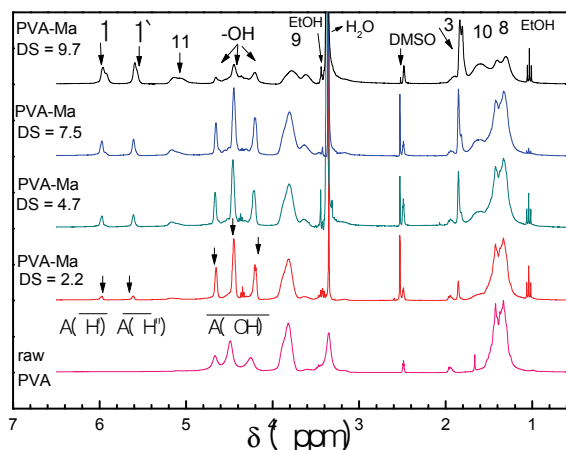

Figure 2. ^{1}H NMR spectra of PVA-Ma possessing different DS.

The DS for the as-obtained PVA-Ma were calculated using the equation (1) based on spectra presented in Figure 2, being the DS values shown in Table 1 where the value of yield for each run is also described. The yields are relatively high, minimum 88 mol-%.

ii) Characterization of PVA-Ma/PNIPAAm IPN hydrogels

Many studies have been performed aiming the obtainment of hydrogels with better properties in response to external stimulus (AZEVEDO et al., 2006; GUILHERME et al., 2005; PEPPAS; KLIER, 1991; SZILÁGYI; ZRÍNYI, 2005). The interpenetrated polymer chains in IPN hydrogel

enhance the mechanical properties, mainly the strength, relative to the not interpenetrated networks (BAJPAI et al., 2008; CRISPIM et al., 2006a). In the case of IPN hydrogel consisting of different polymer networks, it may display, at the same time, properties of different polymers (BAJPAI et al., 2008; DE MOURA et al., 2006).

a) Yields on IPN obtainment

The PVA-Ma/PNIPAAm IPN hydrogels were obtained in two steps. In the first step the PVA-Ma hydrogels were synthesized through reaction evolving double bonds on PVA-Ma, with different DS, using the system persulfate/TEMED, as initiator and catalyst, respectively. Two stepped methodology was also used in our lab for obtaining sandwiched-like thermosensitive membranes (GUILHERME et al., 2006). In this work, the membranes prepared in the first step were swelled up to equilibrium being the swelling ratio (SR) determined in a certain period of time according to the equation (2).

The curve of *SR* as a function of time for each PVA-Ma hydrogel is presented in Figure 3A for a swelling process performed just after synthesis and in Figure 3B for a re-swelling process (the previously swelled samples were dried before be re-swelled up to equilibrium).
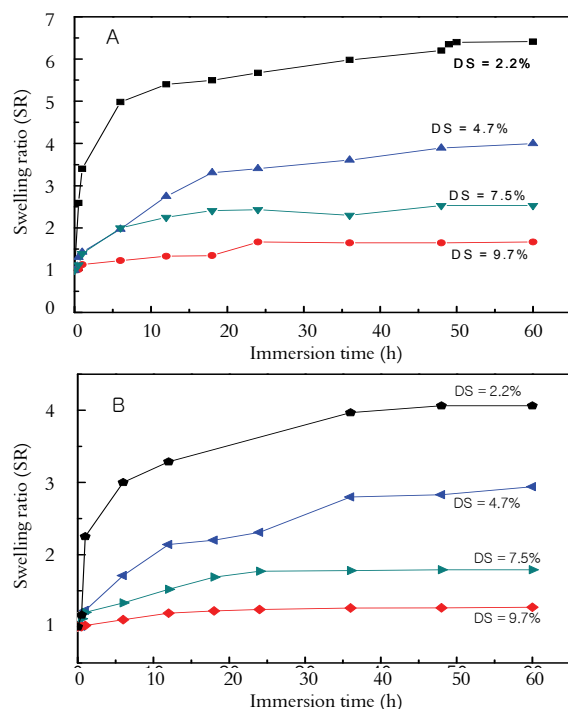

Figure 3. Swelling ratio (SR) as a function of immersion time for PVA-Ma hydrogels obtained from PVA-Ma with different DS. (A) swelled just after synthesis. (B) the samples swelled in first process were dried before be re-swelled up to equilibrium.

Comparing the curves of Figure 3A to the respective 3B, it can be seen that the drying process let the hydrogel to lower swelling capacity. This can be explained by the following: as the swollen hydrogel is dried the polymer chains became close enough for inducing in them the occurrence of new interactions among the groups in sided- or in main-polymer chains (intra and inter chains), what decrease the swelling capacity of the hydrogel. Thus, according to Figures 3A and 3B the swelling degrees at equilibrium are inversely proportional to the DS showing that the cross-linking degree in PVA-Ma matrices is proportional to the amount methacryloyl groups present in the PVA-Ma. Two methacryloyl groups should react themselves to form a single cross-linking. Also, in all cases the equilibrium of swelling is reached under 48h of immersion. It should be emphasized that the curves of Figure 3 were obtained in distilled water.

In the second step, the dried PVA-Ma hydrogels obtained in first step were swelled up to equilibrium in aqueous solution containing NIPAAm/MBAAm monomers in order to obtain PNIPAAm network interpenetrated into PVA-Ma network. The values of the yields for the second step are presented in Table 3 for all runs and ranged from 69 to ca. 78%. This parameter was not calculated for IPNs 5 to 8.

Table 3. Initial and final masses of NIPAAm and the respective yields (%) for second step of PVA-Ma/PNIPAAm IPN hydrogel preparation.

Hydrogel	Mass (g) of NIPAAm and MBAAm used for IPNs preparation	Mass (g) after synthesis of hydrogels	Yield (%)
IPN-1	0.2440	0.1740	77.7
IPN-2	0.1500	0.1050	70.0
IPN-3	0.1279	0.0890	69.9
IPN-4	0.7397	0.5131	69.4

The formation of the PNIPAAm network within the PVA-Ma network was also characterized by FTIR. Bands assigned to functional groups characteristic of PNIPAAm and of PVA-Ma were observed in the FTIR spectra of the IPN hydrogels, confirming the formation of two networks being one of PVA-Ma and other of PNIPAAm.

b) Thermosensibility of PVA-Ma/PNIPAAm IPN hydrogels
Dependence of LCST to the PVA-Ma/NIPAAm ratio

The value of LCST was determined based on change in intensity of light transmitted across the swollen hydrogel while it was warmed from 25 to 50ºC. There is a consensus that the LCST is close to the inflection point in curves of light transmitted as

a function of temperature (CRISPIM et al., 1999; El SHAFEE, 2002; MUNIZ et al., 2009). The value of LCST for each IPN hydrogel is presented in Table 4, for IPN-1 to IPN-8.

Table 4. Values of LCST for IPN-1 to IPN-8.

Hydrogel	PVA-Ma/NIPAAm	LCST (°C)
IPN-1	1.6	34.6
IPN-2	2.0	35.3
IPN-3	2.5	35.6
IPN-4	3.0	38.1
IPN-5	2.0	35.9
IPN-6	2.0	35.6
IPN-7	2.0	36.7
IPN-8	2.0	35.5

There is a plenty of papers on literature showing that the LCST of linear PNIPAAm aqueous solution or swollen network of PNIPAAm falls on 32-33ºC range (SCHILD 1992; CRISPIM, et al., 2006b; GUILHERME et al., 2004; GUILHERME et al., 2006; DE MOURA et al., 2006; MUNIZ et al., 2009). The hydrophilic-hydrophobic phase transition presented by PVA-Ma/PNIPAAm IPN hydrogels obtained in this work occurs at temperatures little bit higher than the observed for PNIPAAm swollen network or aqueous solution of PNIPAAm. This result was attributed to the presence of PVA-Ma matrix that is more hydrophilic than the PNIPAAm one. Due to this characteristic, the presence of PVA-Ma in the IPN hydrogel tends to enlarge the region of miscibility on phase diagram and, thus, raising the value of the LCST.

According to data presented in Table 4, there is a linear dependence of LCST of IPN hydrogels to the PVA-Ma/NIPAAm ratios used in preparation of hydrogels. Important information that comes from these data is that the LCST of PVA-Ma/PNIPAAm IPN hydrogel can be tailored by choosing an appropriated PVA-Ma/NIPAAm ratio. This can be straightly applied to preparation of hydrogel with LCST close to human body temperature, to be used as biomaterials. The evaluation of dependence of LCST to the DS of parent PVA-Ma was performed. In that work it was demonstrated that the DS of PVA-Ma did not influence the value of the LCST of IPN hydrogels. Thus, it can be pointed out that PVA-Ma/NIPAAm ratio used in preparation of IPN hydrogel is the determining factor for the value of LCST of PVA-Ma/PNIPAAm IPN hydrogels.

c) Sensibility of PVA-Ma/PNIPAAm IPN hydrogels to temperature at pH 7-buffer

Due to hydrophobic-hydrophilic transition, polymeric materials that possess LCST-typed phase diagram will present one phase at temperatures lower than LCST. In that condition the hydrogen

bonds formed among the hydrophilic segments of the polymer network and water molecules are dominant and would be the primary responsible for the dissolution of polymers (if not crosslinked) or for the expansion of the network (in the case of hydrogels) (QIU; PARK, 2001). Above the LCST, intramolecular interactions become stronger, while the intermolecular (polymer-water) interactions weaken. Part of water present within the hydrophilic 3D matrix is expelled whether the 3D matrix becomes hydrophobic. This leads to a shrinking of the gel, resulting in a state where the polymer-polymer and solvent-solvent interactions are preferred. The polymer chains of IPN hydrogels that exhibit LCST are, often, composed by moderately hydrophobic and a mixture of hydrophobic/hydrophilic groups (LI et al., 2008).

Curves of swelling ratio (*SR*) of PVA-Ma/PNIPAAm IPN hydrogels as function of temperature obtained at pH 7-buffer are presented in Figure 4. It can be seen that the IPN hydrogels are sensible to temperature. The sensibility to temperature is intensified by the lowering the PVA-Ma/NIPAAm ratio. In this case, hydrogels with lower PVA-Ma/NIPAAm ratio presented higher *SR*, no important is the temperature. For each IPN (IPN-1, IPN-2 IPN-3 and IPN-4) a minimum on *SR* is observed close to 35ºC. The decreasing in *SR* from 25 to 35ºC may be due to collapsing of PNIPAAm segments. The increase of *SR* from 35 to 45ºC was attributed to hydrophilicity of PVA-Ma segments. The PVA-Ma/PNIPAAm IPN hydrogels swell more at temperatures lower to the respective LCST. In these conditions, the H-bonds among the hydrophilic segments and water molecules dominate, leading to a higher *SR* (or expansion of 3D network). However, at temperatures higher than LCST hydrophobic interactions prevail in PNIPAAm segments and at this condition there is a trend in doing intra-chains interactions. Also, at this temperature condition, the H-bonds among water molecules and PNIPAAm segments are less probable to occur. As already mentioned, at 45ºC the PVA-Ma/PNIPAAm hydrogels tend to swell more than at 35ºC due to hydrophilicity of PVA-Ma segments. Molecules of water tend to interact selectively to PVA-Ma segments.

The phase transition of poly(N-isopropyla-crylamide) is the result of unbalance between hydrophilic and hydrophobic groups present in the polymer chain (DE MOURA et al., 2009). That is, with decrease on temperature the hydrophilic character overlaps the hydrophobic one and vice-versa (ZHANG et al., 2004). On this basis, the structure and

properties of PNIPAAm can be changed by modifying the amount of hydrophilic or hydrophobic groups (EL SHAFEE, 2002). In addition to these findings, changes in amount of cross-linking agent used in the hydrogel synthesis may also result in alterations in the characteristics of polymer gel.
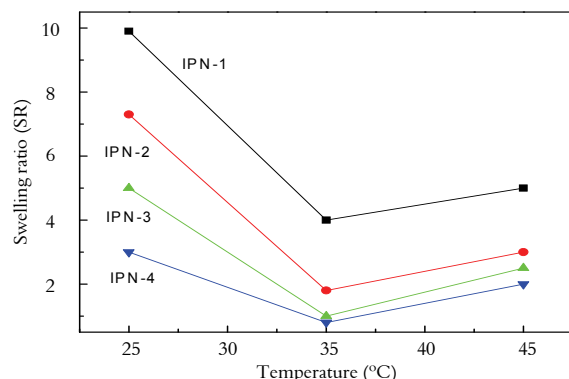

Figure 4. Swelling degree at 25, 35 and 45°C for IPN-1, IPN-2, IPN-3 and IPN-4, on pH 7-buffer.

The differences in hidrophilicity on hydrogels at 25 and at 45°C can be calculated by the respective *SR* at these temperatures. The dependence of the difference in swelling ratio (or hydrophilicity) of PVA-Ma/PNIPAAm IPN hydrogels at 25 and 45°C to the PVA-Ma/NIPAAm ratio is depicted in Figure 5.
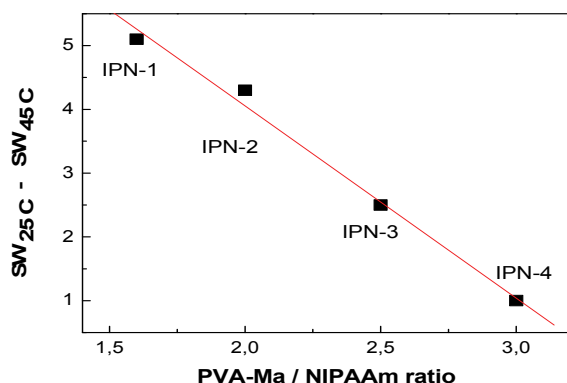

Figure 5. difference in swelling ratio (or hydrophilicity) of PVA-Ma/PNIPAAm IPN hydrogels at 25 and 45°C to the PVA-Ma/NIPAAm ratio.

The difference in swelling ratio at 25 and 45°C becomes lower if the PVA-Ma/NIPAAm ratio increases. So, the high amount of PVA-Ma would increase the swelling ratio at 45°C minimizing the difference in hydrophilicity at the two temperatures.

d) Mechanical properties through compression tests

The elastic modulus is an intrinsic property of solids being dependent of chemical composition and structural of materials. This statement is applied in a significant way to hydrogels. Table 5 shows the

values of elastic modules obtained for IPN-1, IPN-2, IPN-3 and IPN-4 at 25, 35 and 45°C, after applying the equations (3) and (4) to the data of compression tests. It can be seen that the values of elastic modulus increase as the temperature is increased from 25 to 35°C for all IPNs but decrease (excepting for IPN-2) as the temperature is further increased to 45°C. The increase in elastic modulus from 25 to 35°C is related to collapsing of PNIPAAm segments. On the other hand, the decrease of elastic modulus from 35 to 45°C is related to expansion on 3D network due hydrophilicity of PVA-Ma network. Another important aspect for the rigidity of such IPN hydrogels is the DS of parent PVA-Ma. The elastic modulus increases as the DS of parent PVA-Ma and the PVA-Ma/NIPAAm ratio are increased. This behavior matches very well to the data of swelling degree. For temperatures above of LCST of PNIPAAm the elastic modulus is more dependent of amount of NIPAAm used in the hydrogel synthesis due to the collapsing of PNIPAAm chains that tends to form more compacted polymer clusters increasing, in this way, the elastic module. But in same direction, the PVA-Ma matrix in hydrogel increases the density of polymer chains that contribute positively for the elastic modulus. Materials with enhanced elastic modulus are more strength for compressive or tensile deformation.

Table 5. Elastic modules of PVA-Ma/PNIPAAm IPN swollen hydrogels at 25, 35 and 45°C.

Hydrogel	Elastic modulus, kPa		
	@ 25°C	@ 35°C	@ 45°C
IPN1	11.4	26.77	21.32
IPN2	38.7	39.0	49.8
IPN3	41.9	59.0	52.0
IPN4	49.9	76.8	65.7

Conclusion

In this work full IPN hydrogels based on chemically modified poly(vinyl alcohol) poly(N-isopropylacrylamide), (or PVA-Ma/PNIPAAm) were obtained and characterized. The chemically modified PVA (or PVA-Ma), at degrees of substitution (DS, in mol-%) equal to 2.2, 5.3, 7.5, and 9.7 were obtained by reaction of PVA with requested amount of GMA to obtain desired PVA/GMA ratios. Two steps were used for preparation of PVA-Ma/PNIPAAm hydrogels. The network of PNIPAAm was prepared through photo initiated reaction in a second step within the PVA-Ma network. The values of LCST of PVA-Ma/PNIPAAm IPN hydrogels depend in a linear regime to the PVA-Ma/NIPAAm ratio used

for hydrogel preparation. The IPN hydrogels presented sensibility to temperature that was due to the PNIPAAm network. The elastic modulus changed as the temperature is changed. Due to the sensibility of 3D matrix to changes in temperature, these hydrogels can be considered as smart hydrogels. The IPN hydrogels synthesized in this work presented characteristics that potentize their used as biomaterials. Finally, it can be stressed that the LCST of PVA-Ma/PNIPAAm IPN hydrogels can be adjusted to occur close to the human body temperature fact that increases the interest for such materials.

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