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Polymeric nanocomposites made of a conductive polymer and a thermosensitive hydrogel: Strong effect of the preparation procedure on the properties

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ABSTRACT

Nanocomposites are made by loading a conductive polymer (polyaniline, PANI) inside a thermosensitive hydrogel matrix (poly(N-isopropylacrylamide)-co-(2-acrylamido-2-methylpropane sulfonic acid), HG). The composites were obtained by two loading methods: i) in-situ polymerization of aniline inside the hydrogel matrix (ISP) and ii) by swelling of hydrogel in a true solution (SIS) of PANI (base) in N-methylpyrrolidone. Even though the composites have similar chemical composition, scanning electronic microscopy (SEM) shows different morphologies for each material obtained. ISP produces a material with segregated nanodomains of PANI inside HG, building a true nanocomposite (NC). On the other hand, SIS seems to create a semi-interpenetrated (semi-IPN) network of PANI inside the HG. The swelling capacity and volume phase transition temperature (VPTT) of composites are also affected by the loading methods. The segregated nanodomains of PANI in the NC do not affect the thermosensitivity of HG, while the PANI chains are directly interacting with the HG chains in the semi-IPN, affecting the VPTT. The swelling capacity of NC is of %Sweq = 6500 while the semi-IPN is of %Sweq = 8600. Both of them are lower than the one of pure HG (%Sweq = 11,000). The elastic module of both materials is higher than HG. The states of water analyzed by DSC show a high hydrophobic character inside the composite. The amount of water interacting with HG chains decreases with the presence of PANI. Both composites show electronic conductivity which changes when pressure is applied on them. However the NC shows a larger gauge factor. Such property could be applied in a pressure sensor. Additionally, the thermal sensitivity of the matrix is coupled with the electronic conductivity of PANI, allowing to build an electric switch controlled by the temperature.

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1. Introduction

Interpenetrated networks (IPNs) have been conventionally defined as polymers comprising two or more networks that are at least partially interlaced on a molecular scale. They are not covalently bonded to each other and cannot be separated unless chemical bonds are broken. At least one of the components is synthesized or crosslinked in the immediate presence of the other [1]. On the other hand, semi-interpenetrated network (semi-IPN) is a polymer comprising one or more polymer networks and one or more linear or branched polymers characterized by the penetration on a molecular scale of at least one of the networks by some of the linear or branched macromolecules. A semi-IPN is distinguished from an IPN because the constituent linear or branched macromolecules can, in principle, be separated from the constituent polymer network(s) without breaking chemical bonds; it is a polymer blend [2]. By fabrication of IPN networks, the thermodynamic incompatibility between two or more polymers can be overcome due to permanent interlocking of network segments and materials with limited phase separation [3]. IPNs including hydrogel have shown superior performances over the conventional individual polymers and, consequently, the ranges of applications have grown rapidly for such class of materials, tough and highly stretchable hydrogels [4]. Generally, the interpenetration could be

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favoring certain interesting properties of IPN systems such as: to enhance the response rate, to increase the swelling capacity and to improve the mechanical properties [5]. In order to get those results, several synthetic methods to obtain IPN or semi-IPN materials are being researched. It is noteworthy that the interpenetration (or semi-interpenetration) of another polymer inside the crosslinked matrix of a thermosensitive hydrogel could also affect relevant properties such as the swelling ratio, the states of water and the volume phase transition temperature.

Thermosensitive hydrogels are crosslinked matrixes made of polymer chains having a lower critical solution temperature (LCST) in the range accessible in water (0–100 °C). Below the LCST, the polymer chains present between crosslinks are extended in coil form and interacting with the solvent. Above the LCST, the polymer chains turn into globular form, decreasing the interaction with the solvent and increasing the interaction between groups in the chain. In the case of alkyl acrylamides, the main effect behind the transition involves the balance between the rotational entropy due to the alkyl groups and the hydrogen bonding between water and the amide group. Indeed, the volume phase transition temperature (VPTT) can be altered by incorporation of hydrophilic or hydrophobic groups into the polymer chains by copolymerization. The addition of hydrophilic groups increases the transition temperature while the addition of hydrophobic groups decreases the transition temperature [6]. Aoki et al., [7] synthesized IPNs composed of poly(dimethyacrylamide-co-acrylamide) and polyacrylic. The materials showed that the phase transition temperatures, between the shrunken and swollen states, are shifted to higher values as content of dimethylacrylamide increase Thermoresponsive hydrogel composed of poly(N-isopropylacrylamide) (PNIPAM) semi-IPN with chondroitin sulfate (ChS) was synthesized using precipitation polymerization [8]. ChS was introduced to improve the water absorption capacity of the PNIPAM hydrogel and the precipitation polymerization method was used to induce porous network morphology of the hydrogels so as to increase their thermal response rate. In this system, the swelling ratio was greatly enhanced by the addition of ChS and the VPTT of the PNIPAM was virtually unaffected by the formation of semi-IPNs with ChS. The high swelling ratio of the PNIPAM/ChS hydrogels was attributed to both the synergistic effect of the anionic nature of the ChS chains and the interconnected porous morphology. On the other hand, different semi-IPN hydrogels of poly(diallyldimethylammonium chloride)/poly(N,N-diethylacrylamide) (PDADMAC/PDEA) were synthesized from DEA via free-radical polymerization in the presence of crosslinker and PDADMAC aqueous solution [9]. Due to the introduction of PDADMAC component, an interconnected porous structure was generated, and the states of water of PDEA hydrogel was affected. PDEA hydrogel is a typical thermosensitive polymeric network, which exhibits a VPTT about 31 °C [10,11]. The main limitation of the conventional PDEA hydrogel is the slow rate of response to external environment change. PDADMAC polymer is highly hydrophilic and cationic polyelectrolyte with antibacterial properties [12]. For that, the introducing of PDADMAC polymer into PDEA hydrogel to form an interpenetrating polymer network (IPN) was one of the choices to improve the properties. It is well known that the swelling rate of the hydrogels depends not only on the hydrophilic ability of the functional groups but also on the network space of the hydrogels. Other interpenetrating polymer network (IPN) hydrogels based on poly(vinyl alcohol) (PVA) and poly(N-isopropylacrylamide) (PNIPAM) were prepared by the sequential-interpenetration method [13]. The hydrogels with 50% w/w PVA-50% PNIPAM had the highest swelling ratio in time-dependent, while the one with 80%PVA-20% PNIPAM had the lowest. The second material has a more compact complex structure than the other hydrogel because PNIPAM is more hydrophilic than PVA. The

swelling ratio increases with the molar ratio of the hydrophilic groups of PNIPAM in IPNs. We have prepared poly(N-isopropylacrylamide) (PNIPAM) hydrogels and copolymers where polyaniline (PANI) was synthesized inside the hydrogel by *in-situ* polymerization [14]. It seems that the relative higher hydrophobicity of PANI induced the phase-separation and the nanodomains of PANI (18–280 nm) were present. The volume phase transition temperature of PNIPAM hydrogel was unaltered by the presence of PANI and it was possible to obtain a superabsorbent composite with high mechanical resistance and swelling capacity (>25,000%).

In this work, we propose a novel alternative method to incorporate a conductive linear polymer (PANI) inside a network of thermosensitive hydrogel. By combination of both materials, a thermal and conductive composite is possible to obtain. Physicochemical and mechanical properties were measured and compared between two nanocomposite systems obtained by: 1) *in-situ* polymerization of aniline inside the hydrogel to give PANI; and 2) absorption of PANI inside the hydrogel from a true solution. The morphology of nanocomposites has been studied through scanning electron microscopy (SEM). By differential scanning calorimetry (DSC) the states of water were analyzed to provide information about internal micro environment and the behavior of the systems. Volume phase transition temperature and swelling capacity were markedly different for each composite. Elastic modules determined by uniaxial compression increased with loading PANI. Both composites can be useful to build an electronic sensor of pressure and a switch controlled by temperature. However, they show different behavior in spite of containing the same components. It is shown that NC (obtained by *in-situ* polymerization) presents a larger effect of pressure on electric resistivity. On the other hand, the semi-IPN (obtained by absorption of linear PANI) can be used to build an electro-thermal switch to sense temperature changes of aqueous systems. The data presented here suggest that the kind of nanocomposite produced (segregated or molecular mixture) affects considerably the properties and the morphology of composites and depends on the synthetic method for which it was obtained. Therefore, the two synthetic methods allow to obtain a segregated nanocomposite or a semi-interpenetrate network with similar chemical composition but different properties.

2. Materials and experimental methods

2.1. Synthesis of hydrogel matrix

Thermosensitive hydrogels were synthesized via free-radical copolymerization of NIPAM (Scientific Polymer Products) with 2-acrylamido-2-methylpropane sulfonic acid (AMPS) (Scientific Polymer Products). N,N-methylenebisacrylamide (BIS) (Aldrich) was used as cross-linker agent. Ammonium persulfate (APS) (Aldrich) and N,N,N′,N′-tetramethylenediamine (TEMED) (Aldrich) was used as the initiator system of polymerization. BIS as cross-linker agent (2% moles based on NIPAM) was dissolved in aqueous solution of NIPAM monomer (0.5 M) and 2% moles de AMPS based on NIPAM. Next, polymerization initiator system (APS (0.001 g/mL) and TEMED (10 μL/mL)) was added and the solution was purged by bubbling with N_2 gas to eliminate the O_2. The polymerization was carried out in a sealed glass tube at room temperature (20 °C) for 3 h. The resulting cross-linked copolymers was PNIPAM-co-2%AMPS. Scheme 1 represents the chemical structure of hydrogel matrix.

When the polymerization was completed, the hydrogels were immersed in distilled water at room temperature for 48 h and the water was renewed several times in order to remove unreacted chemicals.

R: $CH(CH_3)_2$, R1: $C(CH_3)_2CH_2SO_3H$
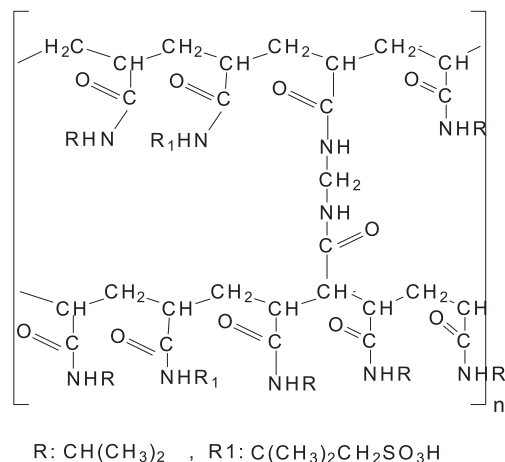
Scheme 1. Chemical structure of hydrogel matrix of PNIPAM-co-AMPS crosslinked with BIS.

2.2. Synthesis of semi-IPN materials

2.2.1. Method 1: in situ polymerization

The *in situ* polymerization was carried out as described before [14]. Experimental steps are resumed in Scheme 2. Small discs of dry hydrogels were immersed into a solution with 0.1 M of ANI (Fluka) in 1 M HCl as solvent, during 12 h. A known amount of APS (equimolar to ANI) was then added as oxidant to produce PANI inside hydrogel. The experience was carried out at room temperature for 3 h. Semi-interpenetrating hydrogels obtained were then immersed in flushing stirred distilled water (>1 L) at room temperature for at least 48 h in order to extract unreacted chemicals. The colorless hydrogel become green–blue color at the end of polymerization indicating that PANI was loaded inside the hydrogel matrix. By visual observation of a sectioned hydrogel piece, it can be checked that PANI is uniformly loaded inside the hydrogel.

2.2.2. Method 2: absorption of linear polymer from solution

Linear PANI was synthesized by oxidation with ammonium persulfate in 1 M HCl as solvent [15]. It was converted into base form (blue color) by treatment with aqueous 0.1 M NH₄OH solution. Then, PANI was purified by dialysis and dried. N-methylpyrrolidone (NMP) was used as solvent to prepare solutions of PANI at different concentrations. Previously, it was found that the NMP solvent is able to swell PNIPAM based hydrogel. Therefore, small discs of dry hydrogels were swelled in true solution of PANI (base form) in NMP as solvent. The absorption was carried out at room temperature for 48 h. After that, the hydrogels were homogeneously colored, as it could be checked by cutting the hydrogel piece. Then, the discs were immersed in flushing stirred distilled water (>1 L) at room temperature for at least 48 h to extract remaining N-methylpyrrolidone. The absence of NMP in the washing solution was checked by UV−vis spectroscopy. The composite was then treated with HCl solution in order to convert PANI base into conductive PANI. Apart from testing the nanocomposite with PANI in the same protonation state, the procedure allows to remove any NMP which could be strongly absorbed inside PANI (see below). Scheme 2 represents the two methods to load PANI inside the hydrogels.

2.3. Morphologic analysis of composites by scanning electron microscopy (SEM)

The nanocomposites were swollen in 1 M HCl solution to protonate the PANI inside the hydrogel. In that way, PANI becomes electric conductive. Then, it was dried under vacuum (50 °C) to remove water and excess HCl. Considering that one of the materials is conductive, the sample was analyzed without metallization by SEM. Scanning electron micrographs were taken at low vacuum and low field in a SEM (Carl Zeiss EVOMA10) or at low vacuum and low field in a LEO 1450VP Variable Field Emission SEM.

2.4. Measurements of swelling kinetic

Dried sample of hydrogel, previously washed and weighed, was placed in solvent (water or NMP) at room temperature. The sample was removed from solution, at certain time intervals, and was superficially dried with tissue paper, weighed in an analytic balance and placed back in the bath. The measurements were repeated until each sample achieved constant weight. The swelling percentage (% Sw) is calculated as a function of time.

$$\%Sw(t) = 100 \times \left[\frac{(W(t) - Wo)}{Wo} \right] \qquad \text{Eq. (1)}$$

where *W(t)* represents the weight of hydrogel in swollen state at
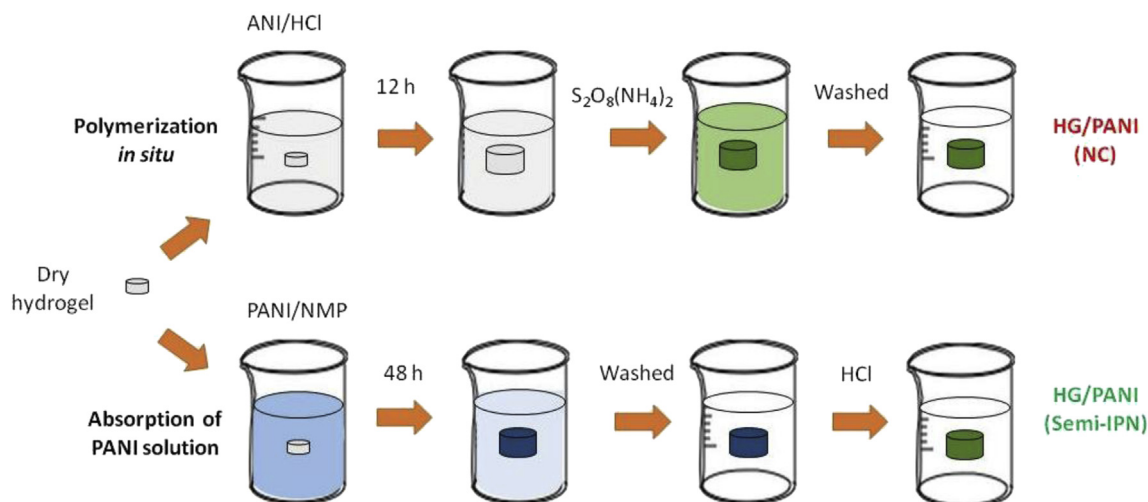
Scheme 2. Schematic representation of the semi-interpenetration steps to load PANI inside PNIPAM-co-2%AMPS hydrogel matrix by two different methods.

time t and *Wo* is the weight of dry hydrogel. Graphics of % Sw vs time were made to analyze the swelling kinetic. Every data of % Sw obtained was the average of five measurement with absolute error around ±150.

2.5. Partition coefficient measurements by UV–vis spectroscopy

The equilibrium distribution of solute between the gel and liquid phases is defined by the partition coefficient (Cp) (Eq. (2)). The Cp value determines the distribution of PANI between two phases, hydrogel and NMP solvent. The Eq. (2) represents the grams of PANI (solute) loaded inside the HG rationed to the grams of PANI in the NMP solution after reaching the equilibrium state:

$$Cp = \frac{\text{grams of PANI/1000grams swollen HG}}{\text{grams of PANI/1000g NMP}} \qquad \text{Eq. (2)}$$

Experimentally, a piece of dry HG of known mass was immersed in 3 mL of PANI in NMP at defined concentration. After 24 h of immersion, the concentration of the remaining PANI in the solution was determined by UV–visible spectroscopy (Hewlett-Packard-8453 UV–visible Spectrophotometer). Previously, a calibration curve of absorbance of PANI versus concentration of PANI in NMP was built at corresponding wavelength (at $\lambda = 328$ nm) (Supporting information-Fig. S1). From the absorbance of PANI in the solution, the molal concentration of PANI in NMP solution was calculated. Knowing the initial gel mass, the grams of PANI in 1000 g of swollen HG could be calculated by differentiation. With such data, Cp values were calculated.

2.6. Volume phase transition temperature and states of water analyzed by differential scanning calorimetric (DSC)

The DSC measurements were conducted using a TA Instruments DSC 2010 under N_2 flow. The samples were previously wetted in water. The sealed pan with the sample (ca. 10 mg) was quickly cooled inside the differential scanning calorimeter (DSC) chamber at $-25\,°C$ by filling the outer reservoir with a frozen solution of 80% w/w $CaCl_2$ in water. Several minutes were taken for the system to get the thermal equilibrium state. The sample holder assembly was then heated from -25 to $60\,°C$, before phase transition and below $100\,°C$ to avoid decomposition of the sample and evaporation of water at a rate of $5\,°C$/min.

2.7. Elastic module (E) determinate by uniaxial compression

Elastic module of an object is defined as the slope of stress–strain curve in the elastic deformation region [16]. *Stress* is the restoring force (F) due to the deformation applied divided by the original cross-sectional area (A) to which the force is applied; and *strain* is the ratio of the change in the length of the object (ΔL) divided by the length from the original state (lo) of the object. When ΔL is small, Hooke's law is obeyed, and the stress σ is proportional to the strain ε. The constant of proportionality is known as the *Young's module* (E).

Uniaxial compression measurements were performed on individual cylindrical hydrogels in swollen states. The temperature of all measurements was $25 \pm 0.5\,°C$. A device was built to measure the module, under compression, which was similar to one described before [17]. A force was applied on the cylindrical hydrogels and the acting force F was calculated as F = m.g, where m is the increasing of mass read on the balance and g is the gravitational acceleration. Next, the *stress* σ was calculated as F/A. The resulting deformation was measured using a digital comparator (Schwyz Electronic indicators, which is sensitive to displacements

of 10^{-3} mm). The comparator length values were read before (L_0) and after (L) the force was applied. For that, ΔL was calculated as the subtractions between l_0 and l, according to Scheme 3. The initial length (L_0) was previously measured using an absolute micrometer. The *strain* was calculated as $\varepsilon = \Delta L/L_0$. The force and the resulting deformation were recorded after 30 s of relaxation. During the measurements, the load increment in successive steps was adjusted so that the gel can be deformed up to about 20–30% compression. Graphing σ vs ε is possible to calculate the elastic module (E) from initial slope. The experiments were performed three times and the results were averaged.

2.8. Measurements of electric resistance and uniaxial compression

Measurements were performed on cylindrical composite in equilibrium swelling state at pH 2. All the measurements were conducted at $20 \pm 0.5\,°C$. The key parts of the apparatus used are shown in Ref. [17] Briefly, a cylindrical gel of 5 mm in diameter and 10–15 mm in height was placed on an analytic digital balance (OHAUS Pioneer, readability and reproducibility = 0.1 mg). A load was transmitted vertically to the gel through a micrometric actuator with a glass end-plate. Previously, above and below of the extremes of the cylinder two aluminum plates (as electrodes) were placed. Aluminum electrodes were connected to homemade resistance meter where the electrical current was measured at defined potential differences. Through the linear slope of potential vs current curve (Ohm's law), the electric resistance (Ω) value were obtained for each compression state. The load was increased in successive steps until the gel was deformed up to about 10%. Then, force and resistance were recorded after 30 s of relaxation.

3. Results and discussions

3.1. Synthesis of composite materials

For absorption of linear PANI inside HG by swelling, it was necessary to find a good solvent of PANI which at the same time was able to swell the HG. It is well known that N-methyl-pyrrolidone (NMP) can interact with the base PANI [18] by hydrogen bonding, leading to an expanded chain configuration of

$$\varepsilon = \frac{\Delta L}{Lo}$$

$$\sigma = \frac{F}{A}$$

$$\sigma = E * \varepsilon$$
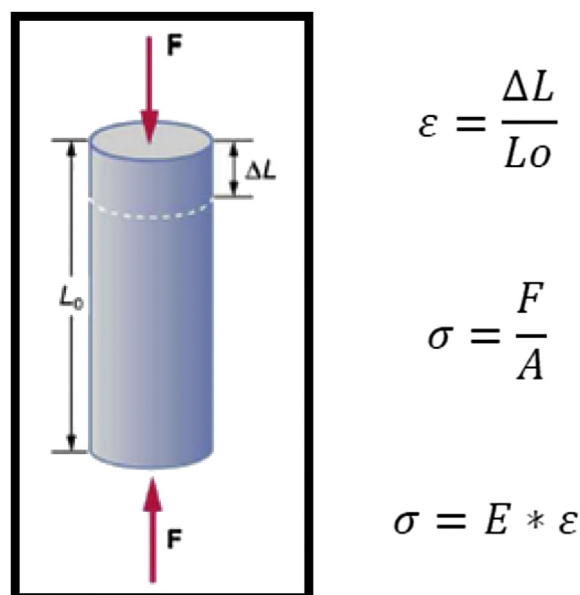
Scheme 3. Equations to define stress (σ) and strain (ε).

PANI in NMP rendering a true solution. Therefore, the swelling of a based HG in NMP was tested (Fig. 1A). As it can be seen, while the swelling of PNIPAM-co-2%AMPS in NMP is slightly lower than in water, it is possible to swell the HG with either water or NMP solvents.

Pieces of HG were swollen in solution of PANI in NMP solvent, during 48 h until achieving the absorption into HG. A dark blue composite colored and homogeneously distributed was obtained. Fig. 2 shows a pure HG and HG loading with PANI/MNP.

However, when the hydrogels were swollen in presence of PANI/ NMP solutions the swelling rate and the equilibrium swelling capacity decreased. (Fig. 1B) Higher concentrations cannot be used because PANI/NMP solution at 10% w/w is unstable. It seems that association among PANI chains eventually leads to the formation of PANI gels outside the HG [15]. Therefore, concentrations below 0.5% w/w were used to avoid gel formation. The UV−visible absorption spectrum coincides with observed for PANI in basic medium [18,19]. When NMP solvent was interchanged with acid aqueous medium the UV−visible spectrum of HG/PANI coincided with free PANI in aqueous medium (Supporting information-Fig. S2).

3.2. Morphology of hydrogels loaded with PANI by scanning electron microscopy (SEM)

The SEM micrograph (Fig. 3) of the HG loaded with PANI by absorption (SIS) shows a cauliflower morphology corresponding to HG matrix. Unlike the SEM micrograph of the nanocomposite made by in-situ polymerization (ISP), which shows conductive (dark)

PANI nanodomains in a dielectric HG (bright) matrix, the nanocomposite made by absorption shows uniform bright topography suggesting a homogeneous blend. Most area was occupied with a material collapsed as cauliflower corresponding to HG matrix. As this material is not conductive, the HG was burnt by the electron beam. The other material was arranged like a fiber and broke through inside collapsed HG. Since fiber-like is in minor proportion, we can say that it corresponds to the electric conductive PANI.

3.3. Partition coefficient of PANI inside HG

According to Eq. (2), the equilibrium distribution of PANI (solute) between the hydrogel and NMP phases is defined as partition coefficient (Cp). Equilibrium state is reached when hydrogel have the maximum capacity to load PANI from NMP solvent. Changing concentration of PANI solution in presence of hydrogel was determined at equilibrium state by UV−visible spectroscopy, through a calibration curve made previously (Supporting information-Fig. S1). Fig. 4 shows Cp values obtained in equilibrium state for different initial concentrations of PANI/NMP solution. Cp increases linearly until reaching a plateau.

The Cp in HG reaches a maximum value when the concentration of PANI in NMP is higher than 0.15 g/L of. The maximum value of Cp agrees with the data shown in Fig. 1 (B) where the maximum swelling capacity is also inhibited when PANI/NMP overcomes 0.4 g/L. Swelling inhibition may be due to osmotic pressure effect.

3.4. Swelling kinetics of the nanocomposite in water

The swelling of the hydrogels is defined by a balance between positive (increase swelling) effect of the solvation of the polymer chains in water and the negative (decrease swelling) effect of the elastic forces due to the hydrogel matrix. The swelling kinetics of the nanocomposite, obtained by two methods, in water and the maximum capacity to take water were determined. Fig. 5 shows that the kinetic behavior in both composites is different. The nanocomposite made by in-situ polymerization (ISP) showed a higher initial swelling rate but a lower swelling capacity in equilibrium state (%Sweq = 6500) than the semi-IPN material obtained by absorption (SIS) (%Sweq = 8600). However, both results are lower than the value obtained for the HG matrix (%Sweq = 11000). Additionally, it should be taken into account that the NC obtained by in-situ polymerization was loaded with 9.7% of PANI, whereas the semi-IPN obtained by in-situ polymerization contained 17.5% of PANI. Therefore, the results could explain why the relatively larger hydrophobicity of PANI compared with HG should decrease the water intake capacity by the nanocomposites.

Although PANI is hydrophobic the increase of amount of PANI enhances the swelling capacity of the HG because its mechanical resistance has been improved. The same was observed for nanocomposite based on superabsorbent hydrogel [20] where PANI increases the mechanical resistance allowing an extremely enlargement of the swelling capacity.

3.5. Volume phase transition temperatures of composites

Phase transition temperatures of hydrogels or volume phase transition temperature (VPTT) were determined by DSC (Table 1). PNIPAM-co-2%AMPS in water shows a VPTT around 37 °C, as it was previously reported [14]. The VPTT of the nanocomposite obtained by ISP (with 9.7% w/w of PANI into HG) has nearly the same value as the HG matrix.

On the other hand, the *VPTT* of the nanocomposite (made by SIS of PANI with 17.5% w/w) from PANI in NMP, swollen in water, is shown to be around 10 °C (47 °C) higher than the HG matrix (37 °C).
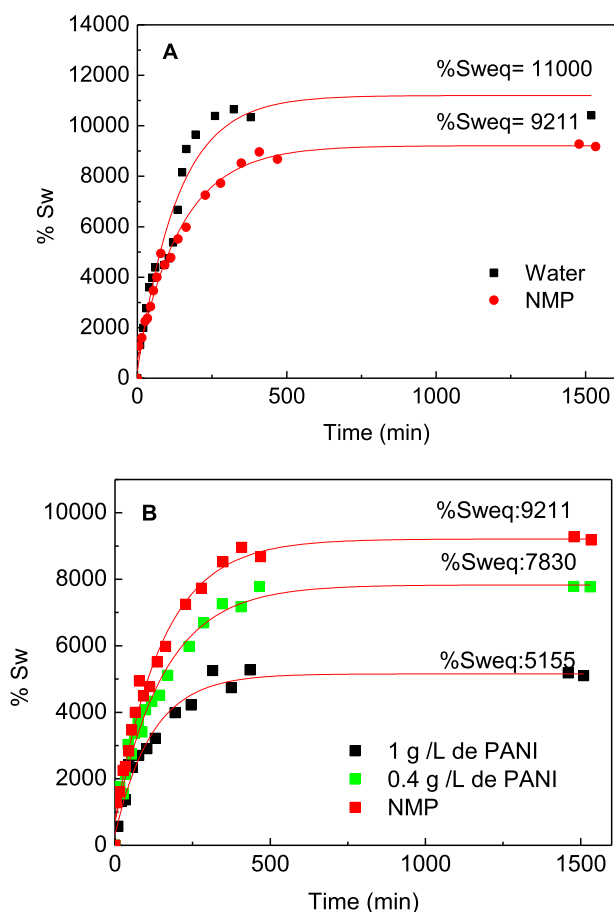

Fig. 1. Swelling kinetic of PNIPAM-co-2%AMPS in water and NMP solvents (A). Swelling kinetic in NMP and PANI in NMP solutions (B).
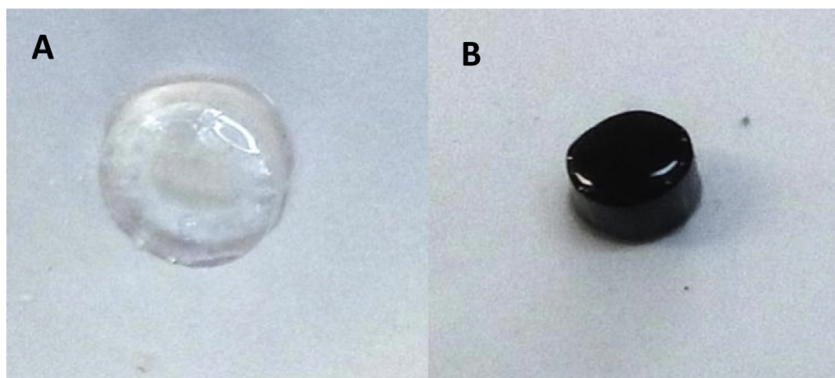
Fig. 2. Photography of PNIPAM-co-2%AMPS hydrogel. A) Swollen in water, B) Swollen in 0.4 g/L of PANI/NMP solution.
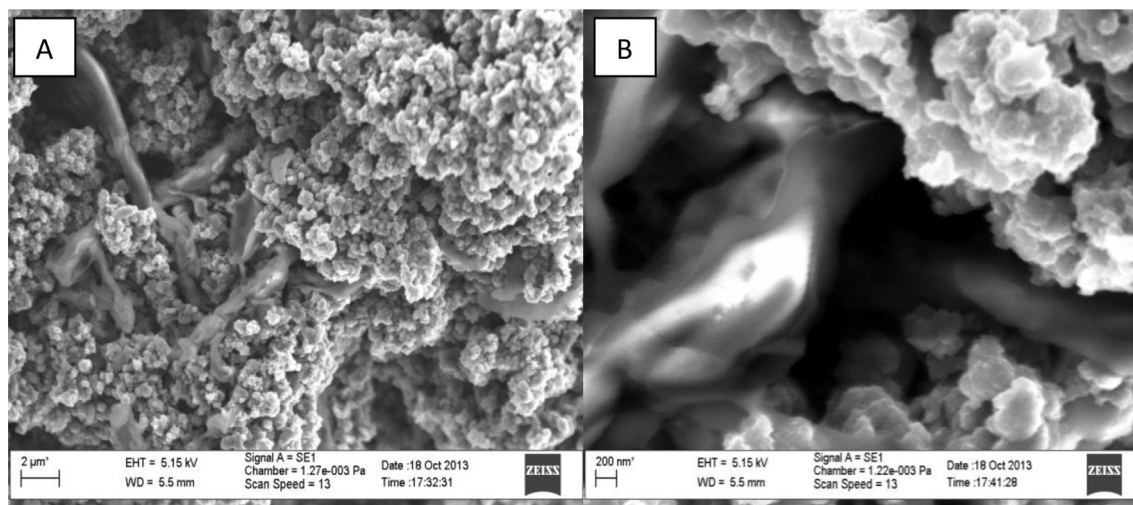

Fig. 3. SEM micrographs of PANI incorporated into a PNIPAM-co-2%AMPS hydrogel by absorption from solution. A) Scale bar: 2 μm and B) Scale bar: 200 nm.
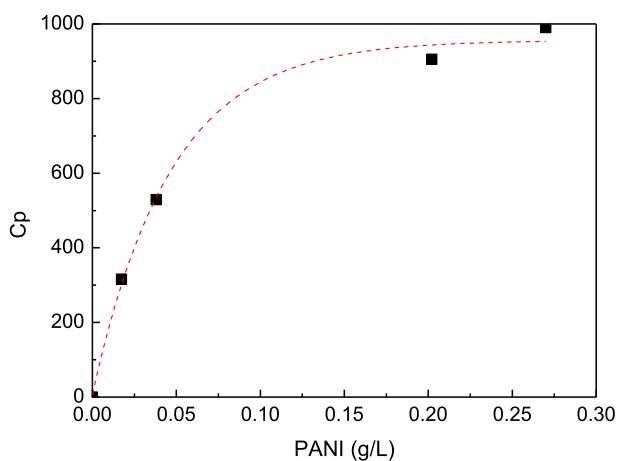

Fig. 4. Partition coefficient of PANI between PNIPAM-co-2%AMPS hydrogel and PANI/NMP solutions, at 20 °C.
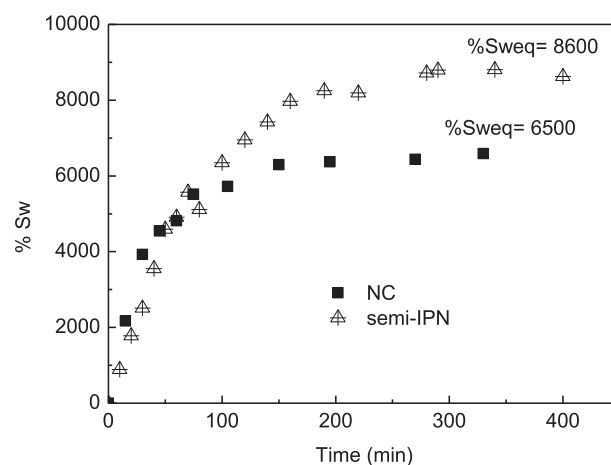

Fig. 5. Swelling kinetic of HG/PANI composites (in water) obtained by both methods. Experimental data of %Sw have an error around ±500.

It seems that PANI and hydrogel chains are intimately mixed and the presence of the PANI chains affects the LCST of the polymer chains in the hydrogel. When the HG was swollen in NMP, the *VPTT* occurs at 56 °C. Therefore, the hydrophobic/hydrophilic balance of HG depends strongly on the nature of the solvent.

3.6. States of water analyzed by DSC

The physical states of the water in the HG are related with the physical interactions between the polymer chains and the swelling medium [13]. The water structure inside the HG can be classified as

Table 1
Volume phase transition temperature of PNIPAM-co-2%AMPS hydrogel and composites of HG/PANI.

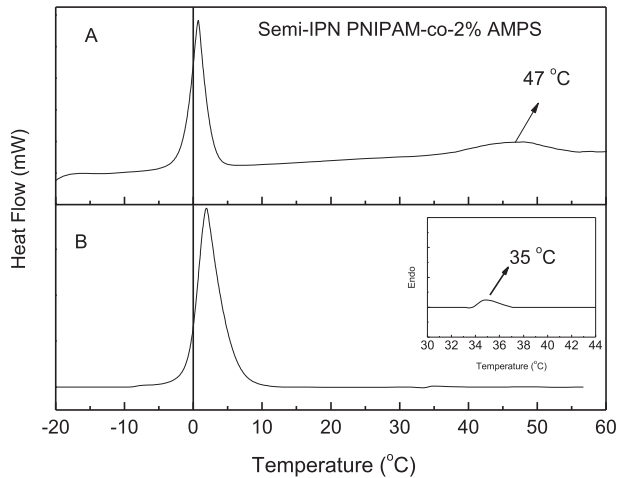| Materials	Solvent	VPTT (°C)[a]
PNIPAM-co-2%AMPS	Water	37.2
PNIPAM-co-2%AMPS/PANI (NC)	Water	35.3
PNIPAM-co-2%AMPS/PANI (SIC)	Water	47.1
PNIPAM-co-2%AMPS	NMP	56.4

[a] Error: ±0.5 °C.

Fig. 6. DSC thermograms of PNIPAM-co-2%AMPS hydrogel with PANI swollen in water. (A) Semi-IPN made by absorption (ISP) from PANI in NMP; (B) NC obtained by *in situ* polymerization (SIS). Inserted plot: peak of the phase transition of the composite.

'free water', 'freezing bound water', and 'non-freezing bound water' [21]. Free water (W_f) does not take part in the interaction with polymer molecules. It has a similar transition temperature, enthalpy and DSC curves as pure water. Freezing bound water (W_{fb}) interacts weakly with polymer molecules, while non-freezing bound water (W_{nfb}) interacts with the polymer chain by hydrogen bonds. The total content of freezing water ($W_{freezing}$) was calculated by DSC, from the area under the endothermic curve for water-swollen hydrogels (Q_{endo}) and the endothermic heat of fusion for pure water ($Q_{pw} = 333.3$ J/g), as described in the following equation:

$$W_{freezing} \ (\%) = W_f \ + \ W_{fb} = \left(Q_{endo} / Q_{pw} \right) \times 100 \qquad \text{Eq (3)}$$

where W_f and W_{fb} are the fractions of "free water" and "freezing bound water", respectively.

On the other hand, the content of "non-freezing bound water" (W_{nfb}) can be determined by subtracting $W_{freezing}$ and considering the equilibrium water content (EWC).

$$EWC \ = \ \left[(w_s \ - \ w_d)/w_s \right] \ \times 100 \qquad \text{Eq (4)}$$

$$W_{nfb} = EWC \ - \ W_{freezing} \qquad \text{Eq (5)}$$

where Ws is the weight of the hydrogel (or composite) sample in the swollen equilibrium state and Wd is the weight of the dried gel (or dry composite).

Fig. 6 shows the DSC thermograms of composites HG obtained by both methods. The states of water were analyzed from melting endothermic peak on heating run and the corresponding parameters were summarized in Table 2.

Firstly and as expected, the equilibrium water content (EWC) was lower in the composites due to hydrophobicity of PANI present inside the matrix. In the case of pure HG the main amount of water is present as non-freezing bound water (W_{nfb}). Almost 96% of water was interacting with HG chains by hydrogen bonding. Q_{endo} is proportional to %$W_{freezing}$ according to eq (3). In that case, the larger values of %$W_{freezing}$ mean that more energy or heat of fusion was measured (See Table 2).

For the composite of PANI/HG a very different distribution of water states was observed. The nanocomposites contained larger amount of free water and freezing bound water (%$W_{freezing}$) than pure HG. Thus, they would have an important competition of water to interact with PANI and/or HG. In addition, the value of %$W_{freezing}$ in semi-IPN is lower than for the NC. Probably the %W_{nfb} is distributed between PANI and HG, making %$W_{freezing}$ smaller. Scheme 4 shows a qualitative representation about distribution of water states.

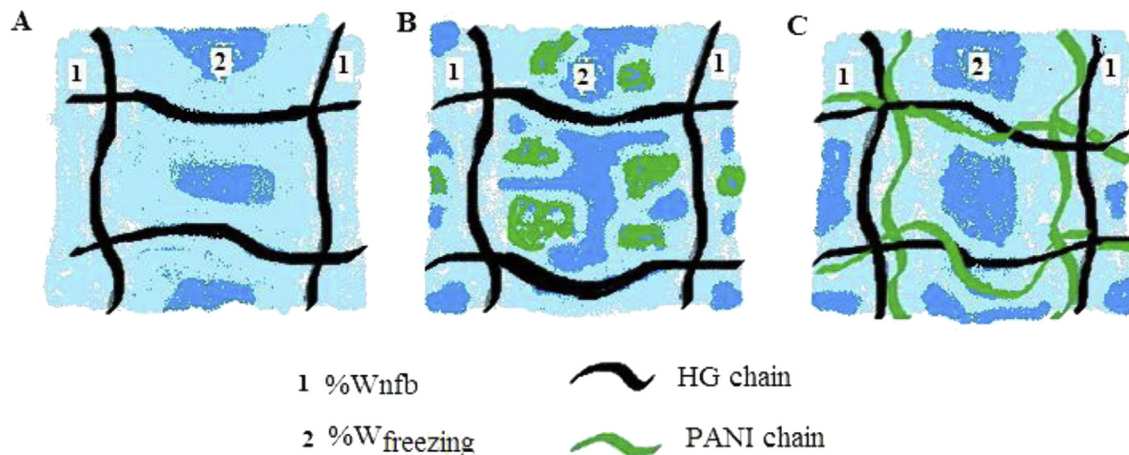### 3.7. Elastic module of the material

If the spatial distribution of PANI into HG is different from the different composites the mechanical properties should be different. Elastic modules were determined by uniaxial compression (Scheme 3) from stress−strain plot (Supporting information, Fig. S3). The E data for the different materials are described in Table 3. The elastic module (E) of the composites is higher than that of the HG matrix and it is according with the increasing swelling capacity previously observed.

If the presence of PANI increases the elastic module of the material, higher PANI loading could further increase the elastic module. Therefore, a way to increase the load of PANI inside the hydrogel was devised. Sequential exposition of the nanocomposites to fresh PANI/NMP solutions for long periods (up to 28 days) allows increasing the elastic module (Fig. 7) of the composite. As it can be seen, E increases up to 18 kPa when exposed during 14 days; longer periods do not improve the mechanical properties.

It is noteworthy that while E increases with PANI loading, the VPTT of all these materials was the same that the one obtained at the first step of loading. Similar behavior was observed for the nanocomposite made by successive steps of in-situ polymerization (Supplementary information, Table S1). It has been shown that the swelling in a solvent strongly affect the mechanical properties of a

Table 2
States of water of PNIPAM-co-2%AMPS and composites with PANI.

Hydrogel systems	Qendo (J/g)	EWC	%Wfreezing	%Wnfb
PNIPAM-co-2%AMPS	11.5	99.04	3.45	95.6
PNIPAM-co-2%AMPS/PANI (NC)	150.7	98.50	45.2	53.3
PNIPAM-co-2%AMPS/PANI (semi-IPN, loaded from 0.4 g/L PANI in NMP)	96.2	98.89	28.9	69.9

Scheme 4. Water states distribution proposed for hydrogel-HG based materials pure hydrogel (A), nanocomposite PANI/HG (B) and semi-IPN PANI/HG (C).

Table 3
Elastic module determined by uniaxial compression.

Material	Elastic module (Pa) (±500)
PNIPAM-co-2%AMPS in water	6500
PNIPAM-co-2%AMPS/PANI (NC)	11,287
PNIPAM-co-2%AMPS/PANI (semi-IPN)[a]	17,756
PNIPAM-co-2%AMPS/PANI (semi-IPN)[b]	9142

[a] Loading 1 g/L of PANI during 7 days.
[b] Loading with 0.4 g/L of PANI in NMP during 7 days.

polymer matrix [22,23]. Therefore, a thorough washing out of NMP from the hydrogel was performed. Moreover, it has been shown that NMP strongly retained inside PANI can be removed by acid washing [19]. So the nanocomposite was treated with acid solution (see experimental section) before measurement of mechanical properties.

3.8. Application of composite as pressure sensor or thermal switch

PANI is turned into an electrical conductor polymer by doping or protonation at pH below 3–4. Before that, it was shown that when a compressive force is applied 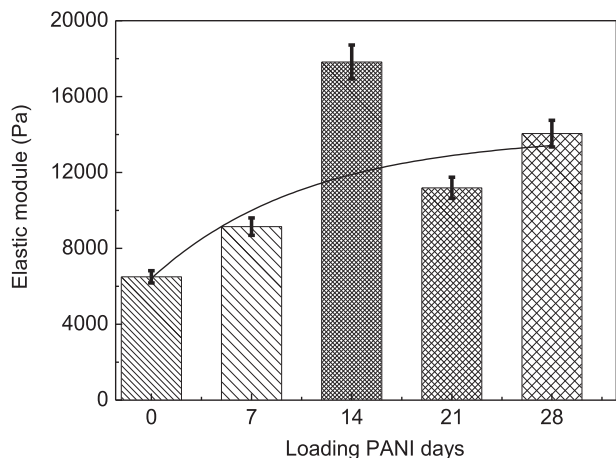on a nanocomposite cylinder (made by in-situ polymerization) the conductivity of material increases [17]. Fig. 8 shows the electrical resistances measured as a function of the compressive stress for semi-IPN with 14 days of PANI loading. As it can be seen, the electrical resistance decreased linearly with the compressive stress applied. The resistance decreased about 5 KΩ for 10% of compression (%C).

The simplest performance metric is the gauge factor (G) [24], which describes how the relative resistance changes depend on strain, ε:

$$\frac{\Delta R}{Ro} = G\varepsilon \qquad \text{Eq (6)}$$

For traditional metals the strain gauge values are around G ~ 2 at low strain [25]. For some materials such as composites, the conductivity is strain-dependent. In a NC the application of strain can change the spacing between conductive filler particles resulting in large resistivity changes. Gauge factor (G) for low compression or stain (ε) = 0.07, was calculated. G values for the NC (dates obtained from Ref. [17]) and semi-IPN are shown in Table 4.

The results indicate that NC is more sensitive to external pressure than semi-IPN. The mechanism of pressure sensitivity could
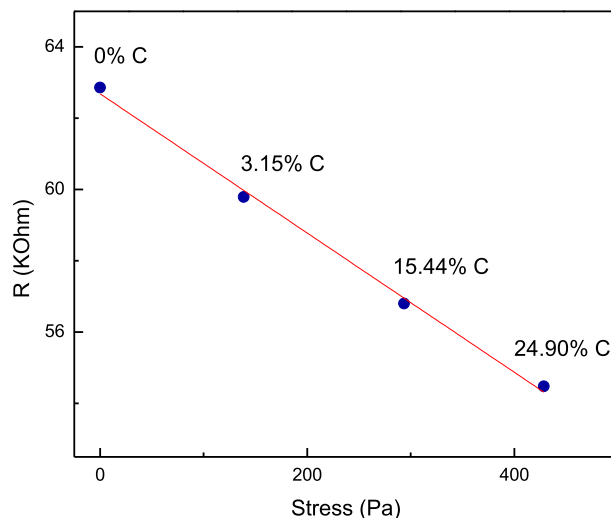

Fig. 7. Elastic module of semi-IPN composite by PANI loading during successive days (method 2, loading with 0.4 g/L of PANI in NMP).

Fig. 8. Electrical resistance vs stress curve of a semi-IPN composite based on PNIPAM-co-2%AMPS with 14 days of PANI loading stabilized at pH 2. Measurements at 20 °C.

Table 4
Strain gauche (G) values obtained from the relative variation of resistance ($\Delta R/R_0$) for a strain (ε) = 0.07.

System	$\Delta R/R_0$	Strain gauge (G)
NC	0.395[a]	5.64
Semi-IPN	0.067	0.95

[a] Ref [17].
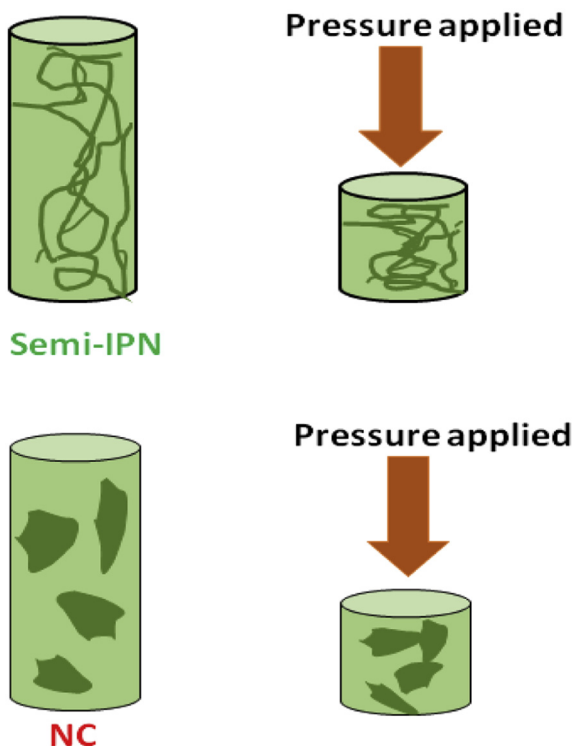
Scheme 5. Representation of spatial distribution of PANI inside HG matrix, before and after external pressure applied.

qualitatively be represented by Scheme 5. In case of semi-IPN, the conductive chains of PANI may be intimately mixed with the HG chains and the pressure decreases the length of the cylinder, decreasing mildly the electric resistance. For the nanocomposite, it is likely that some conductive polymer nanodomains are isolated in the unpressed nanocomposite. When pressure is applied, the material is compressed and the conductive domains contact with each other creating more conducting paths and markedly decreasing resistance.

A thermal switch is possible to be built by placing a cylindrical composite sample between two aluminum plates connected to a multimeter. The system was located in a glass beaker with water at room temperature (20 °C) on a heating plate (Fig. 9). In these conditions, the electric resistance around 540 kΩ was measured. After the temperature was increase at the volume phase transition temperature (47 °C) a decay of the electric resistance (down to 350 kΩ) was observed. This could happen because contact paths increase due to gel collapse. However, at temperatures higher than the volume phase transition temperature (>47 °C) the volume of composite decreased until the contact point is lost and the resistance becomes infinite. In this way, an electric signal switch driven by temperature changes was built. When the system temperature decreases below VPTT, the composite swells again and the electric contact is recovered.

4. Conclusions

Two composites with different mixing properties could be obtained by loading PANI inside a hydrogel matrix based on acrylamide. Apart from the one made by in-situ polymerization (ISP) of aniline inside the hydrogel, we propose a novel method consisting in absorption (SIS) of pre-formed PANI by swelling the HG in a PANI/NMP solution. The SEM investigation of both materials seems to show that, while in-situ polymerization produce a NC with segregated conductive nanodomains in a dielectric matrix, the absorption process seems to produce a semi-IPN material with intimate interaction of PANI and HG chains.

Accordingly, whereas the volumes phase transition temperature (VPTT) of the nanocomposite is nearly the same HG matrix (35—37 °C), the semi-IPN material shows a clearly larger VPTT (47 °C).

The presence of PANI improved the mechanical properties of material but the electric properties were different for NC and semi-IPN when external pressure was applied.

Although the synthesized composite have identical chemical composition and considering the spatial distribution of PANI inside HG matrix, it was possible to demonstrate why NC has more electro-sensitivity to external pressure applied than semi-IPN. However, semi-IPN allowed us to build an electro-thermal switch to sense temperature changes of aqueous systems.

The data presented in this work clearly indicated that molecular interactions affect considerably the properties and morphology of nanocomposites which depend strongly on the synthetic method of the nanocomposite.
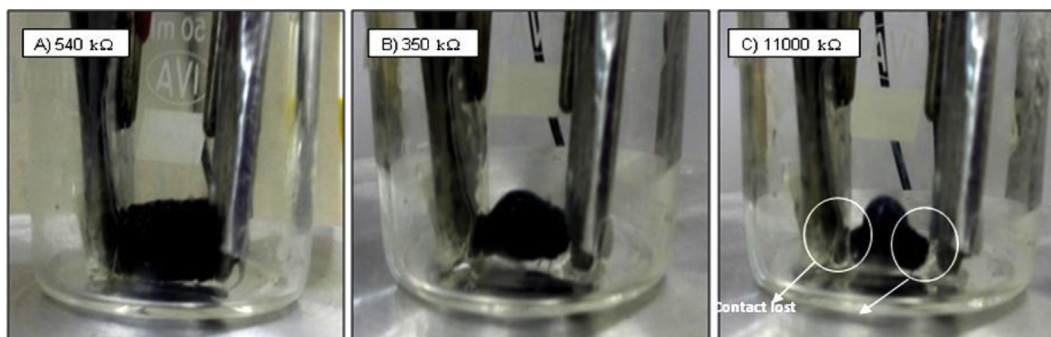

Fig. 9. Photographs of a electric switch built using a semi-IPN made of PANI/HG, A) at 20 °C, B) at 48 °C and C) 55 °C.

Acknowledgments

Appendix. Supporting information

Supporting information related to this article can be found at http://dx.doi.org/10.1016/j.polymer.2015.09.054.

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