



## Pressure and microwave sensors/actuators based on smart hydrogel/conductive polymer nanocomposite



Rebeca E. Rivero, María A. Molina, Claudia R. Rivarola, Cesar A. Barbero\*

Programa de Meso/Nanomateriales, Departamento de Química, Universidad Nacional de Río Cuarto, Ruta 8, km 601, Agencia postal No 3, 5800 Río Cuarto, Argentina

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### ABSTRACT

A nanocomposite is fabricated by formation of a conductive polymer, using in situ oxidative polymerization, inside a thermosensitive crosslinked hydrogel. FE-SEM micrographs show the nanometric domains of the conductive material (polyaniline, PANI) dispersed in the hydrogel matrix based on cross linked poly(N-isopropylacrylamide) (PNIPAm). The thermosensitive properties of PNIPAm and copolymers with 2-acrylamido-2-methyl propane sulfonic acid (AMPS) are not affected by the presence of conductive polymer nanoparticles. The incorporation of PANI improves the mechanical properties of the hydrogel allowing it to swell up to 30,000% without breaking. Since the conductive polymer absorbs strongly microwave radiation at  $\text{pH} < 4$  and heats up, the nanocomposite containing PANI suffer phase transition upon microwave irradiation. At  $\text{pH} > 4$ , PANI is not conductive and the nanocomposite becomes insensitive to microwaves. However, using a pH insensitive conductive polymer (polypyrrole, PPy) in the nanocomposite makes it sensitive to microwaves at all pH values. The nanocomposite is used in a chemomechanical actuator where drug release is driven remotely by microwave irradiation. Since the PNIPAm-co-2%AMPS/PANI nanocomposite is soft and electronically conductive, could be used as pressure/force sensor. It is shown that a compressive force applied on a cylinder of that nanocomposite increases the conductivity of material. Additionally a switch is built which turns off upon microwave irradiation. Therefore, the nanocomposites are potential candidates for different technological applications, such as: a force/pressure electrical sensor, a drug delivery device driven remotely by microwaves, pH or temperature electrical switches and an electric switch driven by microwaves.

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### 1. Introduction

Hydrogels sensitive to external parameters (pH, temperature, ionic force, electric field, etc.) constitute the so-called “smart” hydrogels which could react actively to changes in the environment [1,2]. Crosslinked acrylamide based thermosensitive hydrogels are interesting candidates for biomedical or pharmaceutical applications, such as drug release [3] because they change volume and expel a significant amount of its inner solution when a transition is induced by external action. These kind of materials based on smart hydrogels could also be used in chemical [4] or mechanical [5] actuators as well as environment sensors [6] for technological applications.

\* Corresponding author at: Programa de Meso/Nanomateriales, Departamento de Química, Universidad Nacional de Río Cuarto, Ruta 8, km 601, Agencia postal No 3, 5800 Río Cuarto, Argentina. Tel.: +54 3584676157; fax: +54 3584676233.

E-mail addresses: [rrivero@exa.unrc.edu.ar](mailto:rrivero@exa.unrc.edu.ar) (R.E. Rivero), [mmolina@exa.unrc.edu.ar](mailto:mmolina@exa.unrc.edu.ar) (M.A. Molina), [crivarola@exa.unrc.edu.ar](mailto:crivarola@exa.unrc.edu.ar) (C.R. Rivarola), [cbarbero@exa.unrc.edu.ar](mailto:cbarbero@exa.unrc.edu.ar) (C.A. Barbero).

However, it would be most interesting to induce the volume change at distance using electromagnetic radiation of low energy. In fact, smart nanocomposite hydrogels containing gold nanoparticles and driven by absorption of near infrared radiation-NIR has been proposed [7–10]. It is well known that conductive polymers strongly absorb electromagnetic radiation, specifically in the microwave range, with heating up of the polymer [11].

In addition, we have shown previously that macroporous hydrogels loaded with conductive nanoparticles (including polyaniline nanospheres and nanofibers) could be driven to volume collapse by microwave or laser light (near infrared range) irradiation [12]. At the same time, behavior of semi-interpenetrated system of PANI inside thermosensitive hydrogel showed that properties of both materials were not alters, significantly. That is to say, each component of material could respond by itself.

It is noteworthy that even though the incorporation of conducting polymers to hydrogel network has been described before [13], it have been usually assumed that the conducting polymer form an interpenetrating [14] or semi-interpenetrating networks [15–17]. However, we think this would be the case when a water soluble polymer is made inside a hydrogel network [18].

It is well known that polyaniline is insoluble in the aqueous polymerization solution and precipitates from the solution during polymerization. For that in the present communication we show how a nanocomposite could be easily fabricated by formation of conductive polymer (hydrophobic) inside a nanoporous matrix based on PNIPAm hydrogels. The formation occurs by oxidative polymerization of the appropriate monomer (aniline-ANI or pyrrole-Py), previously loaded inside the hydrogel matrix. Semi-interpenetration of linear polyaniline inside a hydrogel network should involve the formation of isolated PANI chains which have not been detected in water. It is more likely that aggregates of PANI chains, in form of PANI nanoparticles which have been detected in water, also are formed in the water filled pores of the hydrogel. Accordingly, in contrast with previous assumptions, we show clear evidence on the formation of separate nanoscopic domains of PANI incorporated to PNIPAm and copolymers with 2-acrylamido-2-methyl propane sulfonic acid (AMPS). The distinction is quite relevant because the semi-interpenetration of one polymer in a crosslinked matrix alters the physicochemical properties of the gel (e.g. transition temperature) while in a nanocomposite the physicochemical properties are the linear addition of the components properties. The nanocompositing of the conducting polymer and the hydrogel provide novel properties to materials which arise from the synergic combination of each component properties. Using those properties, different sensors and actuators can be built.

The incorporation of a relatively rigid conducting polymer in a soft matrix based on superabsorbent hydrogel enhances the mechanical properties of material. Accordingly, the superabsorbent nanocomposite could swell up to 30,000% without breaking. The conducting polymer absorbs microwaves and heats up, driving the thermal phase transition of the hydrogel. The thermal phase transition is shown as a volume change and the release of the inner solution. Therefore, a drug delivery actuator driven remotely by microwave irradiation is demonstrated.

Besides that, the presence of the conducting polymer makes the nanocomposite electronically conductive while the hydrogel matrix makes the material elastic. In that way, the nanocomposite deforms under pressure and the resistance changes, allowing us to build an electronic pressure/force sensor.

Finally, the volume change upon microwave irradiation combined with the electronic conductivity of the nanocomposite is used to build a microwave actuated electrical switch.

While we built all the actuators as macroscopic devices, the underlying properties are molecular in nature. Therefore, it is likely that the devices can be miniaturized up to nanometric size with success.

## 2. Experimental

### 2.1. Synthesis of nanocomposites

PNIPAm hydrogels were prepared by free radical polymerization dissolving in distilled water 0.5 M N-isopropylacrylamide (NIPAm-Scientific Polymer Products) and 10 mM N'-methylenebisacrylamide (BIS-Scientific Polymer Products) as crosslinker agent, using ammonium persulfate (APS-Cicarelli) (0.001 g/ml) and N,N,N',N'-tetramethylethylenediamine (TEMED-Aldrich) (10  $\mu$ l/ml) as redox initiator and activator, respectively. In other cases, 2-acrylamido-2-methyl propane sulfonic acid (AMPS-Scientific Polymer Products) (2 or 20% moles of NIPAm monomers) was added to NIPAm to synthesize the co-monomer.

The experimental steps of nanocomposite formation are described in [Scheme 1](#). Small discs of dry hydrogels were immersed into a solution with 0.1 M ANI (Fluka)/1 M HCl, until the solution was absorbed. A known amount of APS (equimolar to ANI) was then added as oxidant to produce PANI inside of gel. The experience was

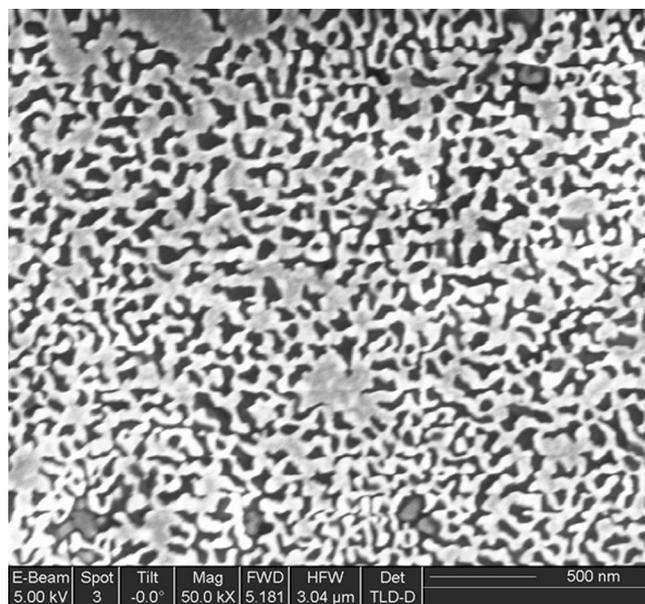


Fig. 1. SEM micrographs of PANI incorporated into a PNIPAm hydrogel.

carried out at room temperature. A similar process was carried out to impregnate hydrogels with polypyrrole (PPy).

### 2.2. Scanning electron microscopy (SEM)

Scanning electron micrographs ([Fig. 1](#)) were taken at low vacuum and low field in a LEO 1450VP Variable Field Emission SEM. The images of porous hydrogels were analyzed using “ImageJ 1.45s” software to ascertain the pore size and distribution. The FE-SEM micrographs were obtained in a dual beam workstation (FEI Helios Nanolab 600) equipped with a field emission gun scanning electron microscope (FE-SEM). The elemental measurements were performed by energy dispersive spectroscopy (EDX) with an accelerating voltage of 20 kV using EDAX instruments detector and EDAX Genesis<sup>®</sup> Software ([Table 2](#)).

### 2.3. Swelling dynamic experience

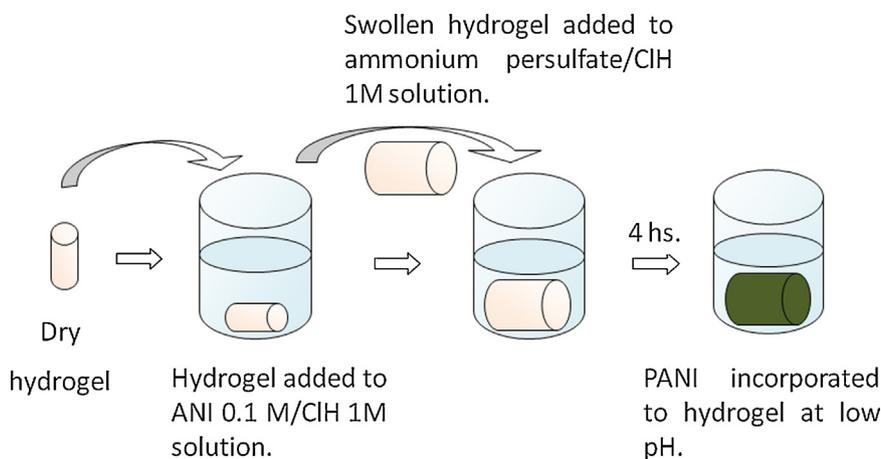
Previously weighted dry hydrogels samples were immersed in solutions. At certain time intervals, the sample was removed from solution and was weighed. The swelling percent can be calculated as a function of time, according to:

$$\%S_w = \frac{W_s - W_d}{W_d} \times 100$$

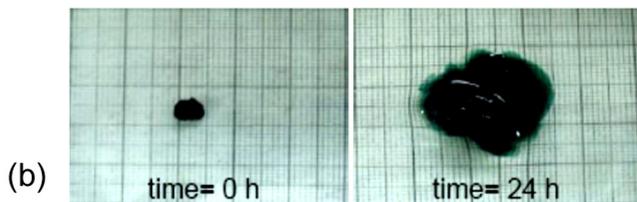
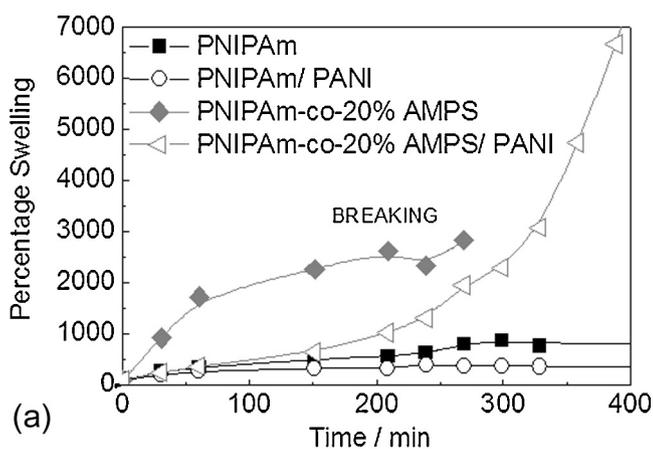
where  $W_s$  represents the weight of the swollen state of the sample at a given time and  $W_d$  is the weight of dry sample. Graphic of  $\%S_w$  vs time were built to analyze the swelling kinetic ([Fig. 2a](#)). Every data of  $\%S_w$  obtained were averaged of five measurement with absolute error around  $\pm 150$ . The experiments were carried out in buffer solution at pH 7 and room temperature. Photography of nanocomposite was taken before and after of equilibrium swelling state to show the extraordinary increase of volume ([Fig. 2b](#)).

### 2.4. Differential scanning calorimeter (DSC)

DSC measurements were performed to determine the phase transition temperature ( $T_{PT}$ ) of hydrogels and nanocomposites swollen in water ([Table 1](#)). The sealed pan with a water swollen hydrogel piece was quickly frozen inside the DSC chamber until  $-25^\circ\text{C}$ . This temperature is reached by an aqueous  $\text{Cl}_2\text{Ca}$  solution



**Scheme 1.** Impregnation process of PANI inside hydrogel.



**Fig. 2.** (a) Swelling kinetic of PNIPAm and PNIPAm-co-20%AMPS, with and without PANI (Error =  $\pm 150$ ). (b) Swelling photography of PNIPAm-co-20%AMPS/PANI after 24 h of water uptake.

previously cooled with liquid  $N_2$ . The system was left without heating for several minutes to allow the system to reach the equilibrium. The sample holder assembly was then heated at a rate of  $10^\circ C/min$  until  $60^\circ C$  (before boiling point of solvent) to avoid sample degradation and evaporation of water. The DCS measurements were conducted using TA Instruments DSC 2010 under  $N_2$  flow.

**Table 1**  
Phase transition temperatures ( $T_{PT}$ ) of PNIPAm based nanocomposites at pH 7, measured by DSC.

Hydrogel	Conducting polymer	$T_{PT}/^\circ C^a$
Poly(NIPAm)	None	33.0
	PANI	32.9
	PPy	34.5
Poly(NIPAm-co-2%AMPS)	None	38.8
	PANI	36.2
Poly(NIPAm-co-20%AMPS)	None	> 100
	PANI	> 100

<sup>a</sup> Average error  $\pm 0.5^\circ C$ .

Similar process was carried out to PNIPAm-co-20%AMPS swollen in ethylene glycol at a rate of  $5^\circ C/min$  until  $150^\circ C$  (before boiling point of solvent) with the purpose to observe phase transition.

### 2.5. UV-vis and FTIR spectroscopy

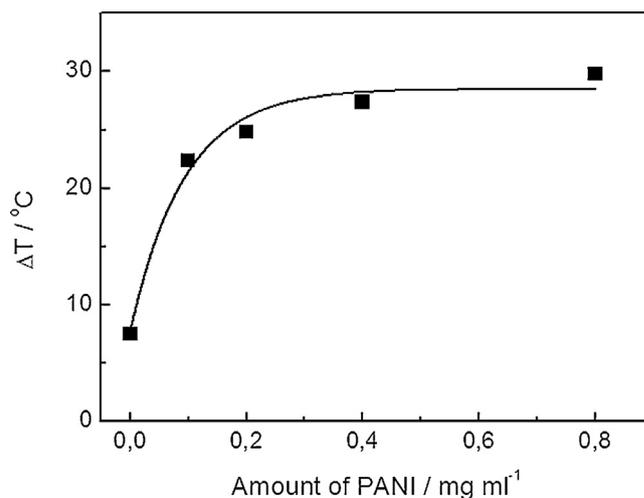
UV Spectra were measured in Hewlett-Packard-8453 UV-vis spectrophotometer. Pieces of hydrogel and nanocomposite were set between two quartz plates and placed in the light beam of the spectrophotometer.

FTIR spectra were measured in an Impact 400 spectrometer (Nicolet) by transmission. The polymers and nanocomposites were dried under vacuum and were crushed in a mortar. After mixing with KBr, the powder was made into pellets by pressing for 15 min at approximately 1500 MPa.

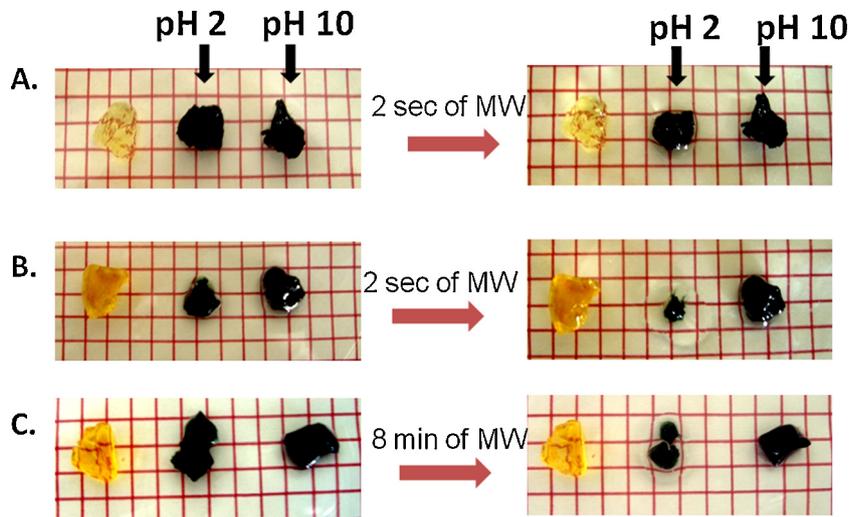
### 2.6. Microwave irradiation experiences

Microwave irradiation was applied both on PANI aqueous dispersions (at different amount) and on swollen nanocomposite pieces (at different pH).

Equal volumes of acid PANI aqueous dispersions were prepared at different concentrations in glass tubes. Every sample was placed in microwave oven. After 30 s of irradiation, those were withdrawn and superficial temperature was measurement with



**Fig. 3.** Increase of temperature ( $\Delta T$ ) by microwave irradiation (during 30 s) on aqueous dispersion containing varying amount of PANI (emeraldine salt form).

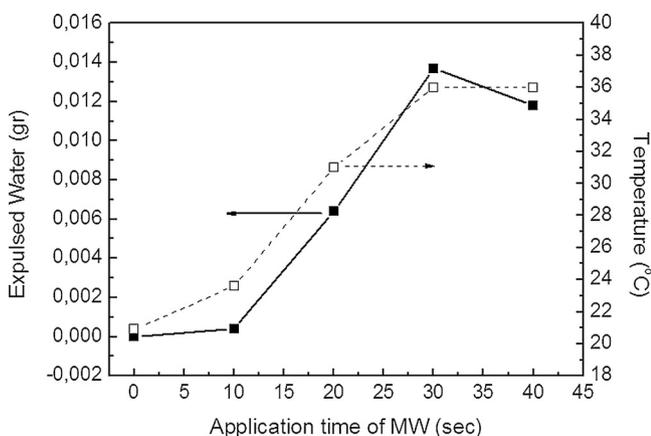


**Fig. 4.** Photographic record of nanocomposite at different pH, before and after microwave (MW) irradiation at low power. (A) PNIPAm with and without PANI. (B) PNIPAm-co-2%AMPS with and without PANI. (C) PNIPAm-co-20%AMPS with and without PANI.

laser IR-thermometer (DeWALT®, DCT414S1), immediately. The increase of temperature ( $\Delta T$ ) induced by microwave absorption of different PANI amounts are shown in Fig. 3.

The microwave irradiation of the nanocomposites was carried out with hydrogel pieces placed in glass Petri dishes below a cover glass in order to see the release of inner solution. Pieces of each hydrogel sample were impregnated in acid or basic solution until they swelled to equilibrium. Optical photographs were taken with an electronic camera before and after exposition of the gels to microwaves, by extracting the samples from the oven and rapidly taking the photographs. The experiments were done with hydrogels alone and nanocomposite with PANI (Fig. 4) and PPy (Fig. 6). The experiments were performed in a commercial microwave oven (2.4 GHz, 700 W nominal power, low power setting).

On the other hand, a swelling nanocomposite piece, with a known weight, was exposed to microwave irradiation and the percent amount of water expelled in function of temperature system were analyzed (Fig. 5). The temperature system was measurement with laser IR-thermometer (DeWALT®, DCT414S1) and the amount of water expelled was determinate by difference between initial weight of the swollen sample and the weight of sample before microwave application.



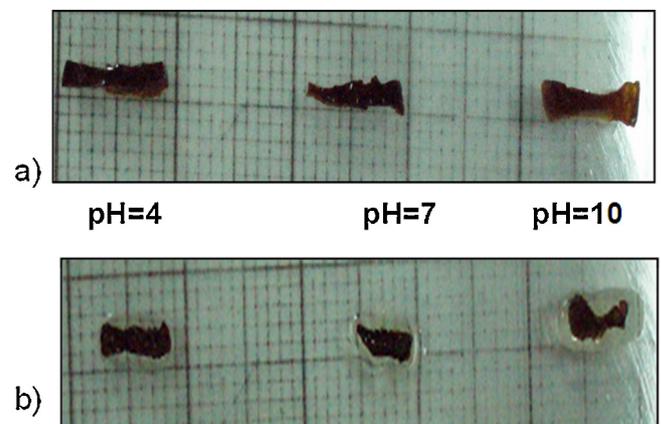
**Fig. 5.** Expelled water amount and surface temperature of a PNIPAm/PANI nanocomposite during application of microwaves at low power.

## 2.7. Electric resistance and uniaxial compression measurements

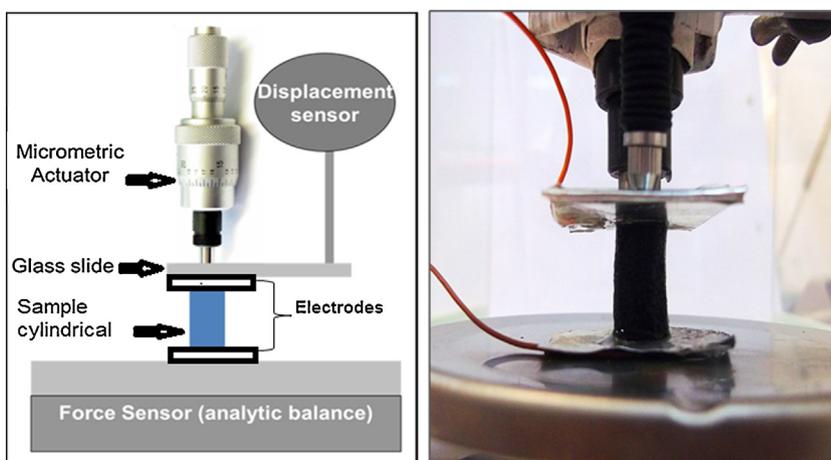
Measurements were performed on cylindrical nanocomposite in equilibrium swelling state at pH 2. All the measurements were conducted at  $20 \pm 0.5$  °C. The key parts of the apparatus used are shown in Scheme 2.

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 extremes of cylinder two aluminum plates (as electrodes) were placed. Stress is defined as the ratio of applied force  $F$  (compressive force) to cross section  $A$ , having the unit of “force per area” ( $F(N)/A(m^2)$ ). The force  $F$  acting on the gel was calculated through mass ( $m$ ) measurement from the reading of the analytic digital balance as  $F = mg$ , where  $g$  is the gravitational acceleration (Hooke’s law). Displacement sensor allows us to determine the percentage compression.

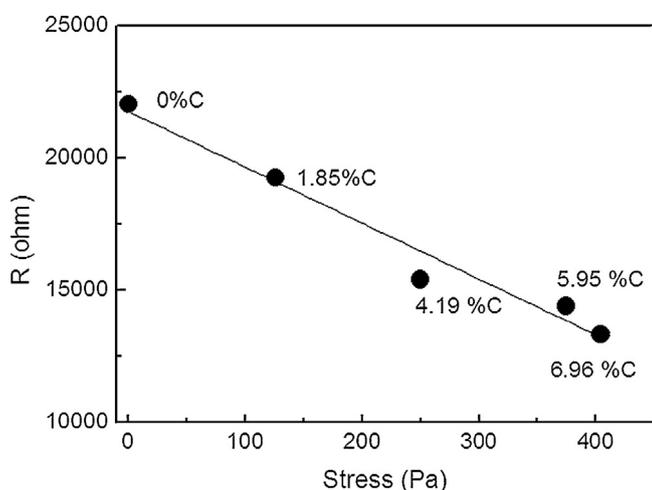
Aluminum electrodes were connected to homemade micropotentiostat where electrical current is measured at defined potential differences. Through the linear slope of potential vs current curve (ohm’s law), the electric resistance ( $\Omega$ ) value were obtained for each compression state. It is possible to measure



**Fig. 6.** Photographic record of a nanocomposite PNIPAm/PPy at different pH, (a) before and (b) after microwave irradiation during 30 s.



**Scheme 2.** Uniaxial compression apparatus: scheme of key parts of the apparatus (left), and original photography of the device (right).



**Fig. 7.** Electrical resistance vs stress curve of a nanocomposite based on PNIPAm-co-2%AMPS/PANI stabilized at pH 2. Measurements at 20 °C.

resistance with a multimeter but the measurement method used here allows us to assure compliance with ohm's law at each state.

The load was incremented in successive steps until the gel was deformed up to about 10%. Then, force and resistance were recorded after 30 s of relaxation. Resistance vs stress curve is shown in Fig. 7.

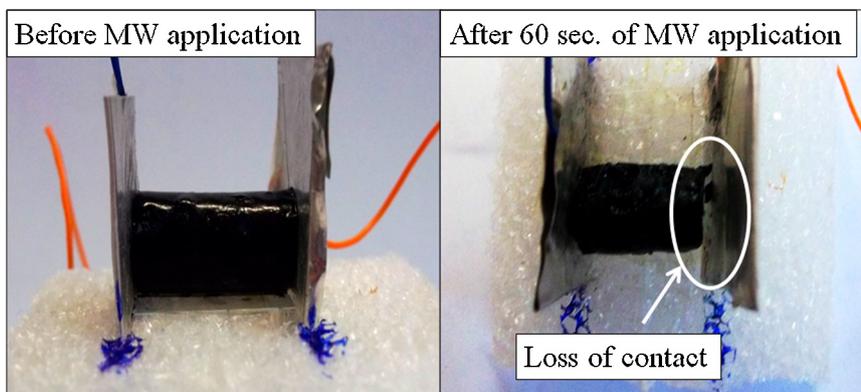
### 2.8. Drug delivery by microwave application

A piece of dry hydrogel was impregnated with tris(2,2'-bipyridine)ruthenium(II) ion (RUBPY) solution for 24 h until reaching equilibrium state. The spectrums of complex in the solution outside the gel and after collapse induced by microwave application (2.4 GHz, 700 W nominal power, low power setting) were taken by a Hewlett-Packard-8453 UV-vis spectrophotometer and quartz cells (Helma).

### 2.9. Electrical switch building and testing

Two glass pieces, covered with aluminum foil and inserted in polystyrene foam were used as electrodes. A PNIPAm/PANI nanocomposite cylinder was swollen in pH 2 solution. Then, the cylinder was attached with conductive epoxy to one of the electrodes while touching the other electrode. The electrodes were connected with alligator clips and the resistance was measured using a multimeter (VA 40B Multimeter-KAISE). The closed circuit was assured by a low (<1 k $\Omega$ ) resistance, revealing good electrical contact between the nanocomposite and the electrodes. The closed circuit photograph was taken (Fig. 8).

The whole device was photographed (closed circuit picture), then placed inside a microwave oven and irradiated with microwaves (2.4 GHz, 700 W nominal power, low power setting), the oven was opened and the resistance was measured. When the



**Fig. 8.** Photography of an electrical switch driven by microwaves. System made of a PNIPAm/PANI nanocomposite contacted to two aluminum electrodes. Closed circuit (left) and open circuit (right) after microwave absorption (2.4 GHz, low power).

resistance surpasses a threshold ( $>1\text{ M}\Omega$ ) the circuit is considered open. Then, the open circuit photograph was taken.

### 3. Results and discussion

#### 3.1. Characterization of nanocomposite synthesized

Isolated nanoscopic domains in PNIPAm matrix with PANI incorporated is shown in Fig. 1. The dark areas correspond to the electronically conductive PANI domains while bright areas correspond to the non conductive hydrogel domains (PNIPAm). The different brightness is related with the electronic charging of the material, which only occurs in the nonconductive domains. Similar topographical images were obtained to PNIPAm-co-20% AMPS nanocomposites (supporting information, Fig. 1-SI). It is say, using a matrix based on PNIPAm allows build a nanocomposite with organic polymer nanoparticles (poorly soluble in water) as PANI.

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.snb.2013.08.054>.

As it can be seen, a uniform distribution of the amorphous PANI particles inside the hydrogel matrix is obtained. The size of the nanometric PANI domains (estimated from the micrographs) is in range of 18–280 nm. This is reasonable since the pore size of hydrogel matrix calculated from Flory–Rehner theory, is of approx. 45 nm. The pores which are bigger than the calculated values have rod-like shape, suggesting that the SEM show some pores (circle-like) cut transversal to the surface and others (rod-like) parallel to the surface. It is noteworthy that similar nanodomains have been observed when poly(2-hydroxyethyl acrylate) and poly(ethyl acrylate) are interpenetrated inside polyacrylamide [19].

FTIR spectrum also suggests that PANI is produced inside the hydrogel with the same chemical structure than in solution. FTIR spectral of subtraction of PNIPAm/PANI nanocomposite and hydrogel, and PANI spectral were added as supporting information (Fig. 2-SI). The spectra obtained show the presence of PANI incorporated into hydrogel matrix.

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.snb.2013.08.054>.

#### 3.2. Swelling capacity of nanocomposites

The hydrogel of PNIPAm-co-AMPS is swelling significantly more than PNIPAm due to the effect of the anionic groups inside the hydrogel [16]. The swelling kinetic of PNIPAm and its copolymer with AMPS (20%) are showed in Fig. 2a. It seems that ionic moieties ( $-\text{SO}_3\text{H}$ ) dissociate and create an overall charge density along the chains, as well as a high concentration of mobile ions in the gel. For that, two new forces appears leading to hydrogel swelling: (i) the osmotic pressure resulting from differences in ion concentration between the swollen gel and the external solution; (ii) the electrostatic repulsion (i.e. coulombic) forces between charged chain segments. However, it can be observed that the ionic hydrogel breaks after approximately 2 h due to the internal pressure of water retained by the superabsorbent matrix containing anionic groups.

The swelling of the nanocomposites was also measured (Fig. 2a), showing that its water uptake capability is smaller than for the hydrogel alone. This could be due to the fact that PANI nanoparticles fill up the volume of the pores leaving only the hydrophilic hydrogel matrix to retain water.

However, the presence of PANI domains increases the nanocomposite resistance to breaking. In that way, the PNIPAm-co-20%AMPS based nanocomposite swells up to 7000% without breaking in approximately 6 h, while the hydrogel alone breaks up at a swelling

degree of about 3000%. After 24 h of swelling, the PNIPAm-co-20%AMPS swell up to 30,000% without breaking (Fig. 2b). This is an important property for the application of hydrogels in water uptake systems [20].

#### 3.3. Phase transition temperature by DSC

Other property which could be altered by incorporation of PANI into hydrogel matrix is the phase transition temperature ( $T_{PT}$ ). The  $T_{PT}$  values were determinate by DSC and registered in Table 1. Results show that there is an increase of  $T_{PT}$  by the presence of hydrophilic AMPS units. When the copolymer contains 20% of AMPS monomer units the  $T_{PT}$  cannot be observed before reaching to measurable range (defined by water boiling point). This happen because the presence of hydrophilic groups ( $\text{SO}_3^-$ ) in the hydrogel chains increases the energy necessary to drive the hydrophilic to hydrophobic transition of the hydrogel. To check the copolymer remains thermosensitive, PNIPAm-co-20%AMPS has to be swollen in a solvent with higher boiling point than water. Ethylene glycol was selected which present a boiling point of  $197^\circ\text{C}$ . By DSC it was observed a  $T_{PT}$  around  $120^\circ\text{C}$ . Therefore, the copolymer remains thermosensitive but the phase transition of PNIPAm-co-20% AMPS swollen in water will be taken place at temperature around or above to boiling point water and could not be experimentally determined.

On the other hand, the presence of PANI or PPy inside the hydrogel shows a negligible effect on the transition temperature ( $T_{PT}$ ). This result is in agreement with the morphology of the nanocomposite material, because we can see how PANI domains are insulated of matrix (Fig. 1) and are not intimately linked to hydrogel network. If the nanocomposite would be a semi-interpenetrated network, the proximity of the two polymers chains should induce some effect on the  $T_{PT}$ .

#### 3.4. Conductive properties of PANI

It is known that PANI is only conductive when it is protonated at pH values below 4. In that way, the samples at pH 2 contain conductive PANI while the ones at pH 10 contain non conductive PANI [21]. The protonation/deprotonation of PANI can be detected by UV–vis spectroscopy. The change in protonation of PANI domains inside the hydrogel is clearly shown in the UV–vis spectra of the nanocomposite (supporting information, Fig. 3-SI), which are in agreement with those previously reported for pure PANI films in the emeraldine state [22]. In addition, measurements of chloride ion (EDX) in a PNIPAm-co-20%AMPS composite treated with HCl (protonated) or NaOH (not protonated) (Table 2) shows the presence of chloride in the protonated material and its absence in the no protonated material. EDX plot is also shown in supporting information (Fig. 4-SI). The results suggest that PANI domains inside the nanocomposite are accessible to ion changes in solution and the conductivity of the PANI can be switched by changing the pH of the external solution.

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.snb.2013.08.054>.

**Table 2**

Elemental distribution obtained by EDX (Energy-dispersive X-ray spectroscopy) of a nanocomposite of PANI formed inside PNIPAm-co-20%AMPS.

Element	Atomic %	
	Equilibrated in HCl 0.1 M	Equilibrated in NaOH 0.1 M
C	50.47	60.28
N	8.31	5.76
O	5.21	6.26
S	2.33	0.56
Cl	3.47	0.00

Therefore, PANI is electrically conductive in the nanocomposite and the hydrogel matrix retains its thermosensitivity.

### 3.5. Effect of microwave applications on nanocomposite

It is well known that PANI absorbs microwave radiation [23]. The property has been used to weld thermoplastics [5] or shield radar signals [24]. However, the microwave absorption capacity has not been studied for PANI immersed in water. To test the microwave absorption in aqueous media, we measured the increase of temperature ( $\Delta T$ ) of aqueous samples containing varying amount of dispersed PANI (emeraldine salt form) powder upon irradiation with microwaves.

The results in Fig. 3 indicate that the heating of water is given mainly by specific microwave absorption of PANI dispersed. The effect reaches a plateau when large amounts of PANI are used. It is likely that in dispersions containing large amount of PANI, the radiation is only absorbed by the external layer of solution. Microwave application during 30 s only increase the temperature of water (without PANI) around 7 °C, while adding 0.2 mg/ml of PANI is enough to increase the microwave absorption and induce a 25 °C change on the temperature of system.

Based on that test, it seems possible to synergically combine the components properties, making PANI to absorb microwaves, heating the nanocomposite and driving the phase transition of the hydrogel.

To test microwave effect on nanocomposite, pieces of hydrogel with or without PANI (stabilized at pH 2 conductive) or pH 10 (non conductive) are swelled and placed in glass Petri dishes. Then, they are set inside a microwave oven and irradiated by some seconds at low power. In Fig. 4 are shown the photographic record of PNIPAm, PNIPAm-co-2%AMPS and PNIPAm-co-20%AMPS, before and after microwave application. As it can be seen, the hydrogels without PANI show negligible volume change indicating that microwave absorption by water inside the gel is not enough to reach the thermal phase transition. The same happens with the nanocomposite containing PANI stabilized at pH 10. At this pH, polyaniline is non protonated and not conductive so it does not absorb enough microwave radiation to heat up the composite and drive the phase transition of the hydrogel. However, the nanocomposite samples containing PANI stabilized at pH 2, where PANI is protonated and conductive, suffers a clear volume change with expulsion of the inner solution upon microwave irradiation during the few seconds of application. Obviously, protonated PANI absorbs enough energy to induce the phase transition by local heating before or near reaching water ebullition temperature. In the best of our knowledge, this is the first successful fabrication of a hydrogel based nanocomposite material which is sensitive to microwave radiation.

On the other hand, when 20% of AMPS is present in the gel, more energy (or application time) is required in order to the collapse happen, because phase transition in water occurs at temperatures around 100 °C or more (it could not be measured by DSC).

Knowing that nanocomposite collapses by absorption of microwaves, the expelled water amount was measured (by mass difference) during application of microwaves at low power. At the same time, the surface temperature of the material was sensed using a laser IR thermometer. Fig. 5 shows that after 10 s of microwave application, the PNIPAm/PANI nanocomposite begins to release an appreciable amount of water when the temperature has reached approximately 30 °C. This result suggests that the expulsion of solution is going on during the phase transition of nanocomposite and that temperature (where no more water is expelled from the hydrogel) is in agreement with dates obtained of  $T_{PT}$  from DSC experience (Table 1). Remembering that

the temperature measurements were taken on the surface of the nanocomposite, the experimental data could have a significant error in this case.

### 3.6. Polymeric nanocomposite applications

#### 3.6.1. Actuator responsive to microwave in a wide range of pH

The sensitivity of PANI based nanocomposite allows detecting the external pH. However, the nanocomposite based on PANI is inactive at neutral pH. This could be limiting its applications for example in biomedical area [25]. To overcome such pH limitation, it is possible to use a conductive polymer much less sensitive to pH than PANI, like polypyrrole (PPy) [26]. Indeed, it was found that PNIPAm/PPy nanocomposites are able to collapse by absorption of microwave even at pH 10, as it is shown in Fig. 6. Therefore, a microactuator responsive to microwave at neutral or basic pH could be built by polymerization of pyrrole inside PNIPAm based hydrogels.

#### 3.6.2. Actuator to drug delivery driven remotely by microwaves

As it was shown in Fig. 5, the gel collapse during phase transition is accompanied with expulsion of a significant amount of the inner solution. The same was seen when the system was collapsed through a thermal heating [20]. Therefore, if a chemical substance is loaded inside the composite, it could be released upon microwave irradiation. To check that possibility, a dye (tris(2,2'-bipyridine)ruthenium(II) ion, RBPY) was loaded into the gels by swelling the dry gels in a 10 mM solution of RBPY. The gels were then subjected to microwave irradiation and the solution expelled analyzed by UV-vis spectrophotometer. The concentration of the probe molecule in the outer solution increases upon irradiation (supporting information, Fig. S-5 I). In addition, the UV-vis spectrum of the released solution is identical to those of freshly prepared solutions, indicating that the probe molecule is not altered by microwave irradiation. Therefore, an actuator based on this composite could release a therapeutic drug driven at distance by microwave irradiation [27].

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.snb.2013.08.054>.

#### 3.6.3. Electrical sensor of force/pressure

Since PANI is an electrical conductor and the hydrogel is a soft matrix. For that, we measured the effect of pressure on nanocomposite conductivity, according to Scheme 2. The electrical resistances are then measured as a function of the compressive stress (Fig. 7). As it can be seen, the electrical resistance decreases linearly with the compressive stress applied. At 7% of uniaxial compression applied on the material, the electric resistance decrease about 9000  $\Omega$  (9 k $\Omega$ ). Therefore, the conductivity increases considerably for small stresses applied.

Knowing the length of the cylinder and the contact area of the cylindrical sample, we can estimate the resistivity ( $\rho$ ) of the nanocomposites. So, when the doped (pH 2) composite was swollen, the resistivity is of 5786.90  $\Omega$  cm and after 7% compression the resistivity decrease to 35.03  $\Omega$  cm. Evidently, the nanocomposite is a poor conductor compared with doped PANI (0.23  $\Omega$  cm at 20 °C) [28] or copper ( $1.7 \times 10^{-6}$   $\Omega$  cm). However, it is very sensitive to external pressure because applying only 50 Pa (1% compression) on the nanocomposite the resistivity decreases about 362  $\Omega$  cm, which could be easily measured. Therefore, an electronic pressure sensor can be built. The mechanism of pressure sensitivity is unclear but it is likely that some conductive polymer nanodomains are isolated in the relaxed polymer and become contacted upon the material deformation creating more conducting paths and decreasing the resistance.

A sample of PNIPAm-co-20%AMPS/PANI swollen at low pH, have an electric resistance of 5.4 k $\Omega$  without stress applied (0% compression (C)). Experimental results show that during uniaxial compression of this nanocomposite, the electric resistance is almost unaltered, suggesting that the PANI nanodomains are already connected in this material and deformation does not increase the conducting paths. The initial resistivity of PNIPAm-co-20%AMPS/PANI (3690  $\Omega$  cm) is larger than that of PNIPAm-co-2%AMPS/PANI (22,044  $\Omega$  cm) in agreement with the presence of more conducting paths in the original state.

### 3.6.4. Electric switch driven by microwave presence

It is possible to build electrical switches using the volume variation upon microwave irradiation. Fig. 8 shows photographs of a device building with two electrodes in contact with the extremes of PNIPAm/PANI nanocomposite. The behavior of device is tested with a multimeter which shows about 250  $\Omega$  of resistance when the electrodes are connected through the swollen hydrogel (stabilized at pH 2) (Fig. 8 – left). After only 30 s of microwave irradiation (low-power), a decrease of resistance was observed (about 50  $\Omega$ ) probably due to the heating of the semiconductor (PANI). After that, microwave application continues, the circuit is opened due to the thermal contraction of the hydrogel cylinder and the resistance becomes infinite (Fig. 8 – right). Therefore, an electrical switch driven by microwave irradiation has been built. The device could be used as microwave irradiation limiter. Up to now, commercial microwave ovens only regulate the power and the irradiation time. Therefore, too much irradiation could be applied. Using the device shown in Fig. 8, adequately calibrated, it is possible to limit the amount of microwaves applied inside the oven.

The same effect is produced on the devices by: (i) pH increase by exposure to ammonia gas, making the nanocomposite no conductive, (ii) ambient temperature increase, making the hydrogel to collapse. It is noteworthy that the temperature of phase transition can be easily changed by including hydrophilic or hydrophobic groups in the polymer chains (Table 1). Therefore, the devices could be tuned to different amounts of microwaves or different temperatures.

## 4. Conclusions

It has been shown that the in situ polymerization water soluble monomers (aniline or pyrrole) inside a hydrogel produces nanocomposite with conductive and dielectric domains. The presence of the conductive polymer does not affect significantly the thermal sensitivity of the hydrogel matrix, but the swelling capacity and rate decrease. However, the mechanical properties seem to improve by the reinforcement effect of the rigid conductive polymer, as PNIPAm-co-20%AMPS/PANI, allowing large swelling (up to 30,000%) without breaking.

The nanocomposite suffers a phase transition by externally changing the temperature of the gel or by microwave absorption. Upon microwave irradiation, the conductive polymer absorbs the radiation and heats up driving the phase transition of hydrogel which involves a clear volume decrease and inner solution expulsion. It is found that the amount of water released correlates well with the surface temperature of the materials upon microwave irradiation. When PANI is the conductive polymer component, the effect is modulated by the pH which controls the conductive/insulator transition of PANI. At pH > 5, the nanocomposite becomes insensitive to microwaves. However when PPy is used the nanocomposite is sensitive to microwaves at neutral or basic pH. The release of a dye absorbed inside the nanocomposite is found to occur by microwave irradiation. Therefore the volume

change induced by microwaves on a thermosensitive nanocomposite (based PNIPAm-co-2%AMPS) can be used in mechanical actuators [29,30], as well in drug delivery devices.

The synergic combination of the electrical conductivity of the conjugated polymer and the sensitivity to uniaxial compression of the hydrogel allows us to build a pressure/force sensor. It is found that the electric resistance of PNIPAm-co-2%AMPS/PANI is linear with the stress applied. Additionally, an electrical switch based on the thermosensitive nanocomposite could be built and driven by microwaves. Moreover, it is possible to use the nanocomposite in biomedical application as photothermal therapy [31] or a drug release system driven remotely.

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## Biographies

**Rebeca E. Rivero** holds a B.Sc in Chemistry (UNRC, 2009) and is presently pursuing a Ph.D. in Chemistry at National University of Rio Cuarto in the subjects of advanced materials based on smart hydrogels. She holds a Ph.D. fellowship from the National Science Council of Argentina (CONICET).

**Maria A. Molina** holds a Ph.D. in Chemistry (UNRC, 2011). She is presently working as a postdoc at the Institut für Chemie und Biochemie, Freie Universität, Berlin (Germany) holding an Alexander von Humboldt Fellowship.

**Claudia R. Rivarola** holds a Ph.D. in Chemistry (UNRC, 2003). She is a permanent research fellow of CONICET.

**Cesar A. Barbero** holds a Ph.D. in Chemistry (UNRC, 1988). He is Full Professor (UNRC) and Program Leader (CONICET). He is director of the Advanced Materials Group (UNRC).