

Stimuli-Responsive Polymer Hydrogels Containing Partially Exfoliated Graphite

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ABSTRACT: In this work, a new stimuli-responsive composite polymer hydrogel containing partially exfoliated graphite was prepared by frontal polymerization. The materials obtained were characterized by differential scanning calorimetry, RAMAN, scan electron microscopy, transmission electron microscopy, atomic force microscopy, and in terms of swelling behavior. It was found that the maximum temperature reached

by the polymerization front and the lower critical solution temperature are affected by the graphite content. © 2010 Wiley Periodicals, Inc. *J Polym Sci Part A: Polym Chem* 48: 5375–5381, 2010

KEYWORDS: composites; frontal polymerization; hydrogels; radical polymerization; stimuli-sensitive polymers; swelling

INTRODUCTION Hydrogels are a class of cross-linked polymer networks that are swollen in water without dissolving.¹ Owing to their biocompatibility, special surface properties and high water content, hydrogels are the materials of choice in many biomedical applications.² Poly(N-alkylacrylamide) hydrogels have been extensively investigated because of their attractive environmentally sensitive characteristics.³ Among them, in aqueous media poly(N-isopropylacrylamide) (PNIPAAm) macromolecular chains can undergo a reversible coil-to-globule transition at the so-called lower critical solution temperature (LCST).⁴

However, these hydrogels have several drawbacks, example, morphological inhomogeneity, mechanical weakness, limited swelling at equilibrium, and slow response to stimuli.^{5–8}

In this work, composite hydrogels of PNIPAAm and graphite were synthesized, and the influence of this filler on the hydrogel properties was investigated. As will be discussed, graphite has been partially exfoliated giving rise to low amounts of graphene.

On this respect, obtained for the first time in 2004, graphene is the name given to one sheet of graphite.^{9–19} It is entirely made up of sp² carbon atoms bonded in a network of repeating hexagons within a single plane that is just one atom thick.

Graphene sheets are predicted to have a variety of unusual and interesting properties that include high values of Young modulus (≈ 1100 GPa),¹¹ fracture strength (125 GPa),¹¹ thermal conductivity (5×10^3 Wm⁻¹ K⁻¹),¹² mobility of charge carriers (2×10^5 cm² V⁻¹ s⁻¹)¹³ and specific surface area (2630 m² g⁻¹).¹⁴

Frontal polymerization (FP) was the synthetic technique used in this work. FP allows the conversion of monomer into polymer by formation and consequent propagation of a front, a reaction zone at high temperature, which is self-sustaining and that propagates throughout the monomeric mixture. There are many advantages in the use of this technique instead of classical polymerization: (i) shorter reaction time (a typical FP run takes only a few minutes, whereas classical polymerization methods often need hours or days); (ii) low energy consumption (it is a consequence of the fact that the external energy source is applied only in the first instant, whereas in classical polymerization techniques, it is necessary for all the experiment duration); (iii) easy protocols.

Since the first pioneering work performed by Chechilo and Enikolopyan,²⁰ an even increasing number of monomers were polymerized by this method. In detail, epoxy resins,²¹ ionic liquid,²² acrylic monomers,^{23–26} glycidyl ethers,^{27,28} 2-hydroxyethyl acrylate,²⁹ N-methylolacrylamide,³⁰ epoxy

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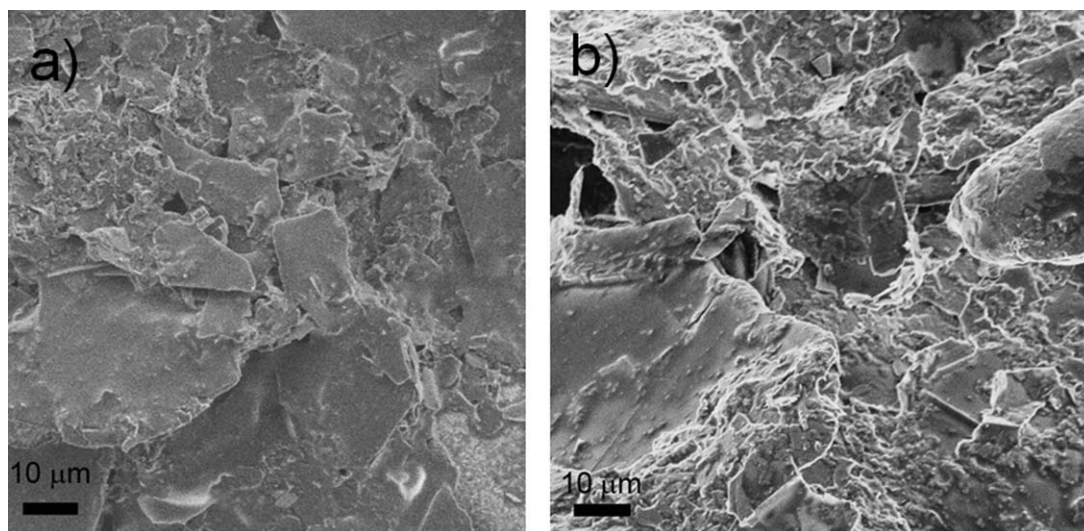


FIGURE 1 FE-SEM images of graphite dispersed in DMSO after solvent removal: (a) 0.2 wt % and (b) 1.0 wt % of graphite in DMSO.

resin/polyurethane networks,³¹ polyurethane-nanosilica hybrid nanocomposites,³² polyvinylpyrrolidone,³³ poly(dicyclopentadiene),³⁴ quantum dot polymer nanocomposites³⁵ were synthesized by different research groups. We obtained polyurethanes,^{36,37} interpenetrating polymer networks,³⁸ unsaturated polyester/styrene resins,³⁹ and poly(diurethane diacrylates).⁴⁰ We also applied FP to the consolidation of porous materials^{41–44}; moreover, we prepared polymer-based nanocomposites with montmorillonite⁴⁵ and polyhedral oligomeric silsesquioxanes,⁴⁶ and synthesized a new class of ionic liquid-based initiators to be used in both classic and frontal radical polymerization.⁴⁷ Recently, we have proposed FP as a new method for developing drug-controlled release systems based on polyacrylamide⁴⁸ and for the preparation of poly(*N,N*-dimethylacrylamide) hydrogels.⁴⁹ In our latest work, a comparison between classical polymerization and FP as techniques to synthesize hydrogel materials was carried out.^{50,51} This technique was already exploited for such a purpose by Fang et al.,⁵² Tu et al.,⁵³ and Washington and Stein-

bock.⁵⁴ Since in these previous works, FP has been found to be a valid alternative technique for polymeric hydrogel synthesis, in this one these materials were obtained via FP only.

RESULTS AND DISCUSSION

As described in the Experimental section, graphite was first sonicated in dimethylsulfoxide (DMSO), before adding monomer, cross-linker, and radical initiator. As a result of this sonication, it was found that graphite underwent partial exfoliation giving rise to graphene sheets. Namely, Figures 1 and 2 show field emission scan electron microscopy (FE-SEM) and atomic force microscopy (AFM) images of graphite dispersed in DMSO after solvent removal. It should be pointed out that Hernandez et al. obtained 0.01 mg/ml graphene in an analogous way from powdered graphite in various solvents.⁵⁵

By operating as described in the Experimental, graphene concentration in DMSO was determined for all graphite-containing samples. It was found that it was almost proportional

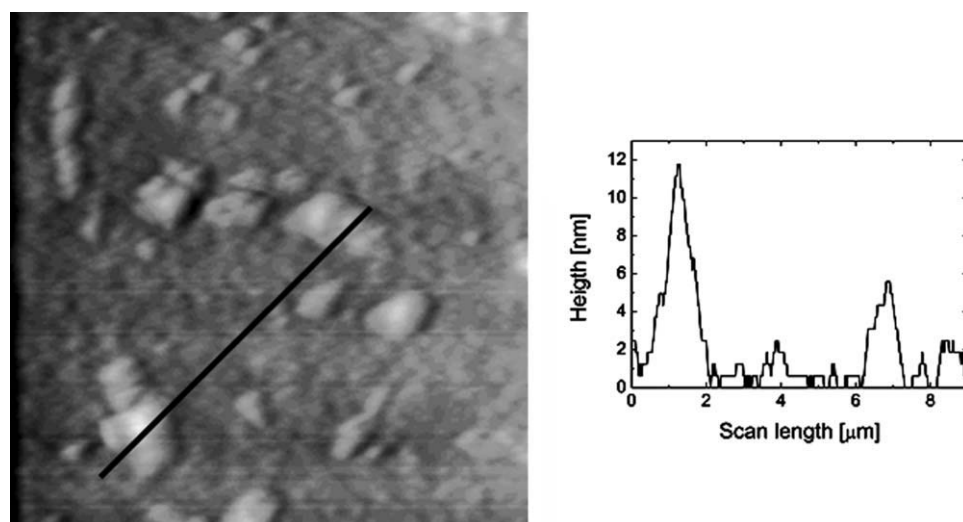


FIGURE 2 2D tapping-mode topography AFM ($10 \times 10 \mu\text{m}$) image and height profile of the graphene flakes obtained from 0.2 wt % dispersion of graphite in DMSO after solvent removal.

TABLE 1 Composition and Some Characteristics of the Synthesized Polymer Samples

Sample	Graphite wt %	LCST (°C)	T_{\max}^a (°C)	V_f^b (cm/min)	T_g (°C)
76.4	0	28	141	1.0	143
76.1	0.01	24	142	1.0	144
76.2	0.05	23	143	1.2	144
76.3	0.07	23	147	1.0	144
70.1	0.1	26	168	0.9	140
70.3	0.2	26	170	1.0	139
70.5	0.5	27	174	–	138
70.7	0.7	26	173	–	138
70.9	1	25	175	–	140

Sample composition: NIPAAm; DMSO = 50 wt % respect to the amount of NIPAAm; TGDMA = 2.5 mol % respect to the molar concentration of NIPAAm; APS = 0.5 mol % respect to the molar concentration of NIPAAm.

^a Maximum temperature reached by the front.

^b Front velocity.

to the initial amount of graphite; namely, the weight ratio graphene:graphite \approx 1:35 (\pm 10%). In particular, graphene concentration in DMSO ranged from 0.005 to 6 μ g/ml, this latter being a value that is in agreement with those reported by Hernandez et al.⁵⁵

Various PNIPAAm samples were synthesized by varying the amount of graphite from 0.01 to 1 wt %, respect to the weight of NIPAAm (Table 1).

Figure 3 shows the maximum temperature reached by the front (T_{\max}) as a function of graphite concentration in the reaction mixture.

As can be seen, T_{\max} values increase as the graphite concentration increases, ranging from 140 °C for the sample without graphite to 175 °C for that containing 1 wt % of it. Moreover, when its content was raised from 0.07 to 0.1 wt %, a sudden increment of T_{\max} was found, with values going from 147 to 168 °C.

As far as the assessment of front velocity (V_f) is concerned, it is worth pointing out that, because of the difficulty to see the position of the front in the graphite-containing polymers, which were too dark for such a purpose, front velocity values were measured only for those samples containing <0.5% graphite (Table 1). For these ones, V_f was always between 0.9 and 1.2 cm/min.

To investigate hydrogel thermal properties, differential scanning calorimetry (DSC) analysis was carried out on dried samples. In detail, a heat/cool/heat cycle was performed from 0 to 250 °C and vice versa: the first heating ramp was carried out to eliminate the thermal history of materials and any possible residual solvent; the second was done to evaluate T_g .

All first heating ramps did not show any residual polymerization heat, thus indicating that conversion was quantitative for all materials independently of the composition used for the preparation.

The second heating ramps show that T_g values remain constant at about 140 °C, independently of the amount of graphite (see Table 1). Recently, similar results were reported by Dubois and coworkers who showed that the glass transition temperatures of composites based on polylactide do not change by varying the concentration of expanded graphite in the polymer matrix.⁵⁶

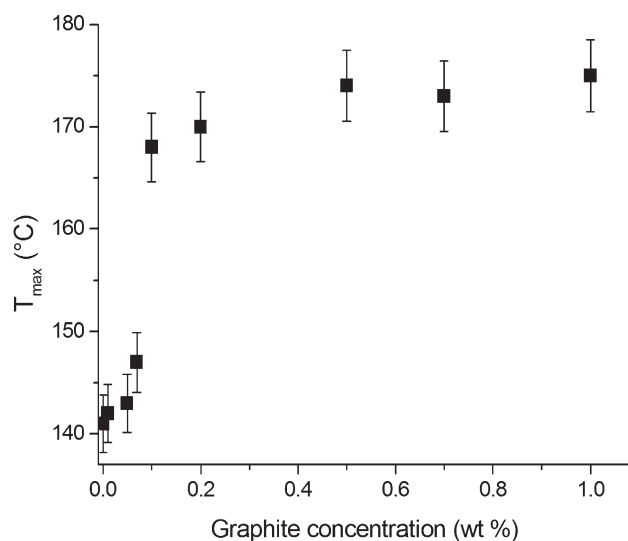
SEM analysis was performed to investigate the morphological structure of hydrogels. As an example, Figure 4 shows SEM micrographs of sample 70.1, which contains 0.1 wt % of graphite. As a comparison, the micrograph of the neat hydrogel is given in Figure 5 (sample 76.4).

As can be seen, the above samples turned out to be characterized by a similar sponge-like structure, with pore diameters between 1 and 8 μ m.

As far as graphite dispersion is concerned, on the surface of sample 70.1 thin graphite aggregates, possibly constituted by few layer graphene, are visible. In all samples, the hydrogel porous structure was found to be not influenced by the graphite content in the dispersion.

To better assess the graphite dispersion in the polymer matrix, transmission electron microscope (TEM) measurements have been carried out. Figure 6 shows two types of objects, typically observed in sample 70.1. Indeed, while a thick aggregate, which consists of several layers is reported in Figure 6a, the micrograph shown in Figure 6b demonstrates that together with the above described aggregates, also few-layer graphite is present in the polymer matrix. In particular, by analyzing the flake edges, this object turns out to be formed by only three-four layers. Similar results were found for all samples.

All samples were further characterized by Raman spectroscopy. A typical spectrum was found to display two main peaks that are characteristic of multilayer graphene: the G band at \sim 1590 cm^{-1} , and the 2D peak at \sim 2700 cm^{-1} , respectively (Figure 7). In particular, the asymmetric shape of 2D peak indicates that graphite and/or multilayer graphene sheets have been obtained.^{57–61}

**FIGURE 3** T_{\max} as a function of graphite concentration.

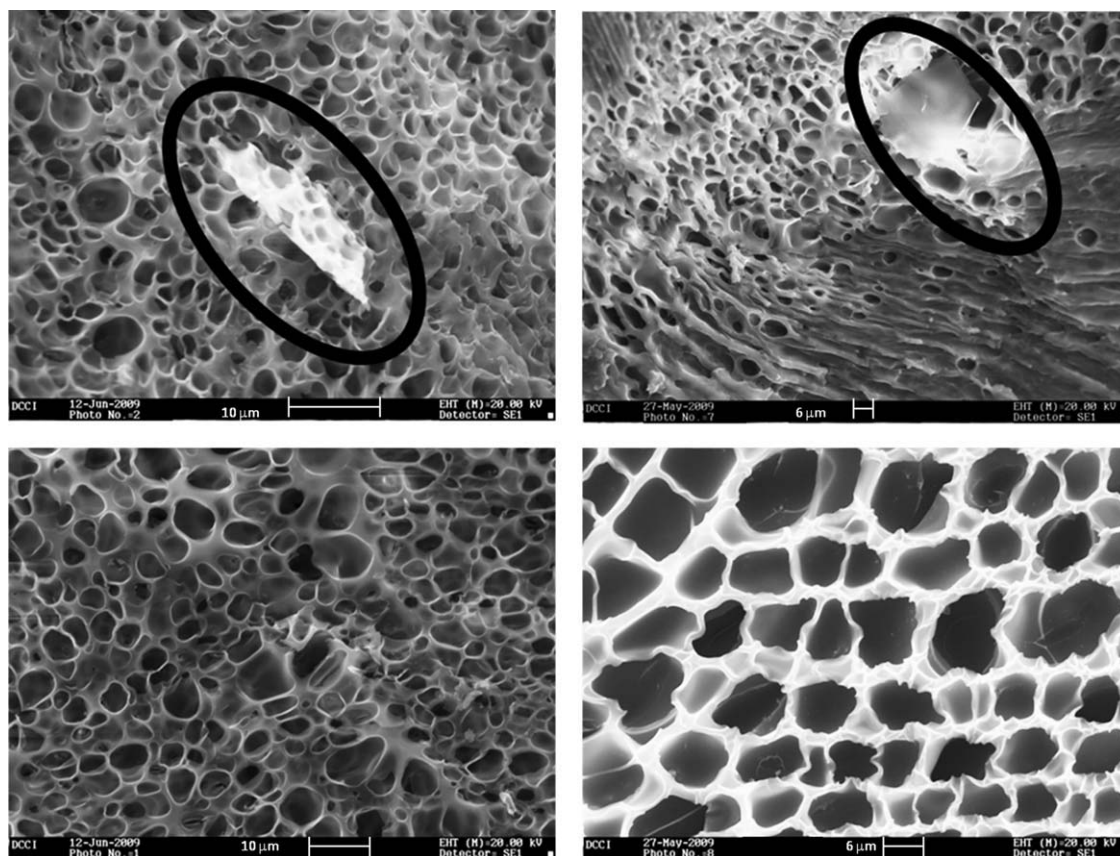


FIGURE 4 SEM micrographs of sample 70.1 (containing 0.1 wt % of graphite).

Swelling Properties

SR% vs. temperature for hydrogels containing different amounts of graphite is reported in Figure 8. The most significant differences of SR% (from 900 to 750%) are only present at the lowest temperature (7 °C). For all other temperatures, the SR% curves are almost superimposed, thus indicating that the degree of swelling is not affected by graphite content. Moreover, it is worth underlining that

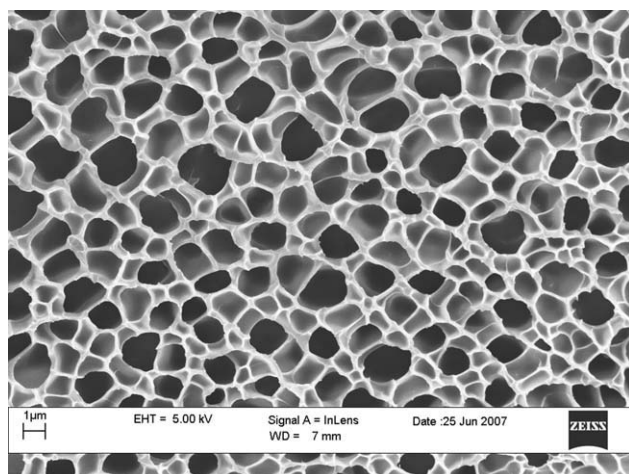


FIGURE 5 SEM micrograph of sample 76.4, which does not contain graphite.

graphite does not influence the stimuli response, which remains as sharp as that of the homopolymer.

Figure 9 shows the trend of LCST by varying the amount of graphite. Indeed, graphite-containing samples exhibit an LCST that is lower than that of the corresponding graphite-free one. Moreover, samples containing an amount of graphite lower than 0.1 wt % show the lowest LCST (at 23–24 °C), thus demonstrating that the above parameter is influenced by graphite concentration, which may affect the thermodynamic interactions among polymer, solvent, and graphite itself.

EXPERIMENTAL

Materials

N-isopropylacrylamide (NIPAAm, FW = 113.16, mp = 60–63 °C), triethylenglycoldimethacrylate (TGDMA, FW = 286.32), and DMSO (FW = 78.13, bp = 189 °C, $d = 1.101$ g/ml) were purchased by Sigma-Aldrich and used as received. Aliquat Persulphate (APS) was synthesized by us according to the method reported in the literature.⁶² Graphite was purchased by Sigma-Aldrich.

Synthesis of Poly(NIPAAm) Hydrogels

Preparation of the monomeric mixture: the desired amount of graphite (from 0.01 to 1 wt % respect to the weight of NIPAAm) was dispersed in DMSO (50 wt % of DMSO respect to the amount of NIPAAm) in an ultrasonic bath at room

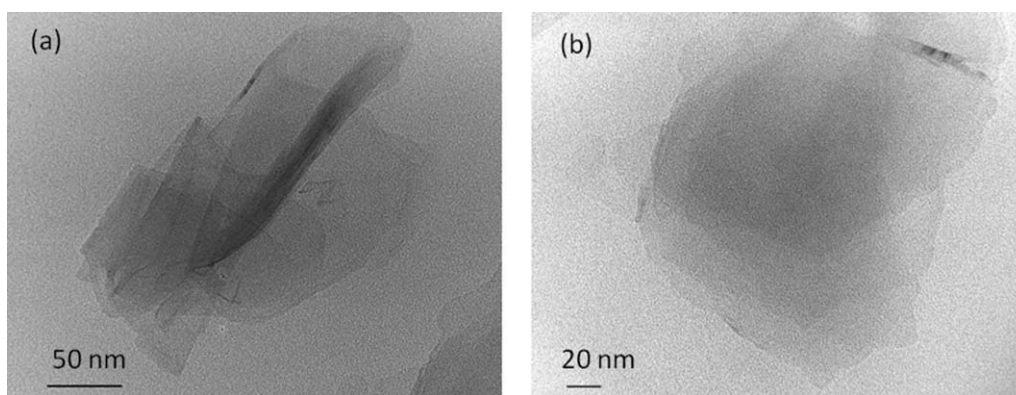


FIGURE 6 TEM micrographs of sample 70.1 (containing 0.1 wt % of graphite). Two objects, formed by few-layer graphite (graphene) are shown.

temperature for 1 h. After, the desired amount of NIPAAm was added to the dispersion of graphite in DMSO and it was sonicated again for 15 min. Then, 2.5 mol % of TGDMA (respect to the molar concentration of NIPAAm) was added, and the mixture was sonicated once more for a few minutes. Finally, 0.5 mol % of APS (respect to the molar concentration of NIPAAm) was added (Table 1).

A common test tube (inner diameter = 1.5 cm, length = 16 cm) was filled with a reagent mixture having the above composition. A K-type thermocouple was located at about 1 cm from the bottom of the tube and connected to a digital temperature recorder (Delta Ohm 9416, ± 1.0 °C), to record T_{\max} ($\pm 2\%$). FP started by heating the external wall of the tube in correspondence of the upper surface of the monomeric mixture. The position of the front (easily visible through the glass wall of test tubes) against time was also measured (± 0.5 mm). For all samples, T_{\max} and V_f were measured.

After, the polymerized samples were washed with water. Eventually, they were allowed to equilibrate in water for swelling studies.

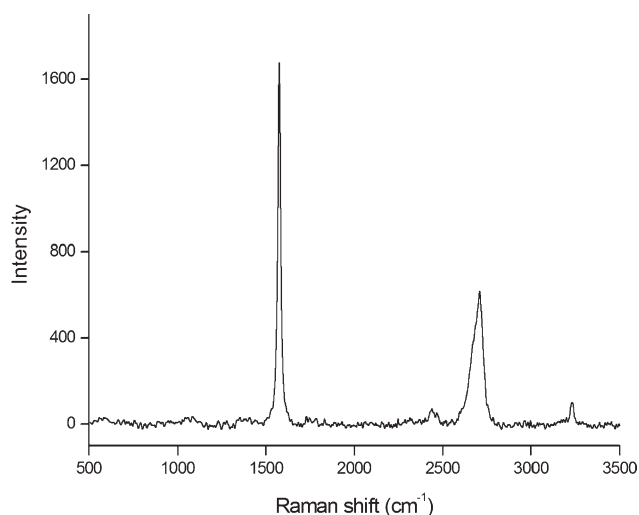


FIGURE 7 Raman spectrum of sample 70.7, containing 0.7 wt % graphite.

Characterization

Graphene concentration in DMSO was determined for all graphite-containing samples by UV analysis, using a Hitachi U-2010 spectrometer (1-mm cuvette) following the method described in the literature.⁶³ Namely, a calibration line for graphene concentration ranging from 0 to 0.15 mg/mL was used, at a wavelength of 660 nm. The calculated absorption coefficient was 1602 mL/(mg m).

Thermal characterization of all samples was performed by DSC analysis by using a Q100 Waters TA Instruments calorimeter, with a TA Universal Analysis 2000 software. Two heating ramps, from 0 to 250 °C, with a heating rate of 10 °C/min, were carried out on dry samples: the first scan was performed to determine possible residual polymerization heat and remove any solvent trace; the second was done to determine glass transition temperatures (T_g).

After freeze-drying, hydrogel morphology was studied by a Leo Stereoscan-440 SEM. Before examination, all samples were fractured in liquid nitrogen, and the fractured surface was coated with gold.

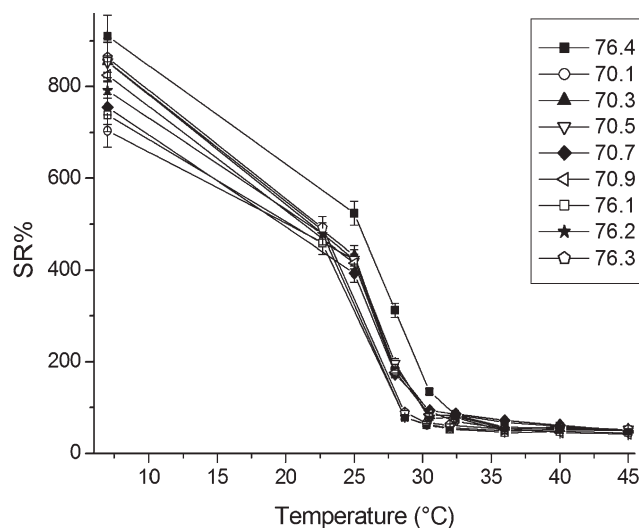


FIGURE 8 SR% as a function of temperature.

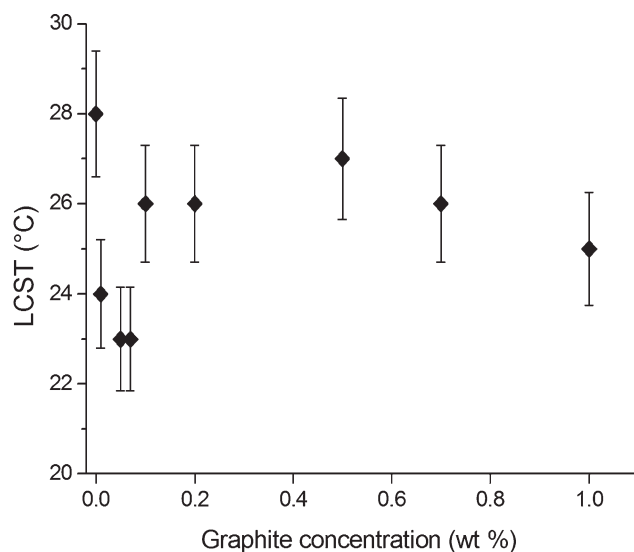


FIGURE 9 LCST as a function of graphite concentration.

The freeze-dried samples were characterized also by TEM analysis. These measurements were performed using a high-resolution transmission electron microscope (JEOL 2010). Ultrathin sections of about 100 nm were cut by a Power TOMO X microtome equipped with a diamond knife and placed on a 200-mesh copper grid.

The morphological features of graphene flakes were investigated using AFM in tapping-mode configuration (AFM, Nanosurf easyScan DFM).

To determine the swelling ratio (SR%) and the critical solution temperature of hydrogels, all samples were immersed in water and heated from 20 to 40 °C, by increasing temperature at a rate of 1 °C/12 h.

SR% was calculated by using the following equation:

$$\text{SR}\% = \frac{M_s - M_d}{M_d} \cdot 100$$

where M_s and M_d are the hydrogel masses in the swollen and in the dry state, respectively.

LCST was determined as the inflection of the curves obtained by interpolating SR% experimental data, which were elaborated by using ORIGIN 6.0 and/or Microsoft Excel software.

Raman analysis was performed by a Bruker Senterra Raman microscope, using an excitation wavelength of 532 nm at 5 mW. The spectra were acquired by averaging five acquisitions of 5 seconds with a 50× objective.

CONCLUSION

Stimuli-responsive polymer hydrogels containing partially exfoliated graphite and little amounts of graphene have been successfully prepared by applying a very easy procedure, namely by sonicating graphite in the presence of the monomer and DMSO, and frontally polymerizing the resulting mix-

ture. It was found that T_{max} and LCST are affected by the graphite content. Namely, the maximum temperature reached by the front increases as the amount of graphite increases. Moreover, a sharp increment of T_{max} was observed when the content of graphite exceeded 0.07 wt %. All graphite-containing samples exhibit an LCST that is lower than that of the neat PNIPAAm hydrogel (28 °C). In detail, a minimum value of 23 °C was found for the samples containing 0.05 and 0.07 wt % graphite. For larger contents of this filler, LCST increases again to 25–27 °C.

It should be also pointed out that T_g , degree of swelling and hydrogel morphology are not influenced by the presence of graphite.

Further studies on nanocomposite polymer hydrogels containing high graphene concentration are in progress and will be reported in a next article.⁶⁴

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