

Graphene-containing thermoresponsive nanocomposite hydrogels of poly(*N*-isopropylacrylamide) prepared by frontal polymerization

Valeria Alzari,^a Daniele Nuvoli,^a Sergio Scognamillo,^a Massimo Piccinini,^b Emilia Gioffredi,^c Giulio Malucelli,^c Salvatore Marceddu,^d Mario Sechi,^e Vanna Sanna^b and Alberto Mariani^{*a}

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Frontal polymerization has been successfully used to synthesize poly(*N*-isopropylacrylamide) nanocomposite hydrogels containing graphene. The latter was directly achieved by ultrasound treatment of a dispersion of graphite in *N*-methylpyrrolidone. The dispersion, having the concentration of 2.21 g L⁻¹, was characterized by TEM analysis and mixed with suitable amounts of *N*-isopropylacrylamide for the synthesis of graphene-containing nanocomposite polymer hydrogels. The nanocomposite hydrogels were analyzed by SEM and Raman spectroscopy, and their swelling and rheological properties were investigated. It was found that graphene strongly influences the swelling ratio, dramatically increasing it, even if present in small amounts. Finally, the rheological properties of the hydrogels were correlated with the graphene content: *G'* modulus and complex viscosity were found to increase with increasing nanofiller concentration, thus indicating the occurrence of good interactions between the two phases. Nevertheless, at a high concentration (*i.e.*, 0.13 wt.%), graphene showed a lubrication effect, lowering the rheological parameters and approaching the same pseudoplastic behaviour of the unfilled material.

Introduction

Hydrogels are three-dimensional polymer networks made up of highly hydrophilic crosslinked macromolecular chains that are able to swell and retain a significant portion of water when placed in an aqueous medium.¹ Hydrogels can be classified into different groups based on their physical structure (amorphous, semicrystalline, hydrogen-bonded or supramolecular), electric charge (ionic or neutral), crosslink type (physical or chemical), possible response to external stimuli, and origin (synthetic or natural).

Research on hydrogels started as early as in 60s with a novel paper on poly(2-hydroxyethyl methacrylate) by Wichterle and Lim.² In 1968, it was successfully predicted that the net repulsion between a polymer network and a poor solvent can cause a phase

transition and a change in the swelling degree (and thus in the hydrogel volume).³ Lately, phase transitions induced by changes in the environment were also reported by other groups.^{4,5}

Poly(*N*-alkylacrylamide) hydrogels have been extensively investigated because of their attractive environmentally sensitive characteristics.⁶ 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).⁷ This finding paved the way to a number of studies on PNIPAAm and its copolymers devoted to find potential applications in various biomedical fields, including embolic agents⁸ and drug delivery.⁹ However, its poor mechanical properties strongly limit the use of pure PNIPAAm in structural applications. Generally, PNIPAAm-based hydrogels exhibit low compressive modulus^{10–13} and weak elastic recovery after loading.

Recently, to overcome these limitations, nanocomposite hydrogels have been synthesized: they show large swelling ratios and rapid deswelling responses to temperature changes, together with high transparency (structural homogeneity), excellent mechanical properties, with astonishingly large elongations.¹⁴

Nowadays, graphene is the nanometric material that attracts most of the interest of both border research and media. That is particularly true after that Andre Geim and Konstantin Novoselov were awarded the 2010 Nobel Prize in Physics “for groundbreaking experiments regarding the two-dimensional material graphene”.¹⁵

^aDipartimento di Chimica, Università di Sassari, and local INSTM unit, Via Vienna 2, 07100 Sassari, Italy. E-mail: mariani@uniss.it; Fax: +39 079 212069; Tel: +39 079 229556

^bPorto Conte Ricerche S.r.l., SP 55 km 8.400 Loc. Tramariglio, 07041 Alghero (SS), Italy

^cDipartimento di Scienza dei Materiali ed Ingegneria Chimica, Politecnico di Torino, sede di Alessandria, and local INSTM unit, Via T. Michel 5, 15121 Alessandria, Italy

^dIstituto di Scienze delle Produzioni Alimentari—Consiglio Nazionale delle Ricerche (ISPA-CNR), Li Punti—Reg. Balduca, Traversa La Crucca, Sassari, 07100, Italy

^eDipartimento di Scienze del Farmaco, Università di Sassari, Via Muroni 23/A, 07100 Sassari, Italy

A graphene crystal is a two-dimensional layer consisting of sp^2 hybridized carbon atoms, which are densely packed in a honeycomb crystal lattice. Actually, a graphene sheet is any single layer that, by π -stacking, constitutes graphite, which, in most cases, is the material from which graphene is prepared.

Graphene is predicted to have remarkable features, such as high thermal conductivity, superior mechanical and excellent electronic transport properties.^{16–20} These have generated enormous interest for its possible implementation in a myriad of apparatuses²¹ including future generations of high speed and radio frequency logic devices, thermally and electrically conducting reinforced nanocomposites, ultra-thin carbon films, electronic circuits, sensors, and transparent and flexible electrodes for displays and solar cells.^{22–27}

Graphene has been produced by several routes, including mechanical exfoliation,¹⁵ growth by chemical vapor deposition (of both discrete monolayers onto a substrate and agglomerated powders),^{28–31} epitaxial growth on crystalline silicon carbide,^{32–35} arc discharge,^{36,37} chemical conversion,^{38,39} reduction of CO,⁴⁰ unzipping of carbon nanotubes,^{41–43} and self-assembly of surfactants.⁴⁴ While these approaches can yield a largely defect-free material with exceptional physical properties, current techniques of making powdered samples of graphene do not yield quantities that are large enough for its use as a composite filler.⁴⁵ The obtainment of graphene from colloidal suspensions is advantageous in terms of simplicity and high volume production, and could be used for a wide range of applications; in particular, two ways for obtaining graphene by this method can be exploited: chemical modification of graphite (*i.e.* obtainment of graphite oxide and its reduction after exfoliation)⁴⁶ and direct exfoliation without chemical modification in suitable organic solvents⁴⁷ or surfactants.⁴⁸ To this aim, our research group has recently succeeded in achieving the highest graphene concentration (up to 5.33 mg mL⁻¹) reported so far in any medium by simple direct graphite exfoliation in an ionic liquid.⁴⁹

The superior properties of graphene are also reflected in polymer/graphene nanocomposites, which show improved mechanical, thermal, barrier, electrical and flame retardant properties compared to neat polymers.^{50–52}

Starting from the above considerations, we devoted this work to the synthesis of nanocomposite polymer hydrogels containing graphene by exploiting the peculiar features of the frontal polymerization (FP) technique. Extensively studied by our research group, FP allows obtaining the conversion of monomer into polymer with many advantages if compared with the classical polymerization methods: (i) shorter reaction time (a typical FP run takes only a few minutes, whereas classical polymerizations 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; (iv) materials having better properties in comparison with those obtained with classical polymerization.

After some fundamental works^{53,54} a large number of systems have been investigated by this technique, namely: epoxy resins,^{55–57} ionic liquids,⁵⁸ acrylic monomers,^{59,60} glycidyl ethers,⁶¹ 2-hydroxyethyl acrylate,⁶² *N*-methylolacrylamide,⁶³ epoxy resin/polyurethane networks,⁶⁴ polyurethane–nanosilica hybrid nanocomposites,⁶⁵ polyvinylpyrrolidone,⁶⁶ poly-

(dicyclopentadiene),⁶⁷ and quantum dot polymer nanocomposites.⁶⁸ We obtained polyurethanes,^{69,70} interpenetrating polymer networks,⁷¹ unsaturated polyester/styrene resins,⁷² and poly(diurethane diacrylates).⁷³ We also applied FP for consolidating porous materials;^{74–77} furthermore, we prepared polymer-based nanocomposites with montmorillonite⁷⁸ and polyhedral oligomeric silsesquioxanes,⁷⁹ and synthesized a new class of ionic liquid-based initiators to be used in both classical and frontal radical polymerizations.⁸⁰ Recently, we have proposed FP as a new method for developing drug-controlled release systems based on polyacrylamide⁸¹ and for the preparation of poly(*N,N*-dimethylacrylamide) hydrogels.⁸² A comparison between classical polymerization and FP for obtaining hydrogel materials was also carried out.^{83,84} Lately, stimuli-responsive hydrogels containing partially exfoliated graphite and thermoresponsive super water absorbent hydrogels of *N*-isopropyl acrylamide and 3-sulfopropyl acrylate potassium salt were synthesized.^{85,86} This technique was already exploited for such a purpose by Fang *et al.*,⁸⁷ Tu *et al.*,⁸⁸ and Washington and Steinbock.⁸⁹

In this work we first investigated the preparation of graphene-containing PNIPAAm hydrogels prepared by FP. The morphologies of the obtained materials were observed through SEM and Raman spectroscopy. In addition, their swelling features and rheological behaviour were investigated and correlated to the nanofiller content.

Experimental methods

Materials

N-Isopropylacrylamide (NIPAAm, $F_w = 113.16$, mp = 60–63 °C), triethylene glycol dimethacrylate (TGDMA, $F_w = 286.32$), *N*-methylpyrrolidone (NMP, $F_w = 99.13$, bp = 202–204 °C, $d = 1.028$ g mL⁻¹) and graphite were purchased by Sigma-Aldrich and used as received. Aliquat Persulfate (APS) was synthesized by us according to the method reported in the literature.⁹⁰

Graphene stock dispersion in NMP

5.0 g of graphite dispersed in 100 g of NMP were introduced in a 250 mL flask; the mixture was sonicated in an ultrasonic bath at room temperature for 24 h. Then, the dispersion was centrifuged for 30 min at 4000 rpm, and the residual solid graphite was removed. The concentration, calculated by gravimetry after filtration through polyvinylidene fluoride filters (pore size 0.22 μ m), was found to be equal to 2.21 g L⁻¹.

Synthesis of poly(NIPAAm) hydrogels

In order to prepare hydrogels containing various amounts of graphene, the above stock dispersion was properly diluted with suitable amounts of NMP and the resulting actual graphene concentrations were determined by UV-VIS spectroscopy. The desired quantities of NIPAAm were added to the obtained graphene dispersion and the new resulting mixture was sonicated for 15 min. Then, the crosslinker TGDMA (2.5 mol% with respect to the molar concentration of NIPAAm) and the initiator APS (0.5 mol% with respect to the molar concentration of NIPAAm) were added. The investigated formulations are collected in Table 1.

Table 1 Samples synthesized in the present work with the indication of graphene concentration in both NMP (after dilution of the stock dispersion) and NIPAAm (before polymerization), and their front temperature and velocity

Sample	Graphene concentration in NMP/g L ⁻¹	Graphene concentration in NIPAAm (wt%)	$T_{\max}/^{\circ}\text{C}$	$V_f/\text{cm min}^{-1}$
3.1	0	0	157	0.85
4.2	0.017	0.0010	161	0.85
4.1	0.041	0.0020	158	0.80
17.5	0.055	0.0030	157	0.75
4.3	0.075	0.0050	158	0.80
17.4	0.11	0.0070	154	0.75
17.3	0.22	0.010	154	0.75
4.5	0.28	0.020	162	0.85
17.2	1.10	0.070	154	—
17.1	2.21	0.13	157	—

Classical polymerization. A common test tube (inner diameter = 1.5 cm, length = 16 cm) was filled with the reacting mixture (Table 1). The polymerization was performed by keeping the tube immersed in an oil bath at 80 °C for 1 hour.

Frontal polymerization. A common test tube (inner diameter = 1.5 cm, length = 16 cm) was filled with the same reacting mixtures as above (Table 1). 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 the front temperature, T_{\max} . 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 monitored in order to determine the front velocity, V_f . The T_{\max} and V_f reproducibility was always within $\pm 2\%$ and ± 0.5 mm, respectively.

Then, the polymerized samples were washed with water. The NMP/water mixtures resulting from this washing were filtered through polyvinylidene fluoride filters (pore size 0.22 μm) and weighed in order to check whether some of the previously dispersed graphene was extracted from the obtained polymer hydrogels. In all cases, no solid residue was found thus confirming that the actual graphene concentration in the polymer samples is that resulting from the initial dispersion in NMP and the following addition of reactants. Eventually, the polymer hydrogels were allowed to equilibrate in water for swelling studies.

Characterization

The graphene stock dispersion in NMP was analyzed by UV-VIS spectroscopy, using a Hitachi U-2010 spectrometer (1 mm cuvette) following the method described in the literature.⁴⁸ Namely, a calibration line for graphene concentration was used, at a wavelength of 660 nm. The calculated absorption coefficient was 1602 mL mg⁻¹ m⁻¹. This was used for determining the actual graphene concentrations in any diluted dispersion derived from the stock one.

After freeze-drying, the hydrogel morphology was studied by a ZEISS DSM 962 CSEM scanning electron microscope. Prior to examination, all the samples were fractured in liquid nitrogen and the fractured surface was coated with gold. The samples were

also characterized by using an Environmental SEM ZEISS EVO LS10 instrument.

TEM images were taken with a ZEISS EM 109 transmission electron microscope, operated at 80 kV. Samples for TEM analysis were prepared by drop-casting a few millilitres of dispersion onto copper grids coated with a pure film of Formvar/carbon (300 mesh).

Raman analysis was performed with 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 \times objective.

To determine the swelling ratio (SR%) and the critical solution temperature of hydrogels, all samples were immersed and equilibrated in water, and heated from 5 to 41 °C (heating rate: 1 °C/12 h). SR% was calculated by using the following equation:

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

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 software.

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.

Rheological measurements were carried out on a strain-controlled rheometer (ARES, TA Instruments Inc., Waters LLC) with a torque transducer range of 0.2–2000 gf cm, using 25 mm parallel plates geometry. The rheometer was equipped with a convection oven in compressed air for temperature control. In order to determine the linear viscoelastic range, strain sweep tests were used within 0.02–1% strain at 25 °C and 1 rad s⁻¹. Thus, frequency sweep tests were carried out in the linear viscoelastic region for all the samples, at 25 °C, 0.1–100 rad s⁻¹, 0.05% strain. In order to assure reproducibility, at least 4 measurements were performed on each sample.

Results and discussion

Before performing all polymerization runs, the graphene formation was confirmed by electron microscopy. Namely, Fig. 1 shows some graphene sheets in the NMP dispersion as evidenced by TEM analysis. Graphene formation is also confirmed by Raman spectroscopy, which is the most commonly used

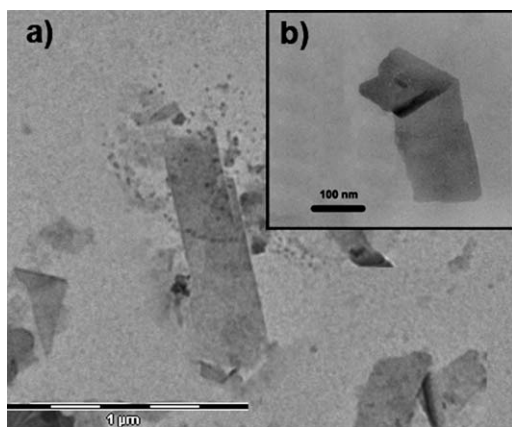


Fig. 1 TEM images showing some graphene sheets found in the stock NMP dispersion (concentration 2.21 g L^{-1}).

analytical technique for assessing the presence of graphene and it allows the identification of single layer, bilayer, and few layer graphene flakes.⁹¹

Fig. 2 shows the spectra of graphite (bottom) and graphene (top) obtained after filtration of its dispersion in NMP. The presence of graphene is clearly visible by comparing the 2D band: in graphite it consists of two components and is upshifted to 2716 cm^{-1} . Moreover, the disorder-related D band at 1350 cm^{-1} is higher in graphene. It should be highlighted that the highest graphene concentration in NMP used in this work was equal to 2.21 g L^{-1} , which is also the highest reported so far in this solvent,⁹² and is the second reported so far after that obtained in an ionic liquid.⁴⁹ Actually, if compared with the method reported by Khan *et al.*,⁹² there are some differences. In particular, while these authors used a starting graphite concentration of 3.3 g L^{-1} , we used the much larger value of 51 g L^{-1} .

A preliminary study was carried out in order to establish whether FP and classical polymerization give rise to actual graphene-based nanocomposites, thus avoiding the possible re-stacking of the sheets to graphite. As can be clearly seen in Fig. 3a, the sample obtained through the classical method is inhomogeneous and shows aggregates visible even to the naked eye; this is a clear evidence that graphene is not stable in the new

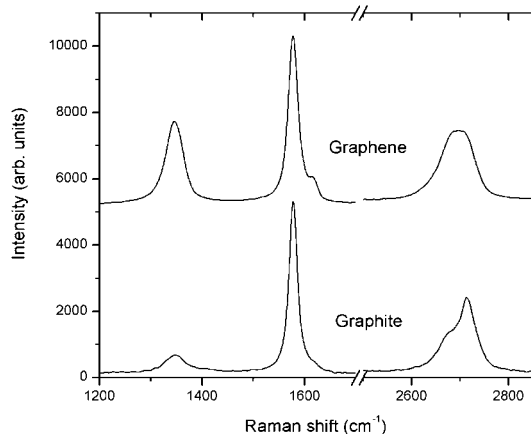


Fig. 2 Raman spectra of graphene obtained after filtration of NMP dispersion (top) and pristine graphite (bottom).

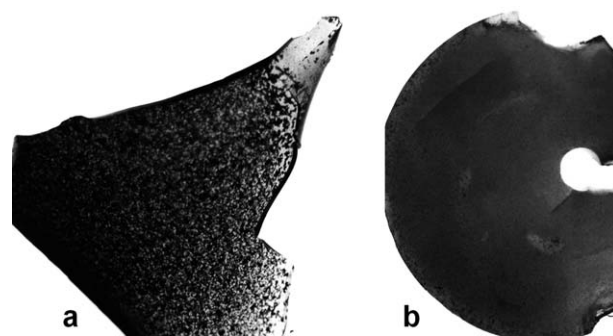


Fig. 3 Photographs of two polymer hydrogels obtained by the same dispersion of graphene in NIPAAm (0.13 wt%): (a) classically polymerized sample (graphene reaggregated); (b) FP sample (graphene is still homogeneously dispersed; little black spots are small bubbles).

polymerizing medium, giving rise to non-nanometric graphite flakes. At variance, the sample prepared by FP is highly homogeneous (Fig. 3b). This result, which is analogous to that previously reported by Pojman *et al.* by dispersing a salt into a monomer,⁹³ is due to the fast conversion reaction of monomer into polymer that characterizes the FP technique, which limits or avoids the occurrence of phase separation that is thermodynamically favoured when a solute is stable in the monomer but is not in the corresponding polymer.

For this reason, the pursuing of the work was focused only on the investigation of the FP samples.

As can be seen in Table 1, T_{max} and V_f values remain almost constant as the graphene concentration increases, namely at about $158 \pm 4 \text{ }^\circ\text{C}$ and $0.80 \pm 0.05 \text{ cm min}^{-1}$ respectively.

Fig. 4 shows the Raman spectra of the neat PNIPAAm (sample 3.1, solid line) and of the PNIPAAm nanocomposite containing 0.13 wt% of graphene (sample 17.1, dash-dotted line) in the $1000\text{--}1800 \text{ cm}^{-1}$ and $2500\text{--}2800 \text{ cm}^{-1}$ spectral ranges; spectra are normalized on the PNIPAAm band peaked at 1455 cm^{-1} . As can be clearly seen, the characteristic peaks of graphene are present:^{91,94,95} the G band at $\sim 1579 \text{ cm}^{-1}$, the 2D band at $\sim 2716 \text{ cm}^{-1}$, and the disorder-related D peak at $\sim 1350 \text{ cm}^{-1}$. The G peak evidences a shoulder at about

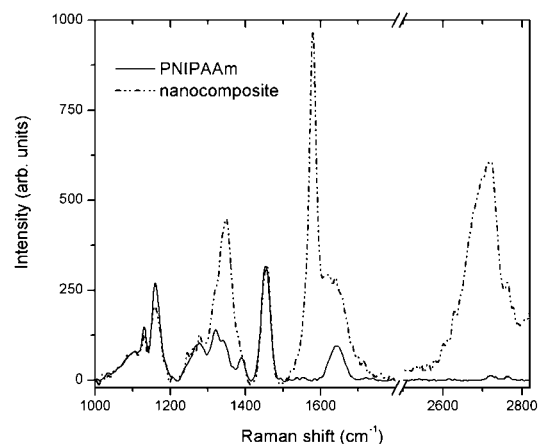


Fig. 4 Raman spectra of neat PNIPAAm used as a blank (sample 3.1, solid line) and PNIPAAm nanocomposite containing 0.13 wt% of graphene (sample 17.1, dash-dotted line).

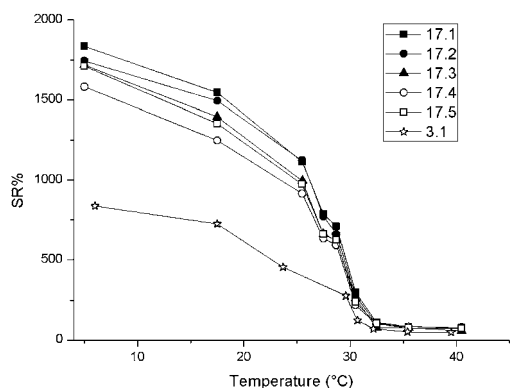


Fig. 5 SR% as a function of temperature for some selected samples (see Table 1 for compositions).

1630 cm^{-1} , which is mainly due to water bending mode. The shape of the 2D band is characteristic of less-than-five-layer graphene.⁹¹

SR% vs. temperature for hydrogels containing different amounts of graphene is reported in Fig. 5. To make the graph more readable, only the curves of some selected samples covering the entire range of graphene concentrations (from 0 to 0.13 wt%) are reported.

The SR% at the lowest temperatures (5–6 °C) clearly shows the influence of the graphene amount on the swelling properties; in particular, SR% increases as graphene concentration increases, from 837% for the neat polymer to 1260% for the nanocomposite hydrogel containing the highest concentration of graphene (0.13 wt%). However, a sharp difference between the neat sample and all the nanocomposites is clearly evident also for the minimum graphene concentration. This difference disappears as the temperature rises beyond LCST (located at *ca.* 27–28 °C), after which all trends superimpose as a result of deswelling. It is worthy to note that graphene does not influence the LCST of hydrogels but only their swelling capacity, increasing it.

A morphological characterization on hydrogels was done through environmental SEM (E-SEM). The image displayed in Fig. 6 evidences the presence of small particles of graphene (<1 μm) uniformly dispersed in the polymer matrix of the sample 4.5, containing 0.02 wt% of graphene.

Since the typical hydrogel porous morphology is not visible because of the vacuum conditions under which the experiment was performed, high vacuum SEM analyses on freeze-dried samples were also carried out.

Fig. 7 shows that the above sample 4.5 is characterized by a sponge-like architecture, with pore diameters at a micrometric level. At variance to the aforementioned E-SEM analysis, by this technique graphene is not visible because of the homogenization due to the metallization that precedes sample characterization.

It is noteworthy that the hydrogel porous structure was not found to be influenced by the graphene content in the dispersion.

Fig. 8 plots the storage modulus G' as a function of frequency for some of the hydrogels investigated. First of all, it is worthy to mention that the unfilled sample (3.1) shows a typical elastic response, due to the presence of a plateau, typically found in cross-linked materials.⁹⁶ When graphene is added to the hydrogel, such plateau tends to disappear, thus indicating that the material behaviour is closer to that of a thermoplastic polymer,

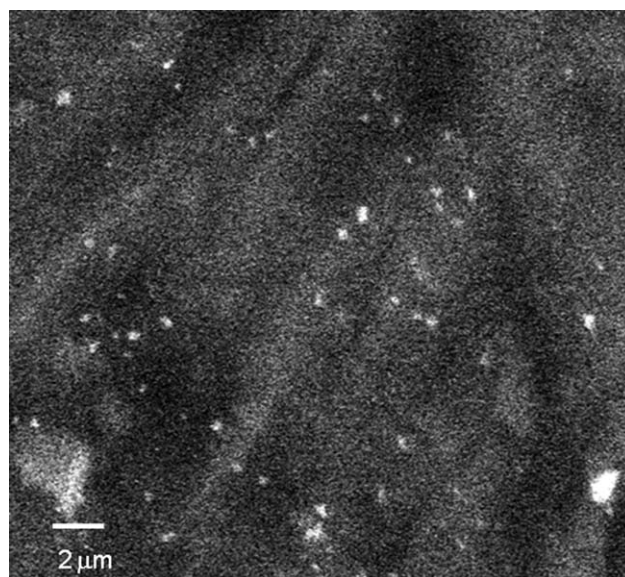


Fig. 6 E-SEM micrograph of the sample 4.5 (0.02 wt% of graphene).

rather than to a thermoset one. In addition, by taking into account the sample with the highest filler content (sample 17.1, graphene concentration 0.13 wt%), the viscoelastic behaviour changes again, approaching that of the unfilled hydrogel.

By comparing the samples with different filler contents, it can be observed that G' increases up to a maximum value (see sample 17.3, graphene concentration 0.01 wt%) and then abruptly slows down: this behaviour is a first clear indication of a lubrication effect exerted by graphene sheets.

The complex viscosity curves are plotted in Fig. 9. They further confirm the results already discussed for G' and in particular the lubrication effect of graphene when present at high concentration: indeed, the complex viscosity tends to increase for samples 17.5 and 17.3 with respect to the unfilled counterpart,

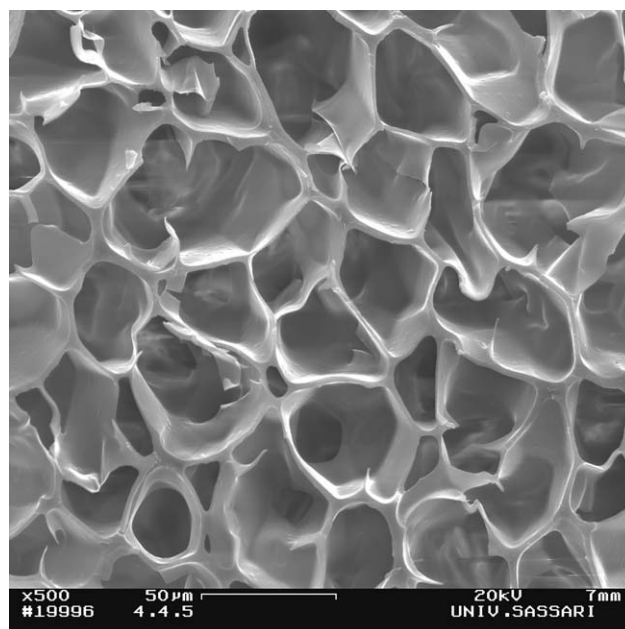


Fig. 7 SEM images of the sample 4.5 (0.02 wt% of graphene).

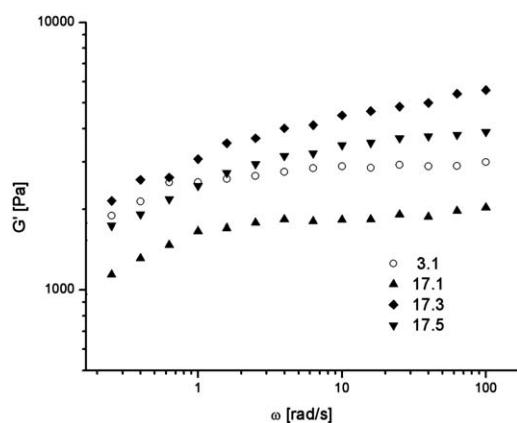


Fig. 8 Modulus G' as a function of frequency for some investigated hydrogels (see Table 1 for compositions).

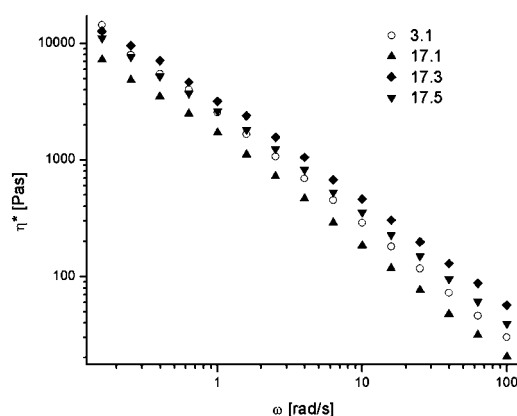


Fig. 9 Viscosity as a function of frequency for some investigated hydrogels (see Table 1 for compositions).

due to the presence of solid filler lamellae. As already evidenced, a further increase of the filler content, acting as a lubricant for the sliding of the sheets, results in a significant decrease of viscosity.

We exploited the complex viscosity curves for assessing the viscoelastic parameters of the materials under study.⁹⁶ To this aim, we determined the slope of the regression lines, which were used for interpolating viscosity data, together with their intercept on the Y axis (η^*): the former gives an indication of a non-Newtonian behaviour of the material, the latter represents the resistance to flow. The obtained values, collected in Table 2, further confirm the previously reported conclusions. The most interesting result concerns the viscoelastic behaviour of sample

Table 2 Viscoelastic parameters of some investigated hydrogels (see Table 1 for compositions)

Sample	Slope	Non-Newtonian behaviour	Intercept	Fluidity of the system ^a (%)
3.1	-0.948	Pseudoplastic	2467	
17.5	-0.875	Less pseudoplastic	2492	-1
17.3	-0.853	Less pseudoplastic	3145	-28
17.1	-0.925	Pseudoplastic	1538	+38

^a With respect to the unfilled sample.

17.1, which exhibits the same pseudoplastic behaviour of the unfilled hydrogel, but is characterized by higher fluidity.

Finally, a DSC characterization was performed on the dried samples. All materials exhibit a glass transition temperature at *ca.* 139.5 °C independently of the graphene content.

Conclusions

In this work, the first nanocomposite polymer hydrogel containing graphene was obtained. This result was achieved thanks to the use of frontal polymerization, which allows fast conversion of monomer into polymer. Indeed, when the classical technique was used, graphene reaggregated to graphite flakes.

It should be highlighted that the highest graphene concentrations in NMP reported so far were achieved by simple graphite sonication without any chemical modification of the latter.

It was found that even small amounts of this nanofiller strongly influence the swelling behaviour of the hydrogel, by dramatically increasing it. On the other hand, LCST was not affected by the presence of graphene.

The nanocomposite hydrogels showed a particular rheological behaviour: G' modulus and complex viscosity were found to increase by increasing the graphene content; in spite of the reinforcing effect exerted by the nanofiller, its highest content promoted a significant decrease of these two parameters, since it acted as a lubricant for the sliding of the sheets, thus approaching the same pseudoplastic behaviour of the unfilled material.

References

- 1 N. A. Peppas, in *Hydrogels in Medicine and Pharmacy*, CRC Press, Boca Raton, Florida, 1986, vol. 1.
- 2 O. Wichterle and D. Lim, *Nature*, 1960, **185**, 117.
- 3 K. Dusek and D. Patterson, *J. Polym. Sci., Part A-2*, 1968, **6**(7), 1209.
- 4 T. Tanaka, I. Nishio, S. T. Sun and S. Ueno-Nishio, *Science*, 1982, **218**(4571), 467.
- 5 S. Hirotsu, *J. Appl. Phys.*, 1985, **24**, 388.
- 6 M. Shibayama, M. Morimoto and S. Nomura, *Macromolecules*, 1994, **27**, 5060.
- 7 X. Z. Zhang, Y. Y. Yang, T. S. Chung and K. X. Ma, *Langmuir*, 2001, **17**, 6094.
- 8 X. Li, W. Liu, G. Ye, B. Zhang, D. Zhu, K. Yao, Z. Liu and X. Sheng, *Biomaterials*, 2005, **26**(34), 7002.
- 9 X. Z. Zhang, L. P. Jo and C. C. Chu, *Biomaterials*, 2005, **26**(16), 3299.
- 10 E. Ho, A. Lowman and M. Marcolongo, *Biomacromolecules*, 2006, **7**, 3223.
- 11 W. F. Lee and Y. C. Yeh, *Eur. Polym. J.*, 2005, **41**, 2488.
- 12 S. Ohya and T. Matsuda, *J. Biomater. Sci., Polym. Ed.*, 2005, **16**(7), 809.
- 13 T. Serizawa, K. Wakita, T. Kaneko and M. Akashi, *J. Polym. Sci., Part A: Polym. Chem.*, 2002, **40**, 4228.
- 14 K. Haraguchi, R. Farnworth, A. Ohbayashi and T. Takehisa, *Macromolecules*, 2003, **36**, 5732.
- 15 K. S. Novoselov, A. K. Geim, S. V. Morozov, D. Jiang, Y. Zhang, S. V. Dubonos, I. V. Grigorieva and A. A. Firsov, *Science*, 2004, **306**, 666.
- 16 R. D. Dreyer, S. Park, C. W. Bielawski and R. S. Ruoff, *Chem. Soc. Rev.*, 2010, **39**, 228.
- 17 G. X. Wang, J. Yang, J. Park, X. L. Gou, B. Wang, H. Liu and J. Yao, *J. Phys. Chem. C*, 2008, **112**, 8192.
- 18 G. Wang, X. Shen, B. Wang, J. Yao and J. Park, *Carbon*, 2009, **47**, 1359.
- 19 X. Li, X. Wang, L. Zhang, S. Lee and H. Dai, *Science*, 2008, **319**, 1229.
- 20 P. Blake, P. D. Brimicombe, R. R. Nair, T. J. Booth, D. Jiang, F. Schedin, L. A. Ponomarenko, S. V. Morozov, H. F. Gleeson, E. W. Hill, A. K. Geim and K. S. Novoselov, *Nano Lett.*, 2008, **8**, 1704.
- 21 M. J. Allen, V. C. Tung and R. B. Kaner, *Chem. Rev.*, 2010, **110**, 132.

- 22 Y. B. Zhang, Y. W. Tan, H. L. Stormer and P. Kim, *Nature*, 2005, **438**, 201.
- 23 K. S. Kim, Y. Zhao, H. Jang, S. Y. Lee, J. M. Kim, K. S. Kim, J. H. Ahn, P. Kim, J. Y. Choi and B. H. Hong, *Nature*, 2009, **457**, 706.
- 24 H. Becerril, J. Mao, Z. Liu, M. Stoltenberg, Z. Bao and Y. Chen, *ACS Nano*, 2008, **2**, 463.
- 25 J. Wu, M. Agrawal, H. A. Becerril, Z. Bao, Z. Liu, Y. Chen and P. Peumans, *ACS Nano*, 2010, **4**, 43.
- 26 H. Li, J. Chen, S. Han, W. Niu, X. Liu and G. Xu, *Talanta*, 2009, **79**, 165.
- 27 X. Wang, L. Zhi and K. Mullen, *Nano Lett.*, 2008, **8**, 323.
- 28 Y. Wang, X. Chen, Y. Zhong, F. Zhu and K. P. Loh, *Appl. Phys. Lett.*, 2009, **95**, 063302/1.
- 29 W. Xianbao, Y. Haijun, L. Fangming, L. Mingjian, W. Li, L. Shaoqing, L. Qin, X. Yang, T. Rong, Y. Ziyong, X. Dong and C. Jing, *Chem. Vap. Deposition*, 2009, **15**, 53.
- 30 E. Dervishi, Z. Li, F. Watanabe, A. Biswas, Y. Xu, A. R. Biris, V. Saini and A. S. Biris, *Chem. Commun.*, 2009, 4061.
- 31 X. Li, W. Cai, J. An, S. Kim, J. Nah, D. Yang, R. Piner, A. Velamakanni, I. Jung, E. Tutuc, S. K. Banerjee, L. Colombo and R. S. Ruoff, *Science*, 2009, **324**, 1312.
- 32 E. Rollings, G. H. Gweon, S. Y. Zhou, B. S. Mun, J. L. McChesney, B. S. Hussain, A. V. Fedorov, P. N. First, W. A. de Heer and A. Lanzar, *J. Phys. Chem. Solids*, 2006, **67**, 2172.
- 33 M. Alexander and P. Oleg, *Phys. Status Solidi B*, 2008, **245**, 1425.
- 34 P. W. Sutter, J. I. Flege and E. A. Sutter, *Nat. Mater.*, 2008, **7**, 406.
- 35 T. Seyller, A. Bostwick, K. V. Emtsev, K. Horn, L. Ley, J. L. McChesney, T. Ohta, J. D. Riley, E. Rotenberg and F. Speck, *Phys. Status Solidi B*, 2008, **245**, 1436.
- 36 N. Li, Z. Wang, K. Zhao, Z. Shi, Z. Gu and S. Xu, *Carbon*, 2009, **48**, 255.
- 37 S. Karmakar, N. V. Kulkarni, A. B. Nawale, N. P. Lalla, R. Mishra, V. G. Sathe, S. V. Bhoraskar and A. K. Das, *J. Phys. D: Appl. Phys.*, 2009, **42**, 115201/1.
- 38 C. Yannick and K. Wim, *ChemPhysChem*, 2006, **7**, 1770.
- 39 X. Yang, X. Dou, A. Rouhanipour, L. Zhi, H. J. Rader and K. Mullen, *J. Am. Chem. Soc.*, 2008, **130**, 4216.
- 40 C. D. Kim, B. K. Min and W. S. Jung, *Carbon*, 2009, **47**, 1610–1612.
- 41 D. V. Kosynkin, A. L. Higginbotham, A. Sinitskii, J. R. Lomeda, A. Dimiev, B. K. Price and J. M. Tour, *Nature*, 2009, **458**, 872.
- 42 A. Hirsch, *Angew. Chem., Int. Ed.*, 2009, **48**, 6594.
- 43 L. Jiao, L. Zhang, X. Wang, G. Diankov and H. Dai, *Nature*, 2009, **458**, 877.
- 44 W. Zhang, J. Cui, C. A. Tao, Y. Wu, Z. Li, L. Ma, Y. Wen and G. Li, *Angew. Chem., Int. Ed.*, 2009, **48**, 5864.
- 45 A. Dato, V. Radmilovic, Z. Lee, J. Phillips and M. Frenklach, *Nano Lett.*, 2008, **8**, 2012.
- 46 S. Stankovich, D. A. Dikin, R. D. Piner, K. A. Kohlhaas, A. Kleinhammes, Y. Jia, Y. Wu, S. Y. Nguyen and R. S. Ruoff, *Carbon*, 2007, **45**, 1558.
- 47 Y. Hernandez, V. Nicolosi, M. Lotya, F. M. Blighe, Z. Sun, S. De, I. T. McGovern, B. Holland, M. Byrne, Y. K. Gun'Ko, J. J. Boland, P. Niraj, G. Duesberg, S. Krishnamurthy, R. Goodhue, J. Hutchison, V. Scardaci, A. C. Ferrari and J. N. Coleman, *Nat. Nanotechnol.*, 2008, **3**, 563.
- 48 M. Lotya, Y. Hernandez, P. J. King, R. J. Smith, V. Nicolosi, L. S. Karlsson, F. M. Blighe, S. De, Z. Wang, I. T. McGovern, G. S. Duesberg and J. N. Coleman, *J. Am. Chem. Soc.*, 2009, **131**, 3611.
- 49 D. Nuvoli, L. Valentini, V. Alzari, S. Scognamillo, S. Bittolo Bon, M. Piccinini, J. Illescas and A. Mariani, *J. Mater. Chem.*, 2011, **21**, 3428.
- 50 H. Kim, A. A. Abdala and C. W. Macosko, *Macromolecules*, 2010, **43**, 6515.
- 51 G. Eda and M. Chhowalla, *Nano Lett.*, 2009, **9**, 814.
- 52 T. Kuilla, S. Bhadra, D. Yao, N. H. Kim, S. Bose and J. H. Lee, *Prog. Polym. Sci.*, 2010, **35**, 1350.
- 53 N. M. Chechilo, R. J. Khvilivitskii and N. S. Enikolopyan, *Dokl. Akad. Nauk SSSR*, 1972, **204**, 1180.
- 54 J. A. Pojman, G. Curtis and V. M. Ilyashenko, *J. Am. Chem. Soc.*, 1996, **118**, 3783.
- 55 A. Mariani, S. Bidali, S. Fiori, M. Sangermano, G. Malucelli, R. Bongiovanni and A. Priola, *J. Polym. Sci., Part A: Polym. Chem.*, 2004, **42**(9), 2066.
- 56 S. Scognamillo, C. Bounds, M. Luger, A. Mariani and J. A. Pojman, *J. Polym. Sci., Part A: Polym. Chem.*, 2010, **48**(9), 2000.
- 57 S. Scognamillo, V. Alzari, D. Nuvoli and A. Mariani, *J. Polym. Sci., Part A: Polym. Chem.*, 2010, **48**(21), 4721.
- 58 Z. Jimenez and J. A. Pojman, *J. Polym. Sci., Part A: Polym. Chem.*, 2007, **45**, 2745.
- 59 D. I. Fortenberry and J. A. Pojman, *J. Polym. Sci., Part A: Polym. Chem.*, 2000, **38**, 1129.
- 60 C. Nason, J. A. Pojman and C. Hoyle, *J. Polym. Sci., Part A: Polym. Chem.*, 2008, **46**, 8091.
- 61 J. V. Crivello, *J. Polym. Sci., Part A: Polym. Chem.*, 2006, **44**, 6435.
- 62 T. Hu, S. Chen, Y. Tian, L. Chen and J. A. Pojman, *J. Polym. Sci., Part A: Polym. Chem.*, 2007, **45**, 873.
- 63 L. Chen, T. Hu, H. Yu, S. Chen and J. A. Pojman, *J. Polym. Sci., Part A: Polym. Chem.*, 2007, **45**, 4322.
- 64 S. Chen, Y. Tian, L. Chen and T. Hu, *Chem. Mater.*, 2006, **18**, 2159.
- 65 S. Chen, J. Sui, L. Chen and J. A. Pojman, *J. Polym. Sci., Part A: Polym. Chem.*, 2005, **43**, 1670.
- 66 X. Cai, S. Chen and L. Chen, *J. Polym. Sci., Part A: Polym. Chem.*, 2008, **46**, 2177.
- 67 A. Mariani, S. Fiori, Y. Chekanov and J. A. Pojman, *Macromolecules*, 2001, **34**, 6539.
- 68 Y. Fang, L. Chen, C. F. Wang and S. Chen, *J. Polym. Sci., Part A: Polym. Chem.*, 2010, **48**, 2170.
- 69 S. Fiori, A. Mariani, L. Ricco and S. Russo, *Macromolecules*, 2003, **36**, 2674.
- 70 A. Mariani, S. Bidali, S. Fiori, G. Malucelli and E. Sanna, *e-Polymers*, 2003, **44**, 1.
- 71 S. Fiori, A. Mariani, L. Ricco and S. Russo, *e-Polymers*, 2002, **29**, 1.
- 72 S. Fiori, G. Malucelli, M. Mariani, L. Ricco and E. Casazza, *e-Polymers*, 2002, **57**, 1.
- 73 A. Mariani, S. Fiori, S. Bidali, V. Alzari and G. Malucelli, *J. Polym. Sci., Part A: Polym. Chem.*, 2008, **46**, 3344.
- 74 A. Mariani, S. Fiori, E. Pedemonte, S. Pincin, E. Princi and S. Vicini, *ACS Polym. Prepr.*, 2002, **43**, 869.
- 75 A. Mariani, S. Bidali, P. Cappelletti, G. Caria, A. Colella, A. Brunetti and V. Alzari, *e-Polymers*, 2009, **64**, 1.
- 76 A. Brunetti, E. Princi, S. Vicini, S. Pincin, S. Bidali and A. Mariani, *Nucl. Instrum. Methods Phys. Res., Sect. B*, 2004, **222**, 235.
- 77 S. Vicini, A. Mariani, E. Princi, S. Bidali, S. Pincin, S. Fiori, E. Pedemonte and A. Brunetti, *Polym. Adv. Technol.*, 2005, **16**, 293.
- 78 A. Mariani, S. Bidali, G. Caria, O. Monticelli, S. Russo and J. M. Kenny, *J. Polym. Sci., Part A: Polym. Chem.*, 2007, **45**, 2204.
- 79 A. Mariani, V. Alzari, O. Monticelli, J. A. Pojman and G. Caria, *J. Polym. Sci., Part A: Polym. Chem.*, 2007, **45**, 4514.
- 80 A. Mariani, D. Nuvoli, V. Alzari and M. Pini, *Macromolecules*, 2008, **41**, 5191.
- 81 E. Gavini, A. Mariani, G. Rasso, S. Bidali, G. Spada, M. C. Bonferoni and P. Giunchedi, *Eur. Polym. J.*, 2009, **45**, 690.
- 82 G. Caria, V. Alzari, O. Monticelli, D. Nuvoli, J. M. Kenny and A. Mariani, *J. Polym. Sci., Part A: Polym. Chem.*, 2009, **47**, 1422.
- 83 V. Alzari, O. Monticelli, D. Nuvoli, J. M. Kenny and A. Mariani, *Biomacromolecules*, 2009, **10**, 2672.
- 84 S. Scognamillo, V. Alzari, D. Nuvoli and A. Mariani, *J. Polym. Sci., Part A: Polym. Chem.*, 2010, **48**, 2486.
- 85 V. Alzari, A. Mariani, O. Monticelli, L. Valentini, D. Nuvoli, M. Piccinini, S. Scognamillo, S. Bittolo Bon and J. Illescas, *J. Polym. Sci., Part A: Polym. Chem.*, 2010, **48**, 5375.
- 86 S. Scognamillo, V. Alzari, D. Nuvoli, J. Illescas and A. Mariani, *J. Polym. Sci., Part A: Polym. Chem.*, 2011, **49**, 1228.
- 87 Y. Fang, H. Yu, L. Chen and S. Chen, *Chem. Mater.*, 2009, **21**, 4711.
- 88 J. Tu, L. Chen, Y. Fang, C. Wang and S. Chen, *J. Polym. Sci., Part A: Polym. Chem.*, 2010, **48**, 823.
- 89 R. P. Washington and O. Steinbock, *J. Am. Chem. Soc.*, 2001, **123**, 7933.
- 90 J. Masere, Y. Chekanov, J. R. Warren, F. D. Stewart, R. Al-Kaysi, J. K. Rasmussen and J. A. Pojman, *J. Polym. Sci., Part A: Polym. Chem.*, 2000, **38**, 3984.
- 91 A. A. Green and M. C. Hersam, *Nano Lett.*, 2009, **9**(12), 4031.
- 92 U. Khan, A. O'Neill, M. Lotya, S. De and J. N. Coleman, *Small*, 2010, **6**(7), 864.
- 93 I. P. Nagy, L. Sike and J. A. Pojman, *J. Am. Chem. Soc.*, 1995, **117**, 3611.
- 94 A. C. Ferrari, *Solid State Commun.*, 2007, **143**, 47.
- 95 R. J. Nemanich and S. A. Solin, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 1979, **20**(2), 392.
- 96 C. Macosko, in *Rheology: Principles, Measurements and Application*, Wiley/VCH, Poughkeepsie, NY, 1994, ISBN: 0-471-18575-2.