Macromolecular Nanotechnology

Graphene derivatives in responsive hydrogels: Effect of concentration and surface chemistry

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ABSTRACT

Reduced graphene oxide (RGO) containing composite hydrogels, based on poly(N-isopropylacrylamide) (PNIPA) were prepared by two different methods: (i) by incorporating RGO directly into the polymer matrix; (ii) applying a post-synthesis reduction of the graphene-oxide (GO) already incorporated into the polymer. The samples were compared by various microscopic (small angle neutron scattering, differential scanning calorimetry, ^{1}H NMR spectroscopy, thermogravimetry) and macroscopic (kinetic and equilibrium swelling properties and mechanical testing) techniques. Results from microscopic and macroscopic measurements show that the dispersity of the nanoparticles as well as their interaction with the polymer chains are influenced by their surface chemistry. Incorporation of nanoparticles limits the shrinkage and slows down the kinetics of the thermal response. Both thermogravimetric and solid-state NMR measurements confirmed strong polymer – nanoparticle interaction when hydrophilic GO was used in the synthesis. In these cases, the slow thermal response may be explained by the decrease of the free volume inside the nanocomposite matrix caused by a hypernodal structure. Our results imply that both the chemistry and the concentration of incorporated graphene derivatives are promising in tuning the thermal responsivity of PNIPA.

1. Introduction

Responsive hydrogels are in the focus of scientific attention in the last few decades owing to their numerous beneficial properties like high water content [1,2] and relatively good deformability. Moreover, thanks to the physiochemical similarity of their network to the native extracellular matrix they are potentially biocompatible. Their responsiveness originates from a reversible volume phase transition (VPT) that can be triggered by changes in certain environmental conditions [3,4] like composition [5] or pH [6] of the swelling medium, temperature [7], electromagnetic field [8], etc. This makes them very attractive for example in drug delivery [9,10], or as sensors [11], actuators [12,13], microvalves [14]. Poly(N-isopropylacrylamide) (PNIPA) is one of the most popular temperature sensitive responsive hydrogel, owing to its peculiar volume phase transition temperature (VPTT) that is at ~34 °C, close to the temperature of the human body [9,15]. Despite the above mentioned advantages hydrogels have several limitations as well (e.g. poor mechanical strength). Carbon nanoparticles (CNP) are widely used for strengthening in polymer nanocomposites. Recently they also got into the focus of interest as components of polymer *hydrogel* nanocomposites, as the CNPs may act not only as

reinforcing agents, but also provide new or modified sensitivity to these complex systems.

Graphene has many specific properties (e.g. excellent heat and electrical conductivity or light sensitivity) which would be beneficial, but its hydrophobicity hinders strongly the use in hydrogels. On the contrary, graphene oxide (GO), which is a damaged graphene layer, decorated with vacations and oxygen containing functional groups, forms stable aqueous suspension. However, due to the corrupted sp^2 structure, its properties are far from those of graphene. Several chemical and physical routes are available for partially restoring the honeycomb structure and removing the functional groups [16]. The resulted reduced graphene oxide (RGO) can have great potential in hydrogel nanocomposites as its properties are close to that of the graphene, but its hydrophobicity is decreased [17].

Nowadays GO containing systems are in the focus of attention [18–21] and few attempts have been already made to prepare various RGO containing composite materials [22–26] as well. In practice, though, the decreased hydrophilicity of RGO (with respect to GO) complicates the preparation of stable aqueous suspensions and consequently causing inhomogeneous distribution of RGO in the composite [27]. If the synthesis procedure of the gel is not too sensitive for the environment, in situ reduction methods (i.e. reduction agent added to the initial precursor mixture) may be used [28,29]. An effective way to make RGO containing gel composites is to reduce the already incorporated GO inside the gel matrix [17,30], however the circumstances of the reduction (e.g. reducing agent, temperature) should be chosen with great care in order not to affect the physical/chemical properties of the gel.

The preparation of RGO containing, PNIPA based, temperature sensitive hydrogels is challenging. As the free radical polymerisation of NIPA is extremely sensitive to the reaction circumstances, the application of even the mildest reducing agent for an eventual in-situ reduction of GO is excluded. On the other hand, incorporation of RGO nanoparticles into the gel matrix is limited owing to the above mentioned reduced hydrophilicity of RGO. In this work we report a novel alternative route to circumvent this challenge. In our paper we show that a treatment with L-ascorbic acid solution, which was proven to be an efficient and environmental friendly reducing agent of GO [31,32], can be used as a post treatment of GO containing PNIPA hydrogel nanocomposites to reduce GO within the gel matrix. In order to compare the microscopic and macroscopic character of the differently prepared GO and RGO containing nanocomposite systems, small-angle neutron scattering (SANS), kinetic and equilibrium swelling properties, macroscopical mechanical tests and differential scanning calorimetry (DSC) measurements were performed on the gels of various nanoparticle content. Our results from solid state NMR spectroscopy and thermal analysis help to shed light on the interactions that are formed between the nanoparticles and the gel matrix.

2. Materials and methods

2.1. Nanoparticle synthesis

Graphene oxide (GO) was obtained by the improved Hummers' method [33] from natural graphite (originated from Madagascar). The GO content of the light brown suspension was ~1 w/w%. The C/O ratio of this GO, determined by XPS, was 1.8.

To prepare RGO we modified the method of Fernandez-Merino et al. [32]. The dry nanoparticles were suspended in L-ascorbic acid (AA) solution in the presence of NH_3 at 20 °C. In the reaction mixture the concentration of the GO, AA and NH_3 was 1 mg/mL; 20 mmol/L and 1.1 mol/L, respectively. After 1 week of soaking the nanoparticles were purified by multiple washing and filtering steps. The resulted RGO was then dried and later stored in a desiccator at ambient temperature. The C/O ratio of RGO, determined by XPS, was 3.6. For nanocomposite gel preparation RGO nanoparticles were re-suspended in water by ultrasonication (Branson B1200R-4) for 15 min with 40 kHz in sweep mode.

2.2. Gel synthesis

The pure PNIPA were synthesised from *N*-isopropylacrylamide (NIPA) monomer (Tokyo Chemical Industry, Japan) and *N,N′*-methylenebisacrylamide (BA) cross-linker (Sigma Aldrich) in aqueous medium at 20 °C by free radical polymerization, as reported previously [34,35]. *N,N,N′,N′*-tetramethylethylenediamine (TEMED) and ammonium persulphate (APS) were used to initiate the system. In the precursor solution the molar ratio of NIPA/BA, NIPA/APS and NIPA/TEMED was 150, 34,2 and 112, respectively.

GO and RGO containing nanocomposite gels (GO@PNIPA and RGO@PNIPA, respectively) were prepared according to the method described earlier [34,35]. The GO loading was varied between 0 and 25 mg GO/g monomer, whereas the highest reachable concentration of RGO was only 11 mg/g monomer due to its poor dispersibility.

The post-reduction treatment of GO@PNIPA gels were made by soaking the dried samples in the AA media (composition is identical as used for GO nanoparticle reduction, described above) for 1 week at 20 °C. The ratio of the solid (S) and liquid (L) phases was kept constant (S/L = 0.012).

In all cases 2 mm thick films and 10 × 10 mm isometric cylinders were prepared. All chemicals were used as received, except NIPA, which was recrystallized from a toluene-hexane mixture. Doubly distilled water was used for the synthesis, purification and measurements, unless stated differently. The nomenclature of the prepared samples is given in Table 1.

2.3. Methods

Equilibrium swelling degree of the samples was measured on dried gel disks with a diameter of 7 mm, cut from the 2 mm thick film. After 1 week in pure water at 20.0 ± 0.2 °C the equilibrium swelling degree was determined as m/m_0, where m and m_0 are the mass of the swollen and dry samples, respectively. Elastic modulus of the fully swollen samples was measured on isometric gel