

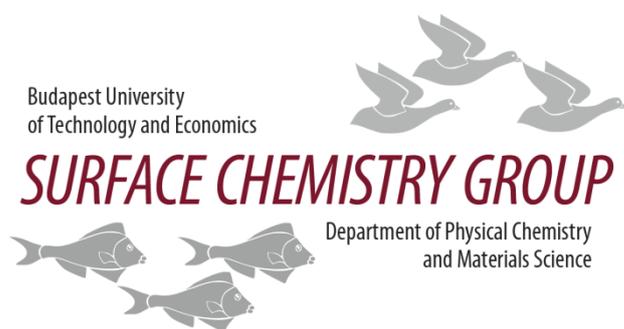


**BUDAPEST UNIVERSITY OF TECHNOLOGY AND ECONOMICS
FACULTY OF CHEMICAL TECHNOLOGY AND BIOTECHNOLOGY
GEORGE OLÁH PHD SCHOOL**

Thermosensitive hydrogel – carbon nanoparticle composites

Extended Abstract for PhD thesis

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1. Introduction

Responsive hydrogels have a wide range of potential applications (e.g., sensors, actuators, microfluidics, drug delivery vehicles, etc.), which can even be further extended through the preparation of composites¹. Carbon nanoparticles (CNPs) are widely used for strengthening in polymer nanocomposites. In responsive systems, CNPs may act not only as reinforcing agents but, by virtue of their special structure, their infrared sensitivity, and their tuneable conductivity, they can also provide new or modified sensitivity to these complex systems. As the nanoparticles may interact differently with the polymer matrix, the final properties of the composites are expected to be tuneable.

In the literature, poly(*N*-isopropylacrylamide) (PNIPAM) based composite systems were investigated with a variety of cross-link densities and/or with different co-monomers, as well as with diverse conditions of synthesis²⁻⁴. Owing to the huge variety of different parameters, it is not possible to evaluate directly the effects of incorporated nanoparticles without a systematic study.

The goal of my PhD work was to investigate systematically the effect of shape and surface chemistry of CNP incorporated into PNIPAM hydrogel systems. I studied two main groups: the rather hydrophobic, oxidized carbon nanotubes (CNTs) and the hydrophilic graphene oxide (GO). Due to its high oxygen content, the physical properties of GO are poorer than those of graphene. I investigated the effect of ascorbic acid reduction under mild conditions on the properties of reduced graphene oxide (RGO) and RGO containing composites prepared by two different procedures.

The shape, size, surface chemistry, concentration and the method of preparation can all influence the character of the resulting material. One of the aims on my thesis is to identify the parameters having the most significant effect on the structure and responsiveness of the composites, and to explore the relation between them. To study the structure as well as the dynamic properties of the composite materials, they are investigated both at macroscopic and microscopic length scales

¹ Kopecek. *Biomaterials* **28**, 5185–92 (2007).; Ionov. *Mater. Today* **17**, 494–503 (2014).

² Li et al.. *Soft Matter* **8**, 3139 (2012).

³ Lo et al. *Soft Matter* **7**, 5604 (2011).

⁴ Ma et al. *Eur. Polym. J.* **49**, 389–396 (2013).

2. Experimental

In this work, the PNIPAM gel and composite samples were synthesized by the free radical polymerization⁵⁻⁷. PNIPAM gel composites of various CNT, GO and RGO compositions were prepared under identical conditions by incorporating the CNPs into the polymer matrix and for RGO containing systems by applying a post-synthesis reduction of the already incorporated GO in the polymer⁸.

The mechanical properties of the gels were characterized by their compressive strength and elastic moduli, measured by uniaxial compression. Their temperature-sensitivity was determined by equilibrium swelling degree measurements at various temperatures in the range 20-50 °C, and by differential scanning microcalorimetry (DSC).

The time-dependent behaviour during the volume phase transition was investigated by temperature-jump induced shrinkage kinetics. During this measurement, gel disks were equilibrated at 20 °C, then plunged into warm water (40 or 50 °C). The mass was measured as a function of time.

The interactions between the CNPs and the polymer matrix were studied by solid-state NMR spectroscopy and thermal analysis

The structure of the prepared systems at the nanoscale-level was studied by small-angle neutron and X-ray scattering (SANS and SAXS, respectively). SANS and SAXS methods are widely used complementary techniques. Via SANS the measured signal comes from the polymer matrix only, the nanoparticles being practically invisible, due to their contrast. Conversely, the SAXS signal is dominated by the scattering of the CNPs.

3. Results

3.1. Macroscopic characterisation

The swelling and the mechanical properties (Figure 1a) of the pure gel systems showed a strong dependence on the cross-link density in accordance with the literature^{5,9}. The elastic modulus of PNIPAM gel is enhanced by GO, while the swelling degree of the GO@PNIPAM systems decreases significantly. Increasing the GO content drastically decreases the swelling degree and increases the elastic modulus. A similar trend is observed in pure PNIPAM gels on increasing the cross-link density, but the shapes of the responses are different. Increasing the

⁵ László et al. *Macromolecules* **37**, 10067–10072 (2004).

⁶ Manek et al.. *Express Polym. Lett.* **10**, 710–720 (2016).

⁷ Berke et al. *European Polymer Journal*, **93**, 717-725 (2017).

⁸ Berke et al. *Soft Matter*, **12** 7166 (2016).

⁹ Chetty et al.. *Express Polym. Lett.* **7**, 95–105 (2013).

cross-link density of the PNIPAM network monotonically changes the swelling degree and the elastic modulus, whereas when GO loading is increased a plateau is observed above the percolation threshold of GO, in both quantities. These differences suggest that the role of the GO was more complex than a simple chemical cross-linker in the polymer matrix. The trends observed with GO are conserved in the post-synthesis reduction, i.e. (GO@PNIPAM)R samples behave similarly (Figure 1b, c).

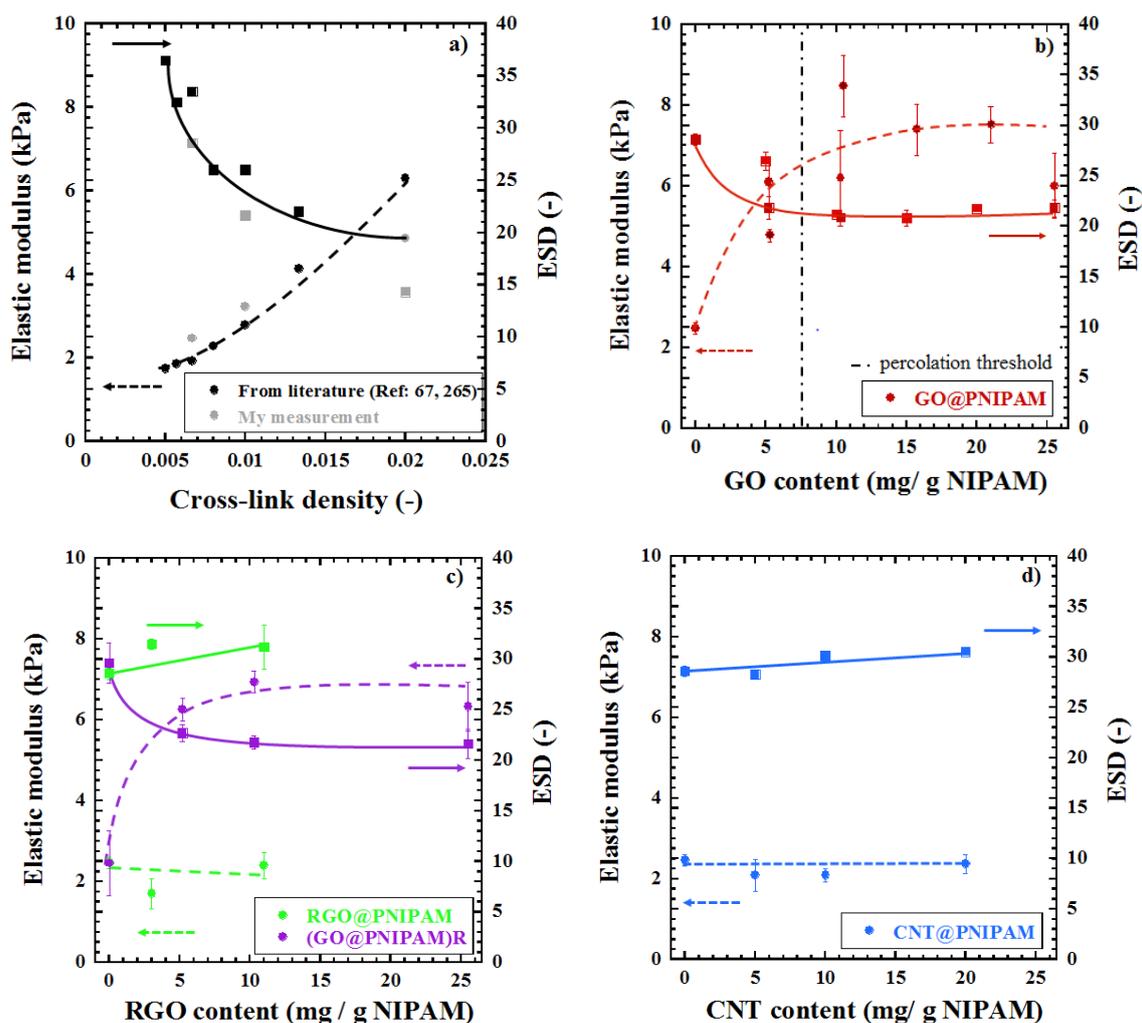


Figure 1. Elastic moduli (squares) and equilibrium swelling degree (ESD) values (circles) at 20 °C of the studied gel system: a) pure PNIPAM systems with different cross-link density values and b-d) GO, RGO and CNT containing composites, respectively. The solid and dashed lines are guides for the eye.

Direct incorporation of RGO is severely limited by its reduced hydrophilicity. The aggregation tendency of CNT and of RGO reduced prior to polymerisation caused only a small modification in the nanocomposites (Figure 1c,d). The swelling and mechanical properties remained almost unchanged with respect to the pure PNIPAM gel.

All types of CNP incorporation improved the fracture strength of the composites in comparison to the pure gel.

The shown macroscopic observations, in accordance with thermogravimetric and NMR measurements, revealed strong interactions between GO and the polymer matrix, which were not influenced by the post-reduction treatment. Our results, however, show no clear evidence of covalent bonds. Further evidence is needed to reveal the real nature of these enhanced interactions. At the same time, when RGO or CNT incorporated directly into the gel, they interact only weakly.

3.2. Structural comparison on microscale

The polymer-polymer correlation length (ξ) characterizes the distance between the cross-links. SANS experiments at performed on gel samples swollen at 25 °C revealed that ξ decreases upon increasing cross-link density (Figure 2a)

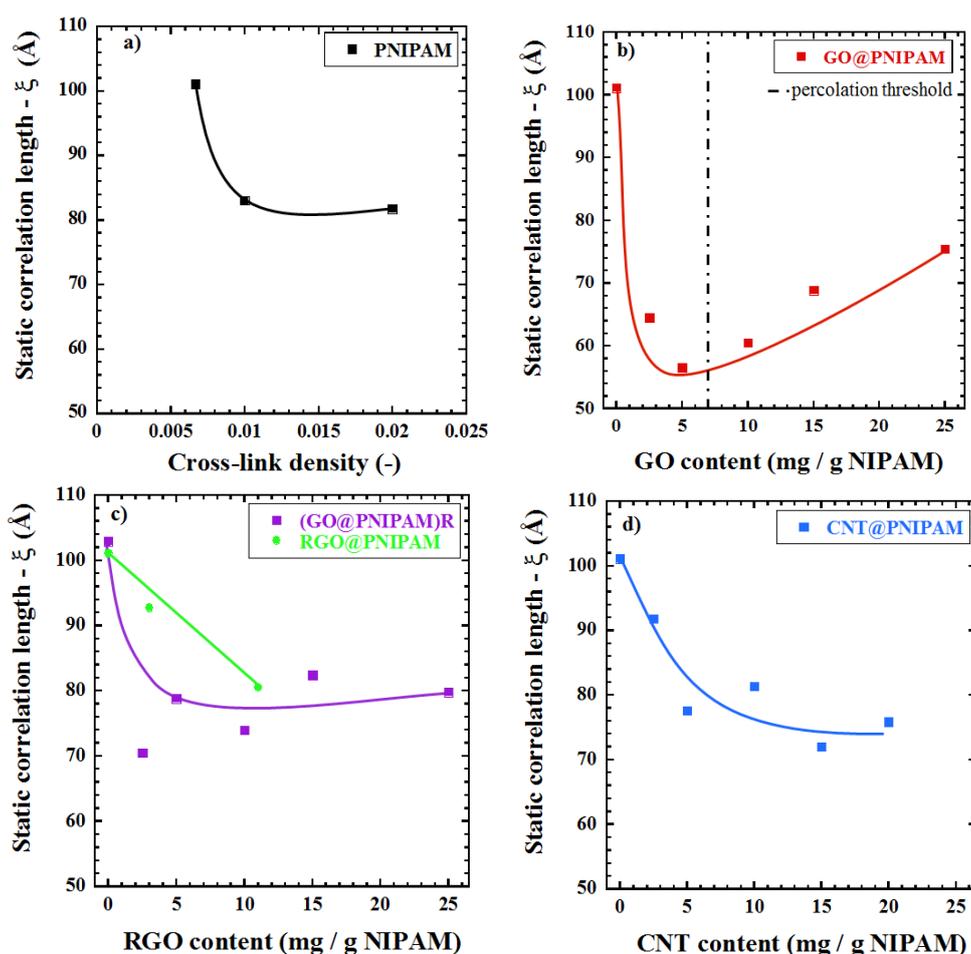


Figure 2. Static correlation length values of the different samples determined by Ornstein Zernike model fits on the SANS curves: a) pure PNIPAM systems with different cross-link densities and b-d) GO, RGO and CNT containing composites, respectively. The solid lines are guides for the eye.

In the case of GO@PNIPAM systems (Figure 2b) a U-shaped curve was observed: but even at the highest GO concentration ξ remained significantly smaller than in the pure PNIPAM. The increasing trend of ξ upon increasing GO loading may indicate that at higher concentrations the GO nanoparticles come into contact with each other and/or stick together, resulting in a smaller effective concentration. This is consistent with the observed macroscopic properties and can be explained by percolation theory.

After the post-reduction treatment ξ increased at all CNP concentrations in comparison with the original GO@PNIPAM systems. Conversely, no significant effect was observed in the pure CNP-free gel after the same treatment, which suggests that the pure polymer matrix was not affected by the reduction procedure, i.e., the chemical cross-links were untouched. When RGO or CNT was directly incorporated into the polymer matrix ξ decreased continuously with increasing concentration (Figure 2c,d).

Information could be gained from the incorporated CNPs from SAXS measurements. It was found that in the suspension state, prior to gelation, the morphology of the GO nanoparticles and CNT aggregates was already approximately the same, and this morphology depended rather on the physicochemical properties of GO, i.e., its interaction with the solvent, as the shape of the SAXS responses displayed no concentration dependence.

Above the VPTT, the gel shrinkage modified the structure. As the internal structure of the gels changed, the corresponding scattering responses changed significantly as well. The phase separation process enhanced the spatial inhomogeneity and gave rise to strong surface scattering. The observed correlation lengths (Θ), which in this case characterized the network inhomogeneities, were found to be significantly larger than the polymer matrix correlation lengths ξ below the VPTT.

From the SAXS studies, the change of the characteristic sizes of the incorporated particles could be followed as well. As a conclusion of the presented structural investigations, the proposition for the internal structure of the composites is shown in Figure 3.

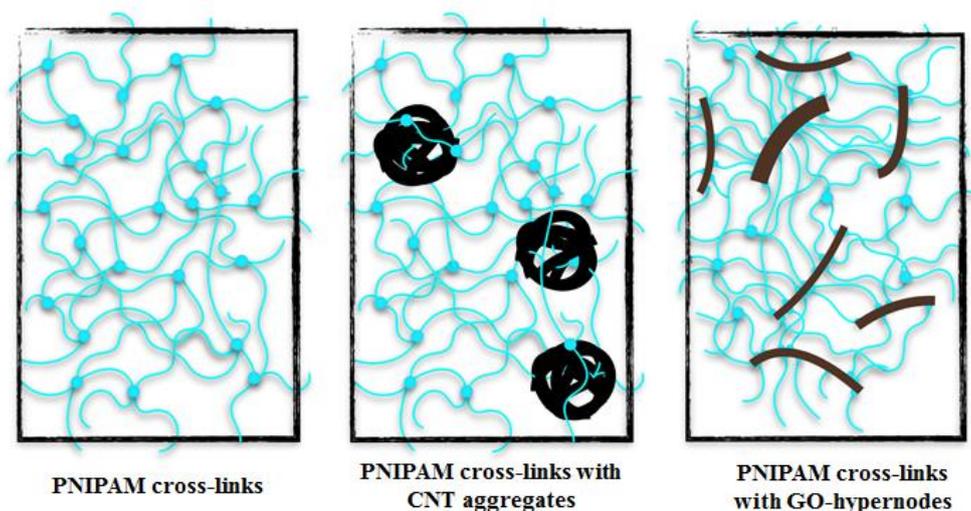


Figure 3. Proposed internal structure of pure gels and CNP containing composites

3.4. Effect of temperature

3.4.1. Static studies

The VPTT was not influenced significantly by the CNP incorporation; the swelling curves of the CNT@PNIPAM and RGO@PNIPAM systems practically overlapped with those of pure PNIPAM. By contrast, despite having an identical VPT value, the GO containing systems deswelled less readily as the temperature was raised to 35 °C. This could partly originate from the hydrophilicity of the GO platelets compensating for the strengthening hydrophobic interactions within the polymer matrix as the temperature increases.

3.4.2. Dynamic properties

Significant differences were observed in the time-dependence of the thermal response of the systems (Figure 4). In pure PNIPAM gels at 50 °C, the resulting hydrophilic – hydrophobic VPT transition involves an abrupt collision of the polymer chains, which hinders their movement and causes jamming. When the VPT takes place at 40 °C owing to the smaller driving force, the observed shrinkage is significantly slowed down, resulting in a jamming-free process.

The hydrophobic character of the CNTs fosters the water expulsion in the early stages of the process. However, the CNT aggregates also act as spacers that physically obstruct the shrinkage and thus impede the motion of the polymer chains. The hindering effect at higher CNT concentrations is more pronounced, and since at 50 °C the gel deswelling is governed by jamming, a more abrupt response provokes stronger hindering at longer time scales.

GO has 2-dimensional morphology and hydrophilic character, which facilitates water expulsion at 40 °C when the process is jamming-free. At 50 °C, by contrast, in the first minutes, the deswelling kinetics is seemingly unaffected by its presence, but is then followed by a significant deceleration. The structure of the GO@PNIPAM composites is different from that of the CNT@PNIPAM systems, and as GO sheets have higher surface area than CNTs, they offer a greater possibility for polymer chains to stick to their surface during the shrinkage. As the polymer chains move during deswelling, they have to drag the GO with them; since other chains may try to move the platelets in the opposite direction, deswelling is significantly slowed. A similar process can occur in the case of the CNT@PNIPAM, but the effect is less pronounced, owing to the smaller number of attached polymer chains.

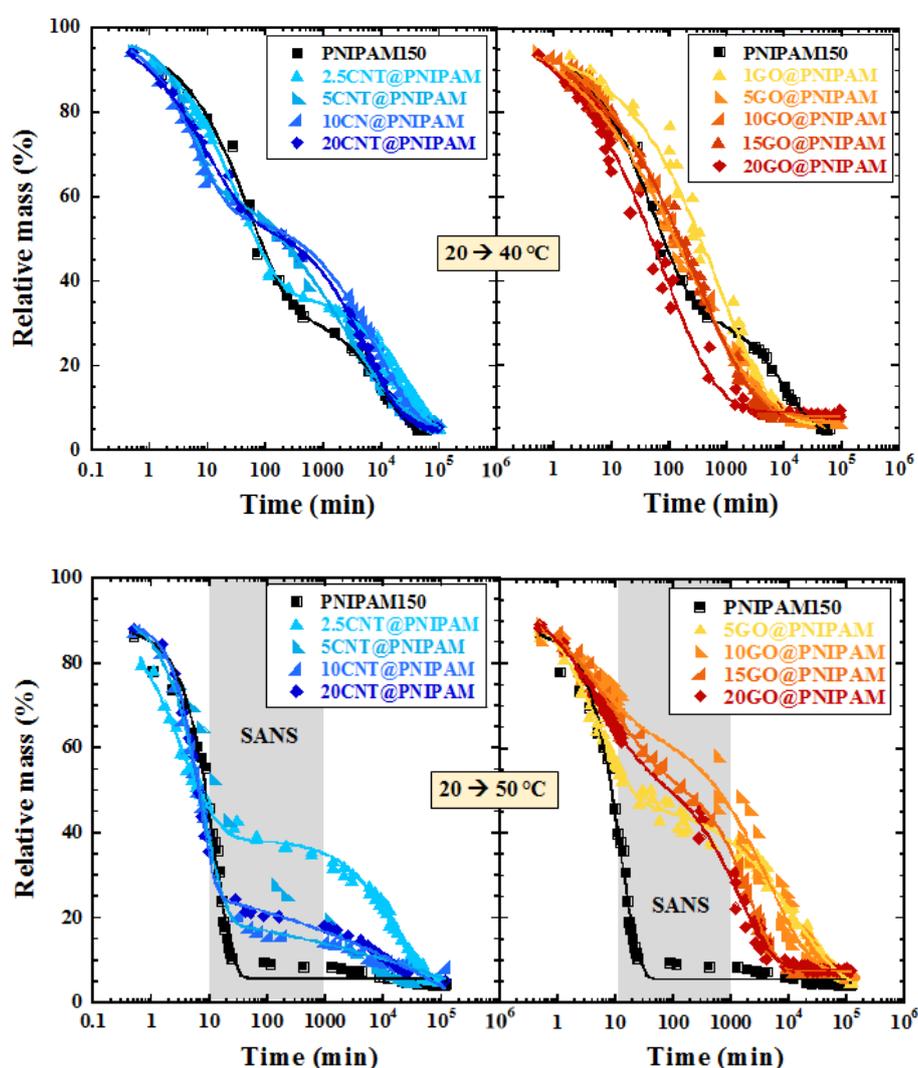


Figure 4. Semi-logarithmic plot of temperature jump ($20 \rightarrow 40 \text{ }^\circ\text{C}$ and $20 \rightarrow 50 \text{ }^\circ\text{C}$) induced shrinkage kinetics of pure PNIPAM gel (\square), and CNT@PNIPAM (blue symbols) and GO@PNIPAM (red symbols) nanocomposite samples.

The results from RGO@PNIPAM and (GO@PNIPAM)_R systems can shed light on the effect of hydrophilicity and available surface area. The RGO@PNIPAM gels contain aggregates, which limit the available surface. As a result, their behaviour is similar to that of the CNT@PNIPAM composites. Conversely, when GO was reduced inside the polymer matrix the available surface area did not change significantly, but the hydrophilicity of the sheets was strongly modified. Owing to these properties, the deswelling of the (GO@PNIPAM)_R systems was slower than for any other of the materials investigated.

4. New scientific results

1. The studied CNPs with various shape and surface chemistry: a slightly surface modified CNT, a hydrophilic GO with high oxygen-content and RGO, had different effects on the *equilibrium* properties and kinetics of the prepared composites systems. [1-4]
2. The CNTs formed aggregates in the aqueous system prior the gel synthesis. The presence of the aggregates yielded an inhomogeneous distribution. It did not significantly influence the elastic modulus and swelling properties of the composites but caused a concentration-dependent increase in the fracture strength and decrease in the polymer-polymer correlation length in the swollen state. [4]
3. Incorporation of GO resulted in a rather homogeneous system. GO reduced the swelling capacity but increased the elastic modulus and the fracture strength of the gels up to a plateau value. The internal gel structure exhibited a strong dependence on GO concentration and revealed the presence of the percolation threshold. [3,4]
4. Reduction of the GO can be carried out efficiently with ascorbic acid even at room temperature. Since the measurements performed (mechanical and swelling properties, microscopic structure) showed that this procedure does not modify the PNIPAM matrix, it was found to be an efficient method for reducing the GO after the composite synthesis. [2]
5. Macroscopic, thermogravimetric and solid-state NMR studies revealed strong interactions between the GO and the polymer matrix, which are practically retained after the post-reduction treatment; however, no clear evidence of covalent bonds was found. The swelling and mechanical properties of the GO@PNIPAM systems were conserved after the post-reduction. At the same time, RGO and CNT interact only weakly when they are incorporated directly into the gel, and cause only minor structural modification in the nanocomposites. [2]
6. Both microscopic and macroscopic observations on the shrinkage kinetics of the system show that both the type and the concentration of the CNP as well as the applied temperature gradient can be used to tune the kinetics of the temperature response of the

nanocomposites. The kinetics of the deswelling found to be altered by the shape and the hydrophilicity/hydrophobicity of the incorporated nanoparticles in a complex manner. [1]

7. Based on the results of the various systems a new structure is proposed for the CNP containing systems. During polymerisation, the GO particles can act not only as network fillers but can also contribute to nucleating the polymerisation reaction at their surfaces, thereby forming strong bonds. With increasing GO content, the gel is reinforced by the filler and the architecture of the network is increasingly dominated by cross-link hypernodes, at the expense of the simple tetrafunctional cross-link structure that prevails with the BA cross-linker alone. Incorporation of the RGO and the CNT occurs in aggregates that do not modify the character of the gel structure; their effect is limited to the characteristic distances inside the matrix. [1]

5. Applications

Thermoresponsive hydrogels have enormous potential e.g., as sensors, actuators, and pollution control remedies or in drug delivery systems.

Incorporated CNP improves their fracture strength and, in some cases, the elastic modulus as well, which is a requirement for load-bearing applications.

The kinetics of the temperature response can be tuned by the quality and quantity of the filler, thereby broadening their possible applications as sensors and drug delivery systems.

The tuneability of the response makes them interesting for microfluidics. For this application faster response rates are required, which can be achieved by the downsizing of the systems investigated.

6. Publications

Related papers

1. **B. Berke**, L. Porcar, O. Czakkel, K. László: Correlation between structure and responsivity in PNIPAM based nanocomposites: a combined nano- and macroscale view. *European Polymer Journal*, 99 (2018) 180-188. - IF: 3.531 (2016/2017) I:-
2. **B. Berke**, L. Sós, V. Bérczes, A. Domján, L. Porcar, O. Czakkel, K. László: Graphene-derivates containing responsive hydrogels: Effect of concentration and surface chemistry. *European Polymer Journal*, 93 (2017) 717-725. - IF: 3.531 (2016/2017) I:-
3. **B. Berke**, O. Czakkel, L. Porcar, E. Geissler, K. László: Static and dynamic behaviour of responsive graphene oxide - poly (N-isopropyl acrylamide) composite gels. *Soft Matter*, 12 (2016) 7166-7173. - IF: 3.889 I:2
4. E. Manek, **B. Berke**, N. Miklósi, M. Sajbán, A. Domán, T. Fukuda, O. Czakkel, K. László: Thermal sensitivity of carbon nanotube and graphene oxide containing responsive hydrogel composites. *Express Polym. Lett.* 10 (2016) 710–720. - IF: 2.983 I:5

Other papers

1. N. Justh, **B. Berke**, K. László, I. M. Szilágyi: Thermal analysis of the improved Hummers' synthesis of graphene oxide. *J. Therm. Anal. Calorim.* (2017) accepted
DOI: 10.1007/s10973-017-6697-2
2. M. Szabó, **B. Berke**, K. László, Zs. Osváth, A. Domján: Non-covalent interactions between Poly(N-isopropylacrylamide) and small aromatic probe molecules studied by NMR spectroscopy. *European Polymer Journal*, 93 (2017) 750-760.
IF: 3.531 (2016/2017) I:-
3. K. Voitko, A. Tóth, E. Demianenko, G. Dobos, **B. Berke**, O. Bakalinska, A. Grebenyuk, E. Tombácz, V. Kuts, Y. Tarasenko, M. Kartel, K. László: Catalytic performance of carbon nanotubes in H₂O₂ decomposition: experimental and quantum chemical study. *Journal of Colloid and Interface Science* 437 (2015) 283-290. - IF: 3.782 I:9
4. P. Podkościelny, A. Tóth, **B. Berke**, K. László, K. Nieszporek: Heterogeneity of multiwalled carbon nanotubes based on adsorption of simple aromatic compounds from aqueous solutions. *ADSORPTION*, 20 (5-6) (2014) 789-800. - IF: 1.771 I:3

Conferences

Oral presentations

1. **B. Berke**, O. Czakkel, L. Porcar, K. László: Thermoresponsive hydrogel nanocomposites with tuneable deswelling kinetics. *International Conference on Neutron Scattering 2017* (9-13.07.2017. Daejeon, Republic of Korea)
2. **B. Berke**, O. Czakkel, L. Porcar, E. Geissler, K. László: Effect of graphene oxide loading on the thermal responsiveness of PNIPA based hydrogels. *3rd International Conference on Bio-based Polymers and Composites* (28.08.-01.09.2016. Szeged, Hungary)
3. **B. Berke**, O. Czakkel, K. László: Carbon nanoparticle containing responsive hydrogel composites. *All You Need Is Neutrons Seminar*, Institut Laue-Langevin (17.05.2016. Grenoble, France)
4. L. Sós, **B. Berke**, K. László: Poly(N-isopropyl-acrylamide) based reduced graphene oxide containing hydrogels – the effect of the reduction route. *13th International Conference „Students for Students”* (13-17.04.2016. Cluj Napoca, Romania)
5. **B. Berke**, L. Sós, O. Czakkel, K. László: Carbon nanoparticle containing responsive gel composites. *Annual PhD Conference of George Oláh Doctoral School of Budapest University of Technology and Economics* (11.02.2016. Budapest, Hungary)
6. **B. Berke**: Carbon nanoparticles and their composites. *BEST (Board of European Students of Technology) summer course: DARE to DATE new MATERIALS - Discover the world of materials sciences!* (15.07.2015. Budapest, Hungary)
7. **B. Berke**: Synthesis and characterization of copper containing lignocellulosic porous carbons. *Students for Students International Conference 7th Edition* (23-25.04.2010. Cluj Napoca, Romania)
8. **B. Berke**: Synthesis and characterization of copper containing lignocellulosic porous carbons. *XXX. National Scientific Students' Associations Conference* (27-29.04.2011. Pécs, Hungary) - **1st prize**
9. **B. Berke**: Synthesis and characterization of copper containing lignocellulosic porous carbons. *Scientific Students' Associations Conference at Budapest University of Technology and Economics* (18.09.2009. Budapest, Hungary) - **2nd place**

Posters

1. **B. Berke**, L. Porcar, O. Czakkel, K. László: Carbon nanoparticle containing hydrogel nanocomposites with enhanced IR sensitivity. *Carbon 2017* (23-28.07.2017. Melbourne, Australia)

2. **B. Berke**, L. Sós, V. Bérczes, A. Domján, L. Porcar, O. Czakkel, K. László: Graphene-derivative containing responsive hydrogels: effect of concentration and surface chemistry. *European Polymer Federation Congress 2017* (2-7.07.2017. Lyon, France)
3. **B. Berke**, L. Porcar, O. Czakkel, K. László: Thermoresponsive hydrogel nanocomposites with tuneable deswelling kinetics. *APME2017: The 12th International Conference on Advanced Polymers via Macromolecular Engineering* (21-25.05.2017. Ghent, Belgium)
4. **B. Berke**, O. Czakkel, L. Porcar, E. Geissler, K. László: Effect of graphene oxide loading on the mechanical and thermoresponsive properties of PNIPA based hydrogels. *4th International Soft Matter Conference* (12-16.09.2016. Grenoble, France)
5. L. Sós, **B. Berke**, O. Czakkel, K. László: Reduced graphene oxide containing responsive hydrogels. *3rd International Conference on Bio-based Polymers and Composites* (28.08.-01.09.2016. Szeged, Hungary)
6. **B. Berke**, L. Sós, O. Czakkel, K. László: Effect of surface chemistry of graphene oxide on its compatibility with organic matrix. *CARBON Conference* (10-15.07.2016. Pennsylvania, USA)
7. **B. Berke**, O. Czakkel, L. Porcar, E. Geissler, K. László: Effect of carbon nanoparticle loading on the mechanical and thermoresponsive properties of PNIPA based hydrogels. *24th Journées de la Diffusion Neutronique* (2-4.05.2016. Carqueiranne, France)
8. V. Bérczes, **B. Berke**, O. Czakkel, K. László: PNIPA-based responsive hydrogels – Effect of the cross-linker. *13th International Conference „Students for Students”* (13-17.04.2016. Cluj Napoca, Romania)
9. **B. Berke**, O. Czakkel, L. Porcar, E. Geissler, K. László: Effect of graphene oxide loading on the mechanical and thermoresponsive properties of PNIPA based hydrogels. *Hercules School* (01.04.2016. Grenoble, France)
10. E. Manek, **B. Berke**, N. Miklósi, M. Sajbán, K. László: Improvement of hydrogel biomedical potentials by the incorporation of carbon nanoparticles. *International Symposium on Amphiphilic polymers, networks, gels and membranes* (30.08.-2.09.2015. Budapest, Hungary)
11. E. Manek, **B. Berke**, N. Miklósi, M. Sajbán, T. Fukuda, M. Trenikhin, T. Maekawa, Y.G. Kryazhev, K. László: Nanoparticle containing soft hybrid materials. *The Fourth Symposium on Future Challenges for Carbon-based Nanoporous Materials* (16-18.03.2015. Nagano, Japan)

12. **B. Berke**, D. Ábrahám, L. Sós, B. Pőcze, G. Dobos, K. László: Effect of temperature on thermal reduction of graphene oxide. *George Oláh Annual Phd Conference* (5.02.2015. Budapest, Hungary)
13. E. Manek, **B. Berke**, N. Miklósi, M. Sajbán, T. Fukuda, M. Trenikhin, T. Maekawa, Y.G. Kryazhev, K. László: Kinetics of temperature induced phase transition of poly(N-isopropylacrylamide)-carbon nanoparticle hybrid hydrogels. *ENSOR workshop* (1-3.03.2015, Brighton, UK)
14. **B. Berke**, D. Ábrahám, L. Sós, B. Pőcze, G. Dobos, K. László: Thermal reduction of graphene oxide. *ENSOR workshop* (1-3.03.2015. Brighton, UK)
15. **B. Berke**, A. Tóth, G. Dobos, M. Heggen, T. Igricz, K. László: Preparation and characterization of surface modified carbon nanotubes. *10th Conference on Colloid Chemistry* (27-29.08.2012. Budapest, Hungary)
16. **B. Berke**, A. Tóth, T. Kulik, B. Palyanytsya, O. Dudik, V. Gun'ko, K. László: A comparative TPD-MS investigation of MWCNT samples. A new method for the chlorination of MWCNT under mild conditions. *10th Conference on Colloid Chemistry* (27-29.08.2012. Budapest, Hungary)
17. **B. Berke**, A. Tóth, Gy. Samu, G. Dobos, M. Heggen, T. Igricz, K. László: Characterization of surface modified carbon nanotubes. *Precarbon Conference* (16-18.06.2012. Budapest, Hungary)
18. A. Tóth, K. Voitko, **B. Berke**, O. Bakalinska, M. Kartel, E. Lőcsei, K. László: Morphology and surface chemistry of air-treated carbon. *Precarbon Conference* (16-18.06.2012. Budapest, Hungary)
19. **B. Berke**, A. Pilbáth, G. Dobos, Gy. Onyestyák, K. László: Transition metal doped lignocellulosic porous carbons for ammonia removal. *4th International Conference on Carbons for Energy Storage/ Conversion and Environment Protection* (24-29.09.2011. Vichy, France)
20. A. Tóth, **B. Berke**, K. V. Voitko, O. Bakalinska, V. Gun'ko, K. László: Nitrogen, propane and water vapour adsorption on O-and N-functionalized multiwalled carbon nanotubes. *Modern Problems of Chemistry and Physics of Surface* (11-13.05.2011. Kiev, Ukraine)
21. **B. Berke**, A. Tóth, Gy. Onyestyák, K. László: Synthesis and characterisation of copper containing lignocellulosic porous carbon. *Modern Problems of Chemistry and Physics of Surface* (18-21.05.2010. Kyiv, Ukraine)