

## Thermo- and pH-sensitive Hydrogels with Incorporated Multi-Walled Carbon Nanotubes

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Carbon nanotubes (CNTs) attract great attention due to the unique combination of physical, chemical, electrical and mechanical properties which have high potential for design of nanocomposite materials with customized properties (electromagnetic shielding, high strength and electroconductivity materials), actuators (e.g. artificial muscles and tissues), sensors, components of microfluidic devices, *etc.* Usage of CNT in practical applications is limited by their lower solubility in most solvents. Remaining primary agglomerates of NT not only increase the amount of filler needed for percolation, but also act as imperfections under mechanical stress. Therefore, in this investigation, the influence of surfactant type and its concentration, along with sonication treating time on sedimentation behavior of multi-walled carbon nanotubes was investigated. To a greater extent, the influence of monomer composition, surface-active substances, and carbon nanotubes on gelation and physicochemical properties of thermo- and pH-sensitive hydrogels and hydrogel nanocomposites based on N-isopropylacrylamide with carbon nanotubes were investigated too.

**Keywords:** Thermosensitive, pH-sensitive, Hydrogels, Carbon Nanotubes, Nanocomposites.

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### 1. INTRODUCTION

Carbon nanotubes (CNTs) attract great attention in the last decades due to the unique combination of physical, chemical, electrical and mechanical properties which have high potential for design of composite materials with customized properties (construction materials, electromagnetic shielding, high strength and electroconductivity materials), actuators (e.g. artificial muscles and tissues), sensors, components of microfluidic devices, *etc.* Usage of CNT in practical applications is limited by their lower solubility in most solvents. However, for reinforcement of different polymeric matrices, CNTs must possess uniform dispersion. In this context, an excellent distribution and dispersion of CNTs is an essential precondition for the effective use of the potential of the nanofiller. Remaining primary agglomerates of carbon NTs not only increase the amount of filler needed for percolation but also act as imperfections under mechanical stress.

Carbon nanotubes can be incorporated into thermosensitive hydrogels based on N-isopropylacrylamide (NIPAAm) with promise to yield significant improvements and new functionalities. Hydrogel system based on NIPAAm has emerged as one of the most extensively studied ones for thermoresponsive applications. A key feature of such system is a lower critical solution temperature (LCST) that occurs in the temperature range of 32-34°C, and it is comparable to the temperature range which can be triggered by both physiological and environmental conditions. Upon heating above the LCST, the phase transition in hydrogel occurs resulting in a drastic change in the hydrogel volume by water expulsion, and it is connected with the transition between two conformation structures of the polymer side groups [1]. Taking into account the fact that the phase

transition temperature or LCST of thermosensitive systems depends on hydrophilic-lipophilic balance, it can be moved to any side during copolymerization of NIPAAm with hydrophilic or hydrophobic monomers. Thus, NIPAAm's copolymerization with hydrophilic monomers leads to the increase of phase transition temperature, while its copolymerization with hydrophobic monomers gives the opposite effect [2]. Furthermore hydrogels systems sensitive to a several stimuli can be obtained copolymerizing of NIPAAm with different stimuli responsive monomers. A rare instance of such copolymeric systems is hydrogels based on NIPAAm and acrylic acid (AA), which possess thermo- and pH-sensitivity.

It have been shown [3] that hydrogel nanocomposites based on NIPAAm with single-walled carbon nanotubes exhibit up to 5 times enhancement in the thermal response time compared to pure NIPAAm hydrogels. Therefore, in this investigation, the influence of surfactant type and its concentration, along with sonication time on sedimentation behavior of multi-walled carbon nanotubes was investigated. To a greater extent, the influence of monomer composition, surface active substances, and carbon nanotubes on gelation and physicochemical properties of thermo- and pH-sensitive hydrogels and hydrogel nanocomposites based on N-isopropylacrylamide with CNTs were investigated too.

### 2. MATERIALS AND METHODS

#### 2.1 Materials

N-isopropylacrylamide (NIPAAm) (Sigma-Aldrich, 97%) was recrystallized from n-hexane and dried under vacuum. Acrylic acid (AA) (Merck) was distilled and then subjected to fractional crystallization. Acrylamide

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(AAm) (Merck, 99.9%), N,N'-methylenebisacrylamide (MBA) (Merck, 98%), ammonium persulfate (PSA) (Sigma, 98%), N,N,N',N'-tetramethylethylenediamine (TMED) (Merck, 99%), multi-walled carbon nanotubes (CNT), Triton X-100 (TX-100) (AppliChem GmbH, M=646.85Da), Tween 80 (T-80), sodium dodecyl sulfate (SDS), and sodium dodecylbenzenesulfonate (SDBS) were used as received without preliminary purification.

## 2.2 Synthesis of hydrogels

(Co)polymeric hydrogels based on NIPAAm, AAm and AA were synthesized by means of radical polymerization in water medium at 15°C. Covalent cross-linking of copolymeric chains was accomplished using bifunctional monomer MBA. Initiation of the polymerization was performed with the help of the redox system composed of ammonium persulfate (PSA) and N,N,N',N'-tetramethylethylenediamine TMED [2].

(Co)polymeric gel composition was determined by the composition of the reaction mixture and was found to be as follows: weight fraction of monomers constituted 10%, 15% or 20%; MBA – 0.20%, 0.10% or 0.05%; concentration of the equimolar initiating mixture was 0.04mol/L for hydrogels based on NIPAAm (NIPAAm with AAm) and 0.08mol/L for hydrogels based on NIPAAm with AA.

## 2.3 Synthesis of nanocomposites

In order to obtain nanocomposites an aqueous dispersion of NT stabilized by surface-active substances (SAS) were added during the synthesis of hydrogels.

(Co)polymeric gel composition with carbon CNTs was determined by the composition of the reaction mixture and was found to be as follows: weight fraction of monomers constituted 20%; MBA – 0.10%; concentration of NTs – 0, 0.05, 0.10 and 0.25%; concentration of the equimolar initiating mixture was 0.04mol/L for hydrogels based on NIPAAm (NIPAAm with AAm) and 0.08mol/L for hydrogels based on NIPAAm with AA.

## 2.4 Dispergation of CNT

The sedimentation behavior of CNTs dispersed in water and aqueous surfactant solutions was investigated. CNTs were added into an aqueous solution of SAS with different concentration, concentration of CNTs was 0.01%, the ratio between SAS and NT was 0:1, 1:1, 2.5:1, 5:1, 7.5:1, 10:1, 15:1, 20:1, 30:1, 40:1, and 50:1. Carbon nanotubes were dispersed at room temperature using ultrasound bath (Transsonic T 460/H, frequency 36 kHz, Elma, Germany) for 5 min and ultrasonic disperser (UZDN-2T, frequency 44 kHz, and the output power of 150 W, Ukrrospribor, Sumy, Ukraine) for 1min. Control pictures were taken in 7 days after dispergation.

## 3. RESULTS AND DISCUSSIONS

The sedimentation stability of CNTs suspensions in water and water solutions of SAS may serve as characteristic of their dispersion ability. The dispersability of carbon nanotubes is mainly influenced by the entanglement structure of the tubes within the as-produced primary CNT agglomerates determining also the ag-

glomerate strength. In general, due to strong van der Waals forces CNTs exhibit a tendency to formation of agglomerates and bundles during synthesis (see Fig. 1), and also during their dispergation and incorporation into the polymeric matrices.

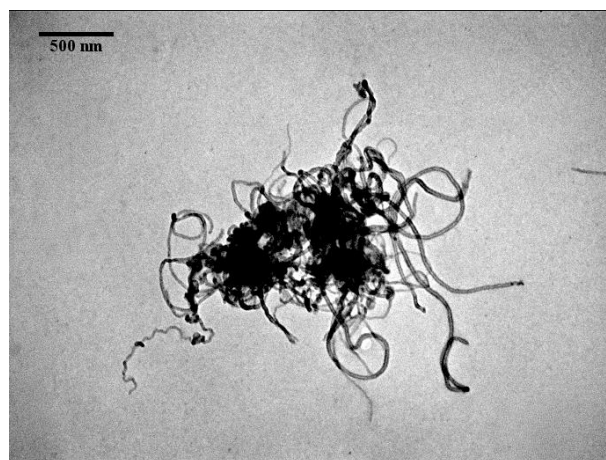


Fig. 1 – Microphotography (TEM) of multi-walled carbon nanotubes.

Pristine CNTs dispersed in water start to precipitate immediately after sonication. As can be seen on Fig. 2 the sedimentation rate increases with increasing of NTs concentration due to so-called swarm sedimentation.

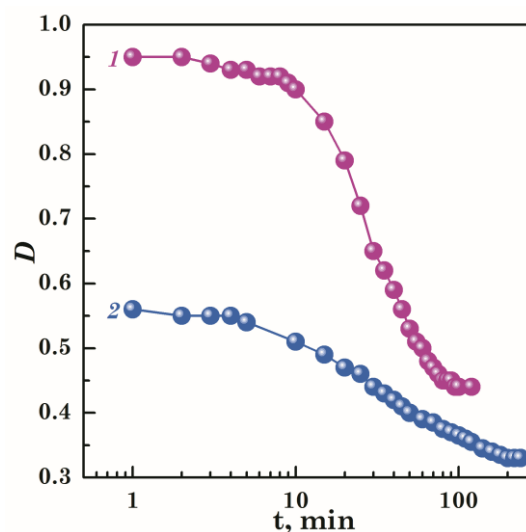
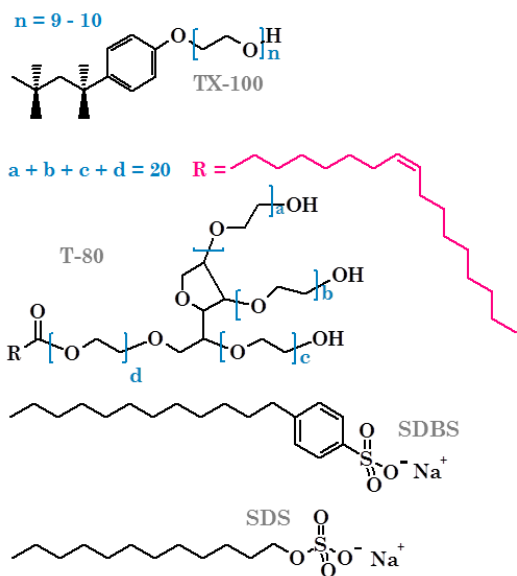


Fig. 2 – Time dependence of optical density at 490nm of CNT suspensions in water with different concentration of nanotubes: 1 – 0.0050%; 2 – 0.0025%.

Dispergation of nanotubes with formation of stable suspensions is of crucial importance for obtaining of hydrogel nanocomposites of high quality. For this purpose CNTs were sonicated in water solutions of four types of SAS (see Fig. 3) at different concentrations. Nonionic (TX-100 and T-80) and anionic (SDBS and SDS) SAS have been used for stabilization of water suspensions of carbon NTs.

The influence of all types of SAS on the stability of aqueous dispersions of CNTs was analyzed using SAS

series (see Fig. 4). Stable dispersions were obtained with certain ratio of SAS to CNTs for all surfactants, e.g. for TX-100 and T-80 it is 2.5:1, for SDBS – 2:1, and for SDS – 3:1. Comparing the results it can be concluded that TX-100 and SDBS stabilized water suspensions of CNTs is the best. High dispersive efficiency of these substances can be explained by the presence of benzene ring combined with the small head group.



**Fig. 3** – Structures of surface-active substances: TX-100, T-80, SDBS, and SDS.



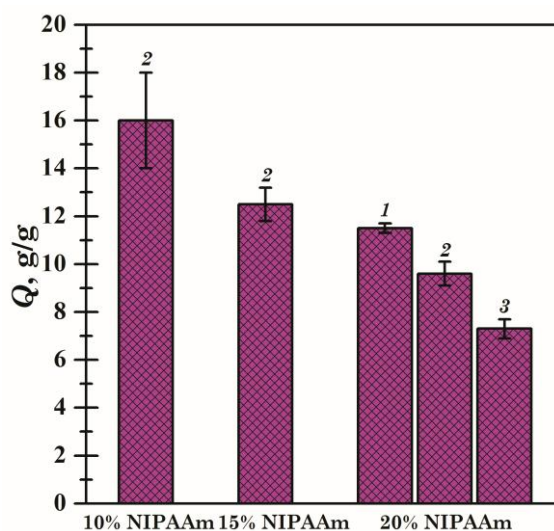
**Fig. 4** – Photo of CNTs suspensions stabilized by TX-100 with different ratio between SAS and NTs. Concentration of CNTs is 0.01%.

Addition of monomers to CNTs suspensions influences on its stability. Thus, AAm improves dispergation of nanotubes and does not change the ratio between SAS and carbon NTs, while NIPAAm and AA have opposite effect. This have to be taken into account for obtaining nanocomposites with CNTs based on NIPAAm and AA.

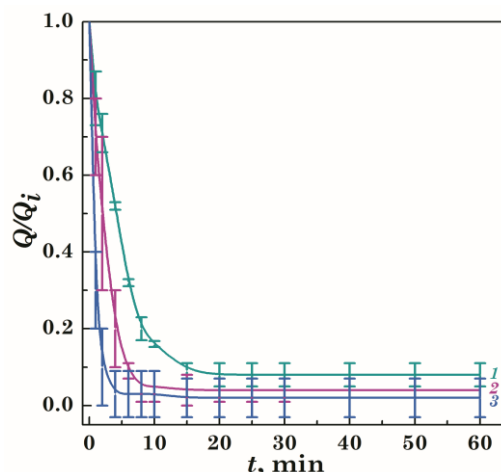
Study of the dependence of hydrogel equilibrium swelling degree on composition allowed choosing matrix, which possess a sufficient strength and have optimal swelling degree (see Fig. 5). Thereby copolymeric hydrogels and nanocomposites with CNTs were synthesized based on matrix with 20%-content of monomers.

Since hydrogels and nanocomposites are promising in terms of their use as actuators, components of microfluidic devices, *etc.* they have quickly respond to external changes. Studying of hydrogel collapse have allowed choosing the suitable matrixes which will be used for obtaining nanocomposites with incorporated NTs based on them. As can be seen on

Fig. 6 homopolyisopropylacrylamide matrix in the initial stage collapses linearly. Furthermore collapse rate decreases with increasing content of MBA and comonomer content.



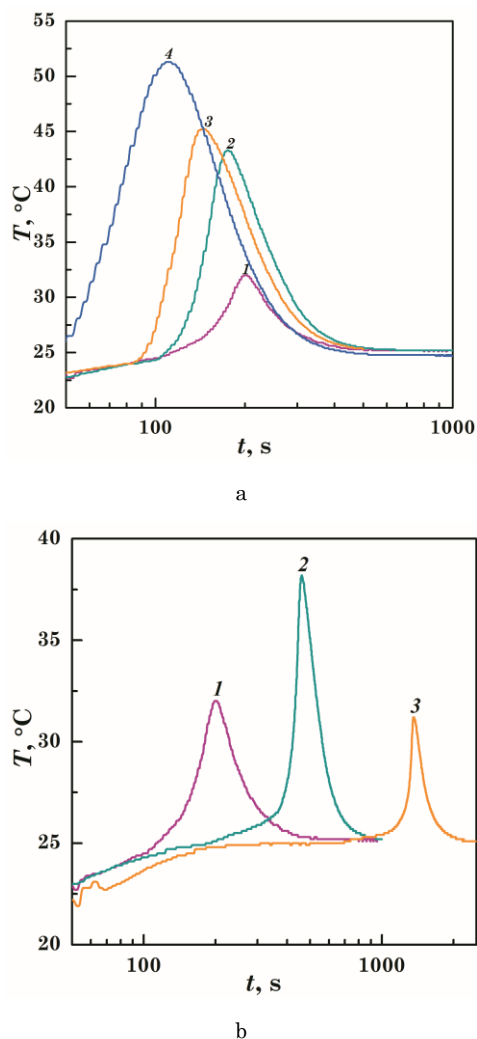
**Fig. 5** – Equilibrium swelling degree of hydrogels based on NIPAAm with different concentration of monomer and at different concentration of MBA: 1 – 0.05%; 2 – 0.10%; 3 – 0.20%.



**Fig. 6** – Time dependence of normalized hydrogel swelling degree of matrixes with 20%-content of NIPAAm and different concentration of MBA when the temperature changes from 25°C to 50°C: 1 – 0.20%; 2 – 0.10%; 3 – 0.05%.

To a greater extent, the influence of monomer composition, SAS and carbon NTs on gelation and physicochemical properties of thermo- and pH-sensitive hydrogels and hydrogel nanocomposites based on N-isopropylacrylamide with CNTs were investigated. It has been shown that different additives to gel composition based on NIPAAm have different effect on the polymerization (gelation). Thus, addition of AAm and CNTs accelerate the polymerization (see Fig. 7.1, Table 1), while AA and SAS have opposite effect (see Fig. 7.2, Table 1).

Hydrogel nanocomposites with incorporated CNTs improve such properties as collapse rate and strength, and increase the electroconductivity of thermo- and pH-sensitive systems.



**Fig. 7** – Temperature ( $T$ ) during the polymerization of (co)polymeric hydrogels based on NIPAAm with AAm (a), and AA (b): 1 – 100% NIPAAm; 2 – 95% NIPAAm; 3 – 90% NIPAAm; and 4 – 0% NIPAAm.

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**Table 2** – Polymerisation time ( $t$ ) for copolymeric hydrogels based on NIPAAm with AAm and AA.

| w(NIPAAm),% | NIPAAm+AAm | NIPAAm+AA |
|-------------|------------|-----------|
|             | $t$ , sec  | $t$ , sec |
| 100         | 200        |           |
| 95          | 175        | 461       |
| 90          | 145        | 1355      |
| 0           | 110        | 4717      |

## 4. CONCLUSIONS

Our study has shown that investigation of the sedimentation behavior of carbon nanotubes dispersed in aqueous surfactant solutions are suitable in order to determine type and ratio between SAS and NTs. It has been shown that TX-100 and SDBS have a high dispersive efficiency with the ratio ca. 2-2.5. Compared to other surfactants, we found SDBS to be more stable in NIPAAm and AA monomer solutions.

Investigating the equilibrium swelling degree and collapse we determined the most suitable composition of polymeric matrixes which can be used as actuators and components of microfluidic devices. It has total content of monomers equal to 20% and 0.10%-content of MBA. Copolymer hydrogel based on NIPAAm with 5%-content of AAm and 10%-content of AA has optimal properties (strength, collapse rate, the value of swelling degree and LCST, etc.) among other copolymeric matrixes.

Hydrogel nanocomposites with incorporated CNTs improve such properties as collapse rate and strength, and increase the electroconductivity of thermo- and pH-sensitive systems.

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