Hydrogel-MWCNT Nanocomposites: Synthesis, Characterization, and Heating with Radiofrequency Fields

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ABSTRACT: Hydrogel nanocomposites are attractive biomaterials for numerous applications including tissue engineering, drug delivery, cancer treatment, sensors, and actuators. Here we present a nanocomposite of multiwalled carbon nanotubes (MWCNT) and temperature responsive *N*-isopropylacrylamide hydrogels. The lower critical solution temperature (LCST) of the nanocomposites was tailored for physiological applications by the addition of varying amounts of acrylamide (AAm). The addition of nanotubes contributed to interesting properties, including tailorability of temperature responsive swelling and mechanical strength of the resultant nanocomposites. The mechanical properties of the nanocomposites were studied over a range of temperatures (25–55°C) to characterize the effect of nanotube addition. A radiofrequency (RF) field of 13.56 MHz was applied to the nanocomposite discs, and the resultant heating was characterized using infrared thermography. This is the first report on the use of RF to remotely heat MWCNT-hydrogel nanocomposites. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 117: 1813–1819, 2010

Key words: hydrogels; nanocomposites; carbon nanotubes; radiofrequency; temperature responsive

INTRODUCTION

Hydrogels are hydrophilic polymeric networks that can imbibe a large amount of biological fluids including water and can swell several times their dry volume. Hydrogels have good biocompatibility and applications in medical and pharmaceutical fields including controlled drug delivery, tissue engineering, diagnostic devices, contact lenses, and biosensors.[1] Responsive hydrogels are a class of hydrogels with swelling properties dependent on the surrounding environment such as pH, temperature, the presence of a particular molecule, or ionic strength. Responsive hydrogels have been demonstrated in various applications such as sensors, pulsatile drug release devices, and valves for active flow control in microfluidic devices.[2,3]

Hydrogel nanocomposites are synthesized by incorporating nanoparticles into a hydrogel matrix. Nanoparticulates can impart unique properties to the matrix, such as enhanced mechanical strength, drug release profile, remote actuation capabilities, and biological interactions. Several researchers have developed hydrogel nanocomposites with different particulates including clay, gold, silver, iron oxide, carbon nanotubes, hydroxyapetite, and tricalcium phosphate.[4] Hydrogel nanocomposites have been demonstrated in numerous biomedical applications such as tissue engineering scaffolds,[5] remote controlled drug delivery systems,[6] sensors,[7] and actuators.[8,9] In recent years, interest in incorporating carbon nanotubes into hydrogel matrices has grown.

Carbon nanotubes (CNTs) are cylindrical graphite hollow tubes with one or more concentric layers. They have high aspect ratios and unique mechanical, thermal, and electrical properties. Superior thermal and electrical properties of CNTs are useful for a wide range of applications including electrochemical and electronic devices, sensors, and probes.[10] The high mechanical strength makes them attractive materials for polymer reinforcement.[11] CNTs have attracted a lot of interest in biological applications including tissue engineering, biosensors, drug delivery, imaging, and cancer treatment.[12] Their ease of surface functionalizations allows for the attachment of desired molecules to enhance solubility, biocompatibility, and applications.[13]

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Incorporation of small amounts of CNTs can significantly enhance the properties of the hydrogel matrix. It was reported that the addition of CNTs to collagen increased the electrical conductivity, and the resultant nanocomposite promoted good cell viability.[14] Bhattacharyya et al. reported fourfold increase in the storage and loss moduli of hyaluronic acid hydrogels by incorporating 0.06 wt % of single-walled carbon nanotubes (SWCNT).[15] Similarly, a few studies have investigated the addition of CNTs into chitosan hydrogels for the purpose of mechanical enhancement,[16] and pH and electrical actuation.[17]

Hydrogel-CNT nanocomposites were also demonstrated for potential applications such as sensors and actuators. Shi et al. demonstrated actuators based on multiwalled carbon nanotubes (MWCNT) and polyvinyl alcohol hydrogels with DC electric field as the stimulus.[18] Due to the fast electron transfer kinetics of CNTs, hydrogel-CNT nanocomposites are being pursued in sensor applications for the detection of a variety of biomolecules including ethanol, glutamate, and glucose.[19,20] In another study, the composite films of poly-*N*-isopropylacrylamide (NIPAAm) and aligned MWCNT arrays showed fast wetting and dewetting behaviors. The electrical conductance of these films was found to be dependent on temperature and water content and, hence, may have applications as temperature and humidity sensors.[7]

In addition, CNTs can be heated by microwaves,[21] radiofrequency (RF) fields,[22] and near-IR light (700–1100 nm).[23] This property can be used for a variety of applications such as cancer treatment,[22,24] antimicrobial agents,[25] and the heating of polymer nanocomposites to drive the polymer transitions.[26–28] Near-IR light was used to remotely trigger shape memory transitions of elastomer-CNT composites.[26,27] Fujigaya et al. embedded SWCNTs into temperature responsive NIPAAm hydrogels and showed that application of a near-IR laser could heat the nanocomposites leading to their collapse.[28] In another study, Miyako et al. showed the near-IR driven thermal transition of composites obtained by incorporating SWCNT in NIPAAm and agarose hydrogels.[29] However, to the best of our knowledge, very little work has been reported so far on the RF heating of CNTs, with no reports on RF heating of CNT-nanocomposites.

In this study, we report synthesis and characterization of the MWCNT nanocomposites of NIPAAm-acrylamide (AAm). NIPAAm is a negative temperature responsive hydrogel, and the addition of AAm to NIPAAm can be used to increase the lower critical solution temperature (LCST), placing it close to the human body temperature (37°C).[30] MWCNT were chosen as the nanoparticulate material because of the potential of enhancements in thermal, electrical, and mechanical properties of the resultant nanocomposites, as well as the capability to remotely heat them with RF. If the heat generated by the nanotubes is sufficient to cause a temperature increase above LCST, the NIPAAm hydrogel matrix will collapse. It is hence possible to remotely heat and actuate the hydrogel-MWCNT nanocomposite. Although there are studies showing toxicity of MWCNT,[31] encapsulation of MWCNT in a nondegradable hydrogel matrix can minimize direct exposure when implanted *in vivo* and reduce their potential toxicity.

The morphology, swelling behavior, and mechanical properties of the nanocomposites were characterized to evaluate the effect of adding different amounts of MWCNT on the hydrogel properties. Finally, a RF field of 13.56 MHz was applied to the hydrogel nanocomposite and the heating effect was characterized for different MWCNT loadings. It is possible to drive the swelling transition of CNT nanocomposites with RF application. To the best of our knowledge, this is the first report on RF heating of MWCNT hydrogel nanocomposites. These nanocomposites can be useful for a range of applications including remote controlled drug delivery, microfluidic valves/pumps, and thermal therapy.

EXPERIMENTAL

Hydrogel synthesis

N-isopropylacrylamide (NIPAAm), acrylamide (AAm), and 2,2-Azobisisobutyronitrile (AIBN) were purchased from Sigma-Aldrich. Tetra (ethylene glycol) dimethacrylate (TEGDMA) was obtained from Polysciences. MWCNT were a generous donation from the Center for Applied Energy Research, at the University of Kentucky. MWCNT had a diameter of 20–30 nm and a length of over 80 μm. TEGO Dispers 710 was obtained from Degussa. All reagents were used as received. Fisher Scientific Sonic Dismembrator Model 500 was used for the mixing of the prepared monomer solutions. Scanning electron microscope Hitachi S4300 was used to investigate the morphology of the nanocomposites.

For the first set of hydrogels, AAm content was gradually increased to obtain gels with molar ratios of NIPAAm:AAm as 100 : 0, 90 : 10, 80 : 20, and 70 : 30. TEGDMA was added as a crosslinker to obtain 1 mol % (NIPAAm and AAm combined). Ethanol was used as the solvent for polymerization and was twice the weight of the combined monomers and crosslinker. Thermal initiator AIBN was then added as 1 wt % of the combined weight of monomers and crosslinker. The mixture was sonicated to ensure complete dissolution and uniformity. The solution was then added to an assembly of clamped glass

plates separated by a 0.75 mm Teflon spacer. The assembly was then placed inside an oven at 60°C for 24 h.

For the second set of hydrogels, NIPAAm: AAm in molar ratio of 80 : 20 were mixed and increasing amounts of MWCNT were added to obtain gels with loadings of 0, 1, 2.5, and 5 wt % of the total of monomer and crosslinker. Ethanol and TEGDMA were added as mentioned above. Surfactant TEGO Dispers 710 was added at four times the weight of MWCNT to enhance their dispersion. Solutions were then sonicated for 5 min to disperse nanotubes uniformly throughout the solution. The initiator was added, and the solutions were polymerized as described above.

After polymerization, the films were removed and washed in deionized water for a week, by changing the water every day to remove unreacted components.

Swelling study analysis

After washing, the gels were cut into 15 mm diameter discs and placed in a vacuum oven until completely dry. The swelling studies were carried out for hydrogels with different NIPAAm: AAm ratios and with different MWCNT loadings by methods described elsewhere.[32] Swelling studies were done in the temperature range of 25–55°C and the volume swelling ratio (Q) was calculated.

Dynamic mechanical analysis (DMA)

All mechanical analyses were completed using dynamic mechanical analysis (DMA) (TA Instruments Q800) in the *DMA multifrequency-Strain* mode on a compression plate setup. The compression plate setup was modified to ensure that gels stay in aqueous environment throughout the analysis. DMA analysis of the nanocomposites with 0, 1, and 5 wt % MWCNT was performed in the temperature range of 25–55°C. The nanocomposites were equilibrated at the set temperature for at least 24 h, cut in circular discs of diameter 3 cm, and promptly placed on the compression plates. The sample chamber of the DMA was heated to the target temperature and held isothermally throughout the experiment. An amplitude of 25 μm was applied to the specimen at a test frequency of 1 Hz. Values of storage modulus, loss modulus, and tan delta were collected and averaged over 15 minutes.

Heating in RF fields

After washing, hydrogel films were placed in a 70°C water bath for at least 24 h to allow them to equilibrate. Hydrogel films were then cut into 15 mm diameter discs and dried in a vacuum oven. Dry hydrogel discs with 0–5 wt % of MWCNT were subjected to RF field of 13.56 MHz and power output of 400 W for 4 min. RF 5S (RF Power Products) power source, with a maximum power output of 550 W, connected to a Variomatch (Dressler) matching network was used to generate the RF field. The solenoid had a diameter of 11 cm, and a total of eight turns. Infrared (IR) camera (SC 4000, FLIR Systems) was used to collect images and record temperatures.

Surface temperatures of the disc were recorded with the IR camera, and results were averaged over three samples. The temperature readings were not affected by the changes in emissivity of samples, because the samples were black in color (with approximate emissivity ~ 1.0). To avoid electrical interference, the IR camera was separately mounted far enough from the solenoid. The IR imaging technique has been used previously and proven to be effective in material characterization.[33]

RESULTS AND DISCUSSION

Hydrogel characterization

The dispersion of nanocomposites appeared uniform to the naked eye. 0 and 5 wt % MWCNT loaded hydrogel nanocomposites were freeze fractured and several cross-sectional SEM pictures were collected. Figure 1 shows the representative images. The 5 wt % loaded nanocomposites show a homogeneous MWCNT dispersion. Uniform dispersion of nanotubes can ensure enhanced mechanical, thermal, and electrical properties. Optimal dispersion will also ensure homogeneous heating of these nanocomposites when exposed to RF fields or near-IR light.

Swelling study analysis

Effect of increasing acrylamide

Swelling studies were performed at varying temperatures to look at the effect of increasing amounts of AAm on swelling transition of the hydrogel system. The purpose of varying the NIPAAm: AAm ratios was to evaluate the effect of AAm on LCST and to obtain a system with desirable actuation around human physiological conditions (37°C). As shown in Figure 2, increasing the amount of AAm shifted the LCST transition to higher temperatures. The hydrogel system without AAm collapsed completely at 32°C, while the system with 30 mol % of AAm collapsed at 55°C. AAm is more hydrophilic than NIPAAm, and it is expected that the addition of AAm would increase the extent of swelling. All systems follow this behavior except NIPAAm:AAm 70 : 30 system in temperature range of 25–32°C. More analysis is needed to further understand the reasons

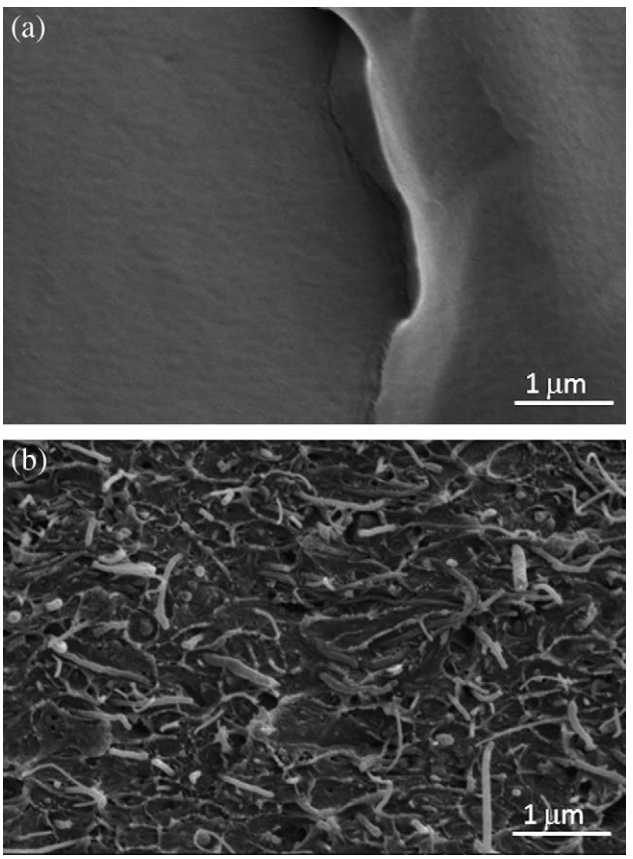

Figure 1 Cross-sectional SEM pictures of NIPAAm-AAm hydrogel matrix with (a) 0 and (b) 5 wt % of MWCNT.

behind this phenomenon. For efficient actuation, it is desirable to have a system that exhibits large volume changes with small changes in temperature. This is controlled to some extent by the amount of cross-linker in the hydrogels. The NIPAAm:AAm 80 : 20 hydrogel with 1 mol % of TEGDMA crosslinker gave significant actuation (ΔQ) around physiological temperature (37°C) and hence was chosen for the addition of varying amounts of MWCNT.

Effect of MWCNT addition

Figure 3 shows the effect of MWCNT addition on the swelling properties of hydrogel with NIPAAm: AAm in 80 : 20 molar ratio and 1 mol % of TEGDMA cross-linking. It is evident that the addition of MWCNT significantly decreased the swelling ratios, with the highest effect on addition of 5 wt % of MWCNT. This could be attributed to the hydrophobic nature of MWCNT and is consistent with other reports in the literature that have looked at the changes in swelling properties due to the addition of MWCNT.[15] On the other hand, the addition of MWCNT did not affect the LCST transition temperature range. The hydrogels were collapsed above 45°C and, hence, there was minimal effect of temperatures or MWCNT loadings above that point. In particular, hydrogel with 5 wt % of MWCNT gave a ΔQ of about 7 between 37 and 45°C, which is significant from the application point of view.

Dynamic mechanical analysis

DMA was performed on hydrated gel discs with three different amounts of MWCNT loadings to compare the effects of increased nanotubes on mechanical properties. It is evident from Figure 4 that for every system, storage modulus increased with increasing temperature up to 45°C. The hydrogels collapsed with increasing temperature, reducing

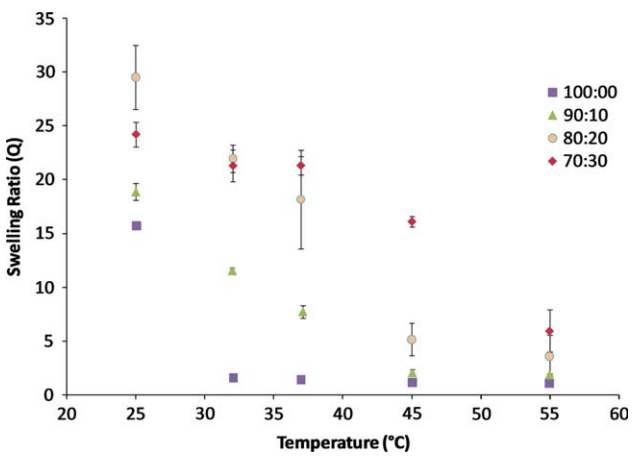

Figure 2 Effect of temperature on equilibrium swelling of hydrogels. The numbers indicate molar ratios of NIPAAm: AAm in hydrogels cross-linked with 1 mol % of TEGDMA. N=3 ±SD. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

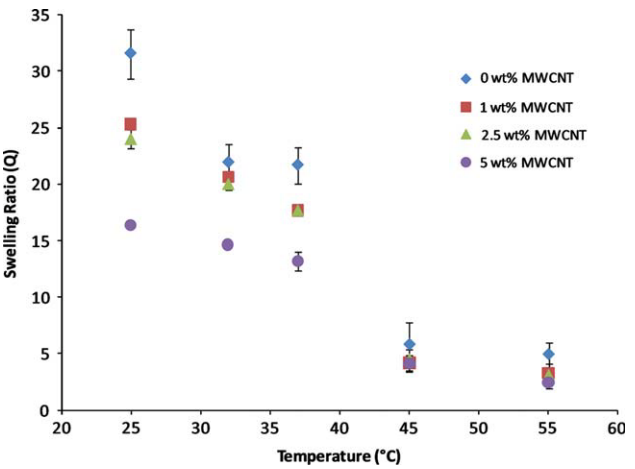

Figure 3 Effect of temperature on the equilibrium swelling of hydrogels with varying amounts of MWCNT. All systems had NIPAAm:AAm in the ratio of 80 : 20 with 1 mol % of TEGDMA as cross-linker. N=3±SD. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

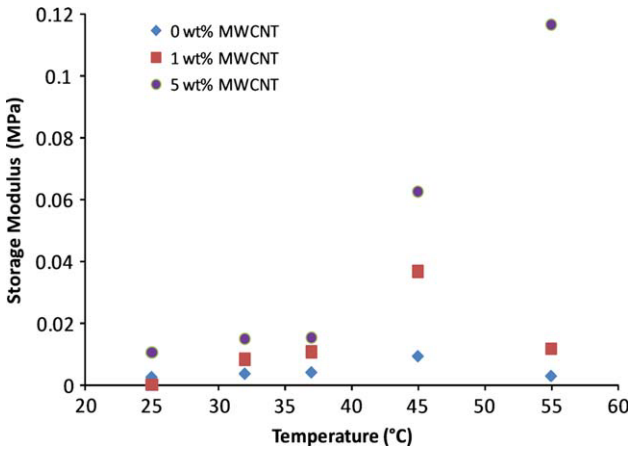

Figure 4 Storage modulus vs. temperature for hydrogels with varying MWCNT loadings. All systems had NIPAAm: AAm in ratio of 80 : 20 with 1 mol % of TEGDMA as crosslinker. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

the amount of water inside them, and thus they exhibited higher mechanical strength. The storage modulus of 0 and 1 wt % of MWCNT loaded gels peaked at 45°C. This effect was not observed for the 5 wt % of MWCNT, and more studies are needed to understand this phenomenon.

There was also an obvious enhancement in storage modulus with increasing amounts of MWCNT. Due to addition of 20 mol % of AAm and low crosslinker content (1 mol %), these hydrogels were highly hydrated at lower temperatures and had low mechanical strength. Manipulation of mechanical properties is crucial for implant applications. MWCNTs possess high mechanical strength and hence their addition leads to better mechanical properties. We see about a fivefold increase in storage moduli with an addition of 5 wt % of MWCNT in temperature range of 25–45°C. In this work, nonfunctionalized MWCNT were physically entrapped in the hydrogel matrix. However, it is expected that the enhancements will be much more if MWCNT were functionalized to enhance the MWCNT-polymer interactions. Favorable nanotube-polymer interfacial interactions can lead to effective load transfer from polymer to nanotubes.[34] Additional studies are on their way to further understand the effect of MWCNT reinforcement.

Heating in RF fields

There are some recent reports on the heating of MWCNT-hydrogel nanocomposites with near-IR light.[28,29] RF at 13.56 MHz can be used as an alternative for near-IR, and has been investigated for cancer therapy applications using CNT.[22] The main advantage of RF over near-IR light is it can penetrate deeper in microfluidic devices or in case of *in vivo* applications. When the MWCNT nanocomposites were subjected to a RF field of 13.56 MHz, there was a significant increase in temperatures. Metallic thermocouples can heat in RF fields, hence infrared (IR) thermography was used to monitor the nanocomposite temperatures. Figure 5 shows the IR images of RF heating of the dry hydrogel nanocomposites containing 2.5 wt % of MWCNT. Starting at 25°C, the

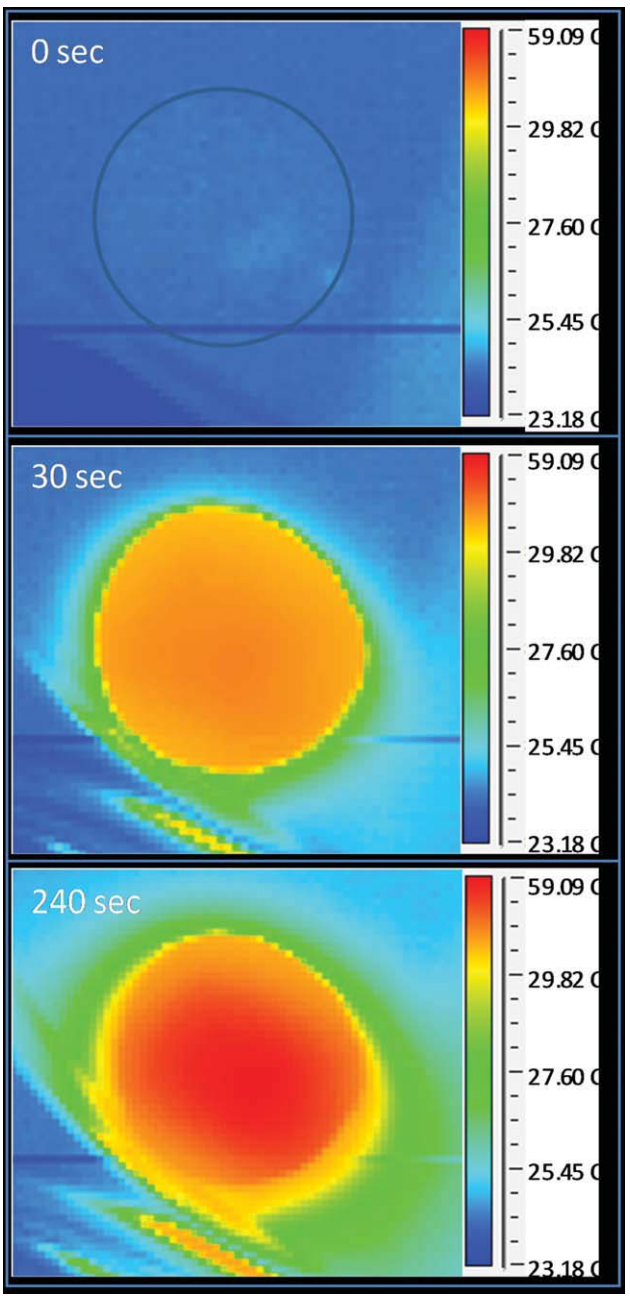

Figure 5 IR images of heating of dry nanocomposites with 2.5 wt % of MWCNT on RF application, at different time points. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

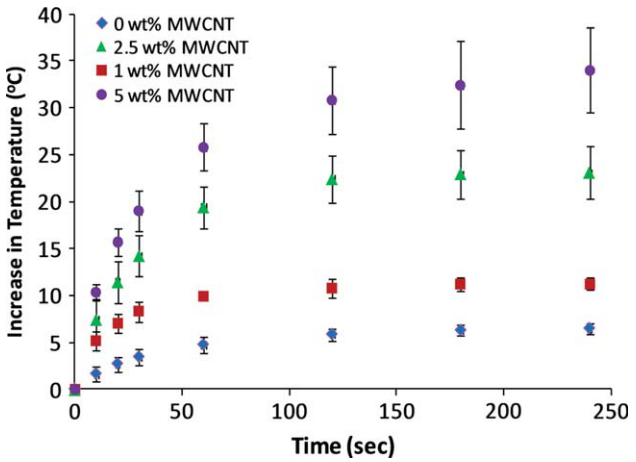

Figure 6 Increase in surface temperatures (ΔT) of dry hydrogel nanocomposites with different loadings of MWCNT during a 4 min RF exposure. N=3±SD. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

surface temperature of the nanocomposite disc increased to about 46°C in 4 min RF exposure.

Increase in temperatures (ΔT) was plotted for dry nanocomposites with 0–5 wt % of MWCNT loadings and is shown in Figure 6. The temperature of the hydrogel with 0 wt % of MWCNT increased by about 5°C, probably due to resistive heating of polymer. The heating ability increased by increasing the amount of MWCNT, with ΔT of about 35°C in 4 min for the samples with 5 wt % of MWCNT.

This study indicates a proof of concept that RF can be potentially used for remote heating of the CNT-hydrogel nanocomposites. The remotely actuated nanocomposites can be useful for a variety of biological and other applications. For example, previous studies have demonstrated that remotely actuated magnetic hydrogel nanocomposites are attractive materials for drug delivery and for microfluidic flow control.[6,8] The study of hydrogel nanocomposite heating in swollen state and the effect of dispersion on heating performance is underway and will be reported in future publications.

CONCLUSIONS

NIPAAm-MWCNT nanocomposites were successfully synthesized. Effect of varying the amount of AAm and MWCNT on temperature responsive swelling properties of NIPAAm hydrogels was characterized. Adding AAm to the hydrogels shifted the swelling transition (LCST) to higher temperatures, which is critical for physiological applications. Adding MWCNT to the hydrogels decreased the extent of swelling due to hydrophobic effects. The addition of MWCNT enhanced mechanical properties of hydrogels, and the enhancement can be tailored by the concentration of MWCNT. Applying a RF field of 13.56 MHz significantly heated the nanocomposites, and the intensity of resultant heating was dependent on MWCNT loadings. The nanocomposites showed unique properties and, therefore, demonstrate great promise for use in different biomedical applications including tissue engineering, remote controlled drug delivery devices, and cancer treatment.

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