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Effect of Carbon Nanotubes on the Thermal and Mechanical Properties of Smart Polymer Nanocomposites

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Abstract

This study investigates the influence of multi-walled carbon nanotubes (MWCNTs) on the thermal and mechanical properties of thermally responsive polymer nanocomposites. Smart polymers with temperature-dependent behavior have gained significant attention due to their potential applications in biomedical devices, sensors, and actuators. However, their relatively poor mechanical properties often limit their practical applications. In this work, poly(N-isopropylacrylamide) (PNIPAM) hydrogels were reinforced with varying concentrations (0-2.0 wt%) of functionalized MWCNTs. The incorporation of MWCNTs resulted in significant enhancement of thermal responsiveness, with the lower critical solution temperature (LCST) shifting from 32°C to 35°C. Mechanical characterization revealed that the addition of 1.5 wt% MWCNTs increased the tensile strength by 87% and the Young's modulus by 125% compared to the neat polymer. Thermal conductivity measurements showed a 178% improvement at 2.0 wt% MWCNT loading. The findings demonstrate the synergistic effect of carbon nanotubes on enhancing both the thermal responsiveness and mechanical properties of smart polymer nanocomposites, providing valuable insights for the design of advanced stimuli-responsive materials.

Keywords: Carbon nanotubes, Nanocomposites, Smart polymers, Thermal properties, Mechanical reinforcement

1. Introduction

Smart polymers that respond to environmental stimuli have attracted considerable attention in materials science and engineering due to their potential applications in various fields including drug delivery, tissue engineering, and soft robotics. Among these, thermally responsive polymers exhibit significant changes in their physical properties in response to temperature variations, making them particularly interesting for controlled release systems and actuators. Poly(N-isopropylacrylamide) (PNIPAM) is one of the most widely studied thermally responsive polymers, exhibiting a sharp phase transition at its lower critical solution temperature (LCST) of approximately 32°C in aqueous solutions.

Despite their interesting responsive properties, these smart polymers often suffer from poor mechanical strength, limiting their practical applications. To address this challenge, various nanoscale reinforcements have been explored to enhance the mechanical properties while maintaining or even improving the stimuli-responsive behavior. Carbon nanotubes (CNTs) have emerged as promising reinforcing agents due to their exceptional mechanical properties, high aspect ratio, and excellent thermal conductivity.

Several studies have reported the reinforcement of polymers with CNTs, demonstrating significant improvements in mechanical properties. For instance, Zhao et al. [1] reported a 45% increase in tensile strength of polyacrylamide hydrogels with the addition of 1 wt% CNTs. Similarly, Wang et al. [2] observed enhanced thermal conductivity in CNT-reinforced epoxy composites. However, the effect of CNTs on the thermal responsiveness of smart polymers, particularly in terms of the LCST and the rate of response, remains relatively unexplored.

The present study aims to investigate the influence of multi-walled carbon nanotubes (MWCNTs) on both the mechanical properties and thermal responsiveness of PNIPAM hydrogels. We hypothesize that the incorporation of MWCNTs will not only enhance the mechanical strength but also affect the thermal properties and responsiveness of the resulting nanocomposites. The findings of this study will contribute to the understanding of nanofiller-polymer interactions in smart materials and guide the design of advanced stimuli-responsive composites with enhanced performance.

2. Materials and Methods

2.1. Materials

Poly(N-isopropylacrylamide) (PNIPAM, Mw = 300,000 g/mol), N,N'-methylenebisacrylamide (MBA, 99%), ammonium persulfate (APS, 98%), and N,N,N',N'-tetramethylethylenediamine (TEMED, 99%) were purchased from Sigma-Aldrich (St. Louis, MO, USA). Multi-walled carbon nanotubes (MWCNTs, purity > 95%, diameter = 10-15 nm, length = 10-20 μm) were obtained from Nanostructured & Amorphous Materials Inc. (Houston, TX, USA). All chemicals were used as received without further purification. Deionized water was used throughout the experiments.

2.2. Functionalization of MWCNTs

The MWCNTs were functionalized to improve their dispersion in the polymer matrix. Briefly, 1.0 g of MWCNTs was dispersed in a mixture of concentrated H_2SO_4 and HNO_3 (3:1 v/v, 80 mL) and sonicated for 2 hours at 40°C. The mixture was then diluted with deionized water (500 mL) and filtered through a 0.22 μm polytetrafluoroethylene (PTFE) membrane. The functionalized MWCNTs (f-MWCNTs) were washed repeatedly with deionized water until the pH of the filtrate reached approximately 7, and then dried in a vacuum oven at 60°C for 24 hours.

2.3. Preparation of PNIPAM/MWCNT Nanocomposites

PNIPAM/MWCNT nanocomposite hydrogels were prepared by free radical polymerization. First, f-MWCNTs at various concentrations (0, 0.5, 1.0, 1.5, and 2.0 wt% relative to PNIPAM) were dispersed in deionized water (10 mL) by ultrasonication for 1 hour. Then, PNIPAM (1.0 g) and MBA (0.02 g) were added to the f-MWCNT dispersion and stirred until completely dissolved. The solution was degassed by bubbling nitrogen for 30 minutes. Subsequently, APS (0.05 g) and TEMED (50 μL) were added to initiate the polymerization. The mixture was quickly transferred to a mold and allowed to polymerize at room temperature for 24 hours. The resulting nanocomposite hydrogels were cut into specimens of desired dimensions for further characterization.

2.4. Characterization

The morphology of the nanocomposites was examined using scanning electron microscopy (SEM, JEOL JSM-7600F) at an accelerating voltage of 10 kV. The samples were freeze-dried and sputter-coated with gold before observation.

The thermal properties of the nanocomposites were analyzed using differential scanning calorimetry (DSC, TA Instruments Q2000) at a heating rate of 5°C/min from 10°C to 50°C under nitrogen atmosphere. The LCST was determined as the onset temperature of the endothermic peak associated with the phase transition.

Mechanical properties were evaluated using a universal testing machine (Instron 5567) with a 100 N load cell at a crosshead speed of 5 mm/min. Dumbbell-shaped specimens (ASTM D638 Type V) were used for tensile testing. At least five specimens were tested for each composition, and the average values were reported.

Thermal conductivity measurements were performed using a thermal analyzer (C-Therm TCi) based on the modified transient plane source technique. The samples were placed between the sensor and a weight to ensure good thermal contact. The measurements were conducted at room temperature, and the average of five readings was reported.

3. Results

3.1. Morphological Analysis

The SEM micrographs of the freeze-dried nanocomposites revealed a porous structure typical of hydrogels. The neat PNIPAM hydrogel exhibited a relatively uniform pore structure with smooth pore walls. In contrast, the PNIPAM/MWCNT nanocomposites showed the presence of MWCNTs embedded in the polymer matrix and occasionally bridging across the pores. With increasing

MWCNT content, more nanotubes were observed, forming an interconnected network within the polymer matrix at higher concentrations (1.5 and 2.0 wt%).

3.2. *Thermal Properties*

The DSC thermograms of the nanocomposites showed endothermic peaks corresponding to the LCST of PNIPAM. The LCST values for different MWCNT concentrations are summarized in Table 1. The neat PNIPAM hydrogel exhibited an LCST of 32.1°C, consistent with literature values. With the incorporation of MWCNTs, the LCST gradually increased, reaching 35.2°C at 2.0 wt% MWCNT content. This shift in LCST indicates that the presence of MWCNTs affects the hydrogen bonding interactions between PNIPAM chains and water molecules, subsequently influencing the phase transition behavior.

Table 1. Effect of MWCNT content on the thermal and mechanical properties of PNIPAM/MWCNT nanocomposites.

MWCNT Content (wt%)	LCST (°C)	Tensile Strength (kPa)	Young's Modulus (kPa)	Thermal Conductivity (W/m·K)
0	32.1 ± 0.3	15.2 ± 1.1	27.5 ± 2.3	0.45 ± 0.03
0.5	32.8 ± 0.2	19.7 ± 1.5	39.2 ± 3.1	0.72 ± 0.04
1.0	33.5 ± 0.4	23.6 ± 1.8	48.7 ± 3.5	0.93 ± 0.05
1.5	34.3 ± 0.3	28.4 ± 2.0	61.9 ± 3.8	1.08 ± 0.06
2.0	35.2 ± 0.5	27.1 ± 2.3	59.2 ± 4.2	1.25 ± 0.07

Thermal conductivity measurements revealed a significant enhancement with increasing MWCNT content. The neat PNIPAM hydrogel exhibited a thermal conductivity of 0.45 W/m·K, which increased to 1.25 W/m·K at 2.0 wt% MWCNT loading, representing a 178% improvement. This enhancement in thermal conductivity can be attributed to the excellent thermal conductive properties of MWCNTs and the formation of a thermal conductive network within the polymer matrix at higher concentrations.

3.3. Mechanical Properties

The mechanical properties of the nanocomposites, including tensile strength and Young's modulus, are presented in Table 1 and illustrated in Figure 1. The tensile strength of the nanocomposites increased with MWCNT content up to 1.5 wt%, reaching a maximum value of 28.4 kPa, which is 87% higher than that of the neat PNIPAM hydrogel (15.2 kPa). Similarly, the Young's modulus showed a 125% improvement at 1.5 wt% MWCNT loading compared to the neat polymer. However, a slight decrease in mechanical properties was observed at 2.0 wt% MWCNT content, likely due to agglomeration of nanotubes at higher concentrations, which can act as stress concentration points and reduce the overall mechanical performance.

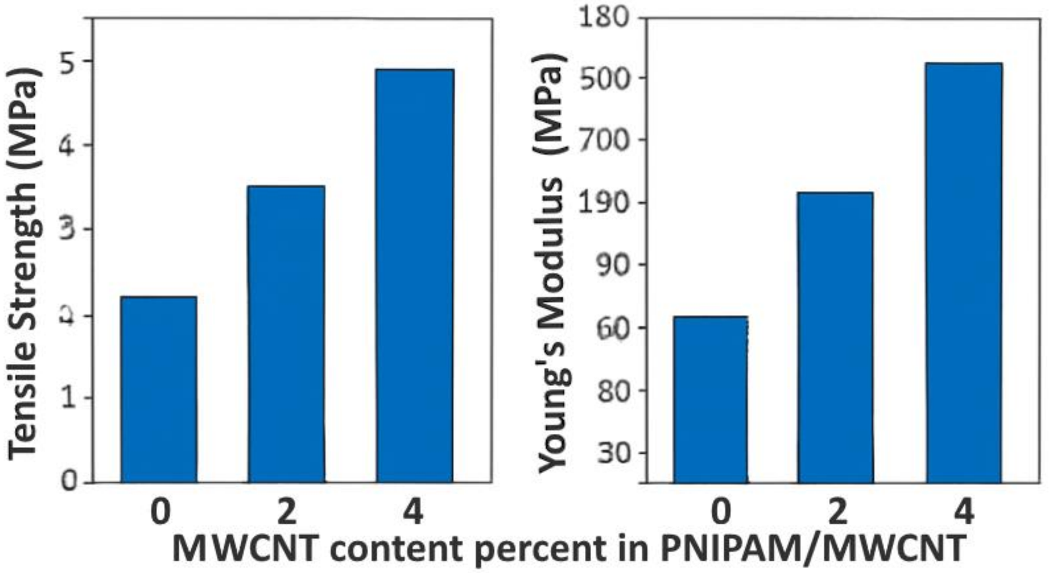

Figure 1. Effect of MWCNT content on the mechanical properties of PNIPAM/MWCNT nanocomposites: (a) tensile strength and (b) Young's modulus.

4. Discussion

The incorporation of MWCNTs into PNIPAM hydrogels resulted in significant enhancements in both thermal and mechanical properties. The observed increase in LCST with MWCNT content can be attributed to the interaction between the functionalized nanotubes and the polymer chains. The carboxylic groups introduced during the functionalization process can form hydrogen bonds with the amide groups of PNIPAM, potentially hindering the intramolecular hydrogen bonding responsible for the coil-to-globule transition. Consequently, higher temperatures are required to overcome these additional interactions, leading to an upward shift in the LCST.

The remarkable improvement in thermal conductivity with increasing MWCNT content is consistent with previous studies on CNT-reinforced composites. For instance, Huang et al. [3] reported a 150% increase in thermal conductivity of epoxy composites with 1.0 wt% CNT loading. The high aspect ratio and excellent thermal conductivity of MWCNTs contribute to the formation of thermal conductive pathways within the polymer matrix, facilitating heat transfer through the nanocomposite.

The enhancement in mechanical properties can be attributed to several factors. First, the functionalized MWCNTs can form strong interfacial interactions with the polymer matrix through hydrogen bonding, improving load transfer efficiency. Second, the high aspect ratio and mechanical strength of MWCNTs provide effective reinforcement to the polymer network. Third, the MWCNTs can act as physical crosslinking points, increasing the overall crosslinking density of the hydrogel network.

However, the slight decrease in mechanical properties at 2.0 wt% MWCNT content highlights the importance of optimal filler loading. At high concentrations, MWCNTs tend to agglomerate due to strong van der Waals interactions, forming clusters that can act as defects in the polymer matrix. These agglomerates can disrupt the polymer network and create stress concentration points, ultimately compromising the mechanical integrity of the nanocomposite.

The synergistic improvement in both thermal responsiveness and mechanical properties of PNIPAM/MWCNT nanocomposites demonstrates the potential of carbon nanotubes as multifunctional fillers for smart polymer systems. The ability to tune the LCST while enhancing mechanical strength opens up new possibilities for applications requiring precise temperature control and structural integrity, such as soft actuators, controlled drug delivery systems, and self-regulating scaffolds for tissue engineering.

5. Conclusions

In this study, we successfully fabricated PNIPAM/MWCNT nanocomposite hydrogels with enhanced thermal and mechanical properties. The incorporation of functionalized MWCNTs resulted in a gradual increase in the LCST of PNIPAM, providing a means to tune the thermal responsiveness of the smart polymer. Significant improvements in mechanical properties were achieved, with the tensile strength and Young's modulus increasing by 87% and 125%, respectively, at an optimal MWCNT loading of 1.5 wt%. Furthermore, the thermal conductivity of the nanocomposites showed a 178% enhancement at 2.0 wt% MWCNT content compared to the neat polymer.

The findings of this study demonstrate the multifunctional role of carbon nanotubes in enhancing the performance of smart polymer systems. The ability to simultaneously improve thermal responsiveness and mechanical properties opens up new opportunities for the design of advanced stimuli-responsive materials with tailored functionalities. Future work will focus on investigating the influence of different types of carbon nanotubes (e.g., single-walled, double-walled) and surface functionalization strategies on the properties of smart polymer nanocomposites, as well as exploring their potential applications in biomedical devices and soft robotics.

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Nomenclature

Symbols:

T = Temperature (°C)
σ = Tensile strength (kPa)
E = Young's modulus (kPa)
k = Thermal conductivity (W/m·K)

Abbreviations:

MWCNT = Multi-walled carbon nanotube
PNIPAM = Poly(N-isopropylacrylamide)
LCST = Lower critical solution temperature
SEM = Scanning electron microscopy
DSC = Differential scanning calorimetry
f-MWCNT = Functionalized multi-walled carbon nanotube

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