

Research Article

MWCNTs/Cellulose Hydrogels Prepared from NaOH/Urea Aqueous Solution with Improved Mechanical Properties

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Novel high strength composite hydrogels were designed and synthesized by introducing multiwalled carbon nanotubes (MWCNTs) into cellulose/NaOH/urea aqueous solution and then cross-linked by epichlorohydrin. MWCNTs were used to modify the matrix of cellulose. The structure and morphology of the hydrogels were characterized by Fourier transform infrared (FT-IR) spectroscopy, high resolution transmission electron microscopy (HR-TEM), and scanning electron microscopy (SEM). The results from swelling testing revealed that the equilibrium swelling ratio of hydrogels decreased with the increment of MWCNTs content. Thermogravimetric analysis (TGA) and dynamic mechanical analysis (DMA) results demonstrated that the introduction of MWCNT into cellulose hydrogel networks remarkably improved both thermal and mechanical properties of the composite hydrogels. The preparation of MWCNTs modified cellulose-based composites with improved mechanical properties was the first important step towards the development of advanced functional materials.

1. Introduction

Hydrogels, because of their excellent hydrophilic properties, biocompatibilities, permeability, and high swelling ratio [1–3], have attracted considerable interest from the industry and scientific community. So far, they have been widely applied in food, cosmetics, and biomedical field especially in drug delivery [4] and tissue engineering [5]. They are defined as three-dimensional network of hydrophilic polymers which could absorb and retain large quantities of water. Compared with hydrogels prepared from synthetic polymers, hydrogels from natural polymers, especially polysaccharides, exhibit distinct characteristics such as better biocompatibility and biodegradability, as well as more biological functions but less latent toxic effect [2].

As mentioned above, cellulose, the most abundant natural polymer in nature, is renewable, biodegradable, and biocompatible [6, 7]. Therefore, people are increasingly paying attention to this natural polymer, considering it

an almost inexhaustible source of raw material to replace petrochemically derived compounds in many cases [8]. The widespread applications of cellulose hydrogels in different fields have brought about higher requirements for their properties. Hence, the development of high-performance cellulose is of great importance. Though some researchers have centered a considerable attention on the synthesis of cellulose-based hydrogels [5] and achieved encouraging breakthrough [9], few have reported on the fabrication of cellulose hydrogels directly from unsubstituted cellulose due to the insolubility of cellulose in aqueous solutions and in most organic solvents resulted from its large proportion of intra- and intermolecular hydrogen bonds. To solve this problem, Zhou et al. have reported a novel “one-step” method to fabricate cellulose hydrogels from unsubstituted cellulose by dissolving cellulose in NaOH/urea aqueous solution with cross-linker (epichlorohydrin, ECH) [10]. However, weak mechanical strength and poor durability of cellulose hydrogels have limited their practical application to a great extent.

At present, some contributions have focused on nanoscale reinforcements for improving the mechanical and electrical performance of cellulose effectively.

To date, nanoparticles especially carbon nanotubes (CNTs) and their composites [11] have earned great attention for the modification of polymers in the field of material science during the last decade [12]. They are very effective fillers in terms of high specific surface area (SSA) and excellent mechanical properties, especially toughness [13]. Wang et al. reported that incorporation of 0.8% CNTs into the CS matrix greatly improved the mechanical properties of the composites, and the tensile modulus and strength of the composite increased by about 93% and 99% compared with those of neat CS [14]. It has also been reported that the mechanical properties of the CNTs/PMMA composite films improved as the concentration of CNTs increased [15].

With the combination of low density, high aspect ratio, high stiffness, and extremely high strength [16], multiwalled carbon nanotubes (MWCNTs) have been commonly considered as interesting nanofillers for reinforcing various organic polymers [17, 18]. Besides, the load on the PMMA composites could be transferred to the PMMA-grafted MWCNTs when used as the reinforcement in the previous literature [19]. In addition, MWCNTs show good communication with redox proteins, including those where the redox center is embedded into the glycoprotein cell, such as glucose oxidase [20, 21]. Based on the above reasons, the MWCNTs are expected to improve the mechanical property of cellulose materials.

To achieve the predicted goal, we used a simple method in which MWCNTs interpenetrate cellulose hydrogels to control their mechanical strength. In the present work, novel high strength hydrogels were successfully fabricated from cellulose and MWCNTs in the NaOH/urea aqueous system by using epichlorohydrin [22] as cross-linker. Fourier transform infrared (FT-IR) spectroscopy, scanning electron microscope (SEM), transmission electron microscope (TEM), and thermogravimetric analysis (TGA) were applied to characterize the intermolecular interaction, morphology, and thermal stability of hydrogels. Besides, the swelling behavior and mechanical property were evaluated by measuring the equilibrium swelling ratios and compressive modulus, which might open doors for their potential applications in the field of advanced biomaterials.

2. Experimental

2.1. Materials. Whatman CF-11 cellulose powder (catalog number 4021050) was used as the starting material. Its weight-average molecular weight (M_w) was determined in NaOH/urea aqueous solution to be 3.46×10^4 with static laser light scattering (DAWN DSP, Wyatt Technology Co., US). Epichlorohydrin [22] (1.18 g/mL) was of analytical grade; multiwalled carbon nanotubes (MWCNTs, 99.9% purity; outer diameter, 10 nm; inner diameter, 3–5 nm; length, 5–15 μm) were purchased from the Department of Chemical Engineering, Tsinghua University. All water used was purified by Milli-Q plus water purification system (Millipore Corporate, Billerica, MA).

2.2. Synthesis of Cellulose/MWCNTs Hydrogels. Cellulose solution (5 g, 2 wt%) was prepared in NaOH/urea aqueous solution according to our previous work as follows [1, 2]. Firstly, stoichiometric amount of MWCNTs was added into the cellulose solution with stirring for 0.5 h, and then these mixtures were ultrasonic-treated for 0.5 h. Subsequently, ECH (1.184 g/mL, 500 μL) was added to the cellulose solution as a cross-linking agent. The resultant mixtures were stirred for 0.5 h to yield a homogeneous solution. After reacting at 60°C for 3 h, cellulose/MWCNTs hydrogels were taken out carefully and stored for further testing. The appearance of the prepared hydrogels is shown in Figure 1. The samples were encoded as Gel 1, Gel 2, Gel 3, Gel 4, and Gel 5 when the weight ratios of cellulose/MWCNTs were 20 : 1, 10 : 1, 4 : 1, 3 : 1, and 2 : 1, respectively.

2.3. Characterization. The hydrogel samples were ground into small particles and dried in vacuum at 50°C for 24 h. The dried samples were analyzed in KBr discs by Fourier transform infrared spectroscopy (Perkin Elmer Spectrum one, Wellesley, MA, USA). FT-IR spectra were recorded at a resolution of 4 cm^{-1} and 64 scans. TEM studies of the hydrogel samples were carried out using a JEM-2010 FEF (UHR) transmission electron microscope (JEOL TEM, Japan). The internal morphology of the hydrogels was studied using SEM (Hitachi X-650 microscope, Mountain View, CA, Japan). Prior to SEM observation, the hydrogels were firstly immersed in distilled water for equilibrium at 37°C for 24 h. Then they were frozen in liquid nitrogen, snapped immediately, and further freeze-dried in a Virtis Freeze Drier (Gardiner, NY) for 24 h until all the solvent was sublimed. The fracture surface (cross section) of the hydrogel was sputtered with gold and then observed and photographed. Thermogravimetric analysis (TGA) was performed by a Pyris TGA linked to a Pyris diamond TA Lab System (Perkin-Elmer Co., USA) at a heating rate of 10°C/min from 40 to 500°C under nitrogen atmospheres.

2.4. Swelling Measurements. The equilibrium swelling ratios (SR) of hydrogels were investigated in distilled water. The SR value was calculated from the following formula:

$$\text{SR} = \frac{W_s}{W_d}, \quad (1)$$

where W_s is the weight of the wet hydrogel at swelling equilibrium (37°C) and W_d is the weight of the hydrogel in the dry state.

2.5. Mechanical Strength Measurements. Dynamic mechanical analysis (DMA, TA instrument Q800 series) was used to determine the mechanical properties of the swollen hydrogel samples. The hydrogel samples were fully swollen in distilled water at room temperature, and then the hydrogels were cut into circular disks (diameter, 5 mm; thickness, 3 mm) using a cutter. The compression stress-strain experiments were conducted using a step mode at a rate of 0.250 N min^{-1} till the samples were broken against a stainless steel platform [23].

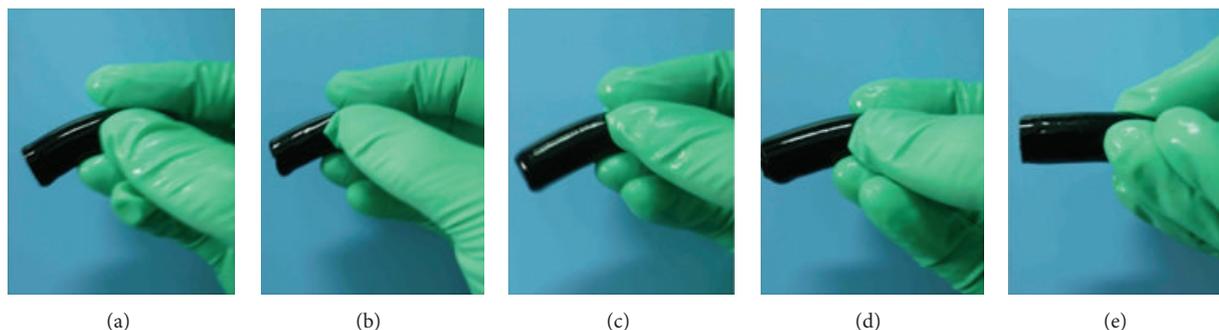


FIGURE 1: The appearance of cellulose/MWCNTs hydrogels with different weight ratios: (a) Gel 1 (20:1), (b) Gel 2 (10:1), (c) Gel 3 (4:1), (d) Gel 4 (3:1), and (e) Gel 5 (2:1).

TABLE 1: Reaction conditions and material compositions of the various cellulose/MWCNTs hydrogels.

Code	MWCNTs (g)	Cellulose solution (g)	ECH (mL)	Time (h)	T ($^{\circ}\text{C}$)
Gel 1	0.25	5	3	3	60
Gel 2	0.50	5	3	3	60
Gel 3	1.25	5	3	3	60
Gel 4	1.67	5	3	3	60
Gel 5	2.50	5	3	3	60

3. Results and Discussion

3.1. Appearance and Structure of the Hydrogels. The reaction conditions and chemical compositions of the cellulose/MWCNTs hydrogels are displayed in Table 1. The hydrogel samples of Gels 1–5 with different weight ratios of MWCNTs to cellulose were prepared by using ECH as cross-linker [4]. Figure 1 is the top view of five hydrogels with various MWCNTs concentrations. It could be seen that all samples had black sections with enhanced interpenetrating MWCNT concentration, and these black sections are homogeneously dispersed throughout the entire Gels 1–5 hydrogels. Interestingly, we found that all samples exhibited excellent formability and high mechanical strength. Besides, Gel 1 presented as black bending tubular gel, but the extent of the bending gradually reduced with the increment of MWCNTs content, which might mainly be attributed to the stiffness of MWCNTs.

To characterize the chemical structure of samples, the FT-IR spectra of cellulose/MWCNTs hydrogels are given in Figure 2. Obviously, the molecular structure did not obviously change with the variation of MWCNT concentrations. The broad absorption bands of the hydrogels at 3300–3500 cm^{-1} were assigned to stretching of the large number of hydroxyl groups on the cellulose backbone. For Gels 1–5, the absorption peaks at 2920 cm^{-1} and 2880 cm^{-1} were attributed to the asymmetric and symmetric stretching vibration of CH_2 and C–H, and another absorption peak at 1640 cm^{-1} was assigned to COO^- stretching. However, the typical C–H stretching absorption at around 3000–2800 cm^{-1} caused

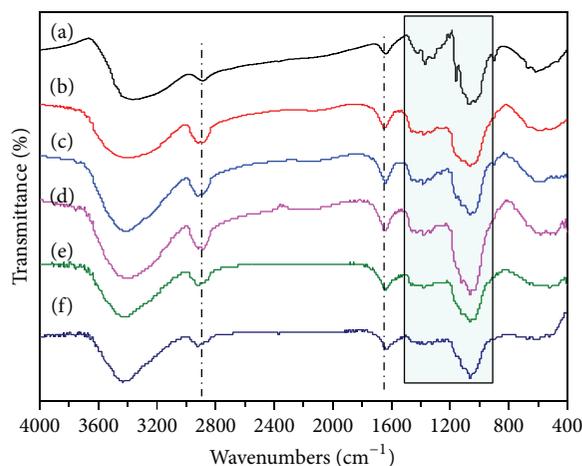


FIGURE 2: FT-IR spectra of cellulose hydrogel (a) and cellulose/MWCNTs hydrogels: (b) Gel 1, (c) Gel 2, (d) Gel 3, (e) Gel 4, and (f) Gel 5.

by MWCNTs was too weak to be observed for Gels 1, 2, 3, 4, and 5, because the ratios of MWCNTs to cellulose were too small. Compared to neat cellulose hydrogel (see Figure 2(a)), the band observed at 1420 cm^{-1} and 1371 cm^{-1} in the cellulose/MWCNTs hydrogels became indistinguishable (Figures 2(b)–2(f)). On the other hand, the interpenetrating of MWCNTs also had an impact on the absorption bands. With the addition of MWCNTs, the typical band in the range of 3454–3200 cm^{-1} became narrower than pure cellulose (curve (a)). The experimental results further demonstrated that a cellulose/MWCNTs composite structure was created.

HR-TEM images of the purified MWCNTs and cellulose/MWCNTs are shown in Figure 3. It could be observed that the purified MWCNTs were generally well dispersed, but agglomerates of about 10 nm diameter could be observed frequently (Figure 3(a)) due to the intrinsic van der Waals forces [24]. The compact walls of the MWCNTs and well-defined lattice fringes were clearly observed in Figure 3(b). Compared with neat MWCNTs, cellulose/MWCNTs with weight ratio of 2:1 (Gel 5) exhibited lower entanglement degree. No large aggregates of CNTs were observed, but small and individual aggregates composed of a few MWCNTs were

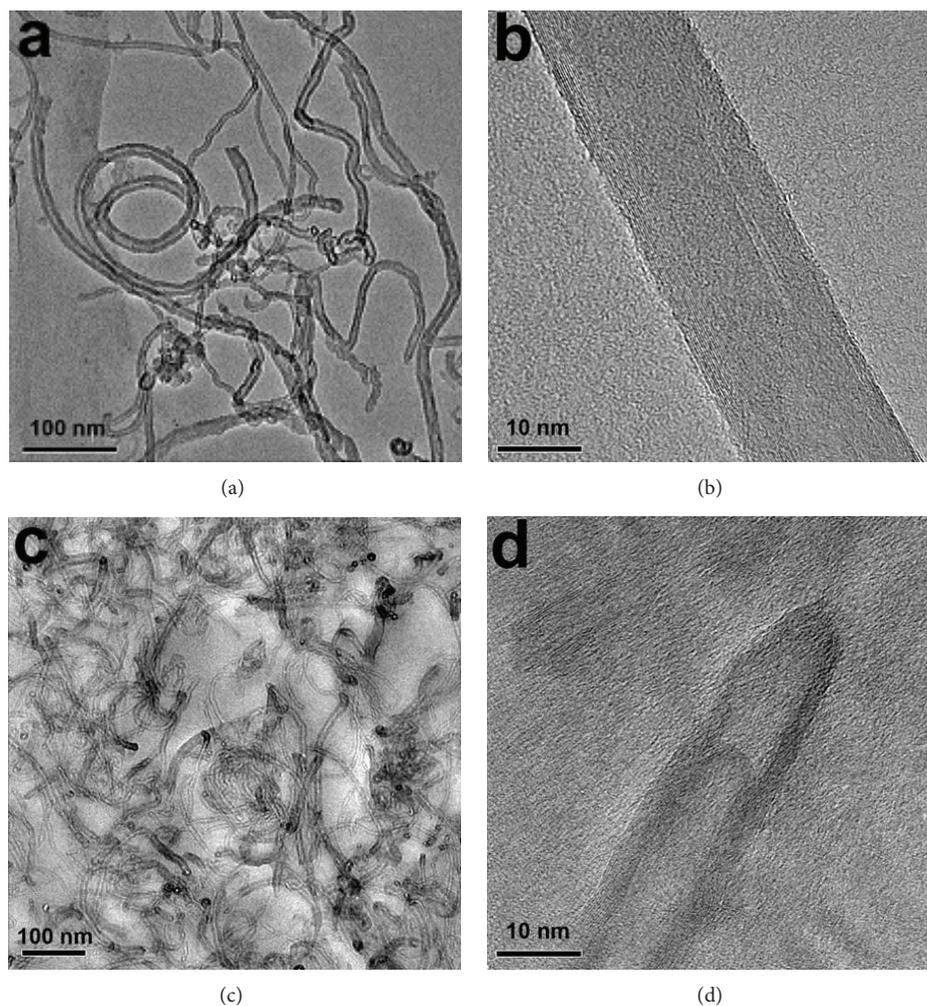


FIGURE 3: HR-TEM images of the purified MWCNTs ((a), (b)) and the cellulose/MWCNTs hydrogel Gel 5 ((c), (d)).

scattered separately in the cellulose matrix. Besides, a piece of cellulose/MWCNTs fibril was found with smaller diameter and rougher surface, which implied that the MWCNTs were wrapped by cellulose. The core-shell structure formed between the compact walls of the MWCNTs and the relatively loose cellulose layers, with the MWCNTs as the core and the cellulose as the shell (Figures 3(c) and 3(d)), might result from the covalent bond formed between cellulose and MWCNTs.

To investigate the effect of MWCNTs on the internal structure of the hydrogels, we used a freeze-drying method to generate a honeycomb structure of the gel and SEM to study their internal structure. Figure 4 presents the FE-SEM images of Gel 5 hydrogel at two different magnifications. Both surface and cross section of the hydrogel exhibited a homogeneous and dense architecture with obvious porosity. Interestingly, uniformly porous structures with large size were produced in the internal networks of Gel 5 (Figures 4(b) and 4(d)). The uniformly porous structure suggested that the MWCNTs were well distributed and incorporated into the hydrogels, which was in agreement with the result in Figures 3(c) and 3(d). The porosity of Gel 5 was consistent with

a previous result that the internal structures of hydrogels were more porous for higher concentrations of interpenetrating polymers [25]. The high-magnification image of the internal structure (Figures 4(c) and 4(d)) revealed many filaments which were consistent with the filamentous morphology of the MWCNTs in Figure 3(b), which provided strong evidence that the MWCNTs interpenetrate into the hydrogel network to help construct a scaffold structure. Since hydrophobic MWCNTs were dispersed in the hydrogel solution and displace hydrophilic components, the incorporated MWCNTs decreased the density of the hydrophilic hydrogel frameworks and created a network with thinner walls and a porous structure [26].

3.2. Swelling Behavior of Cellulose/MWCNTs Hydrogels. The effect of compositions of the hydrogels on equilibrium swelling ratios (ESR) in distilled water at a temperature of 37°C is illustrated in Figure 5. The swelling ratio of the prepared composite hydrogels decreased with increasing MWCNTs content. The order of the swelling ratio was Gel 1 > Gel 2 > Gel 3 > Gel 4 > Gel 5. The results elucidated

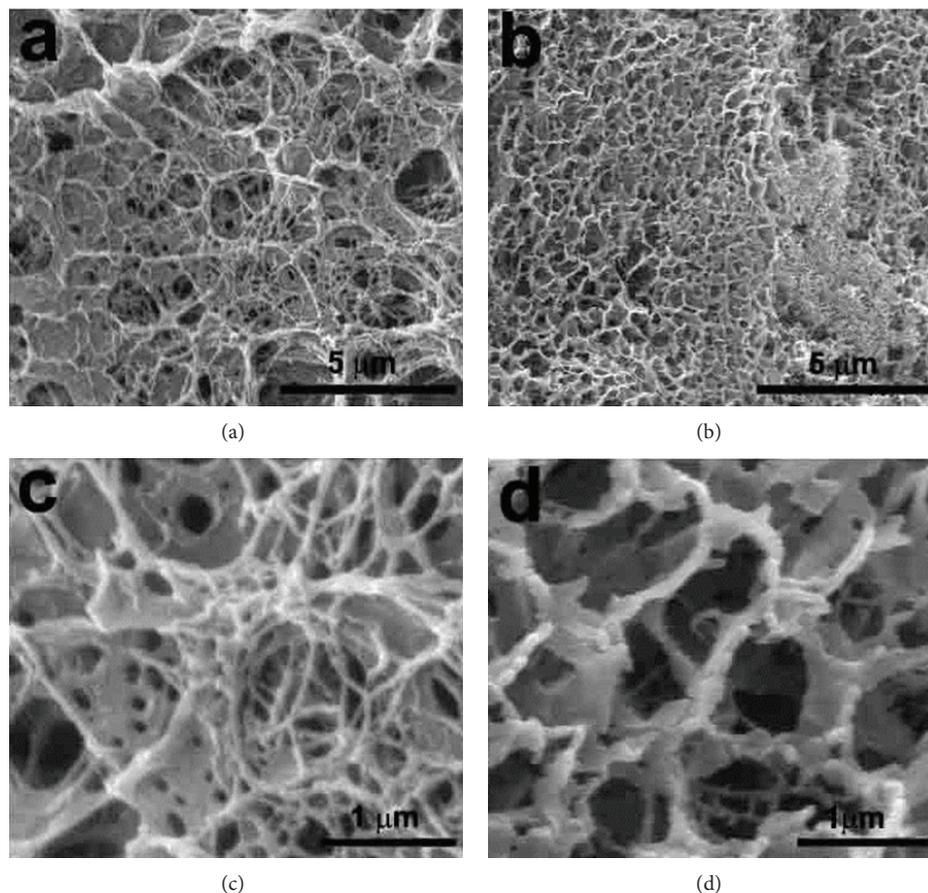


FIGURE 4: FE-SEM images of cellulose/MWCNTs hydrogel Gel 5: surface ((a), (c)) and cross section ((b), (d)).

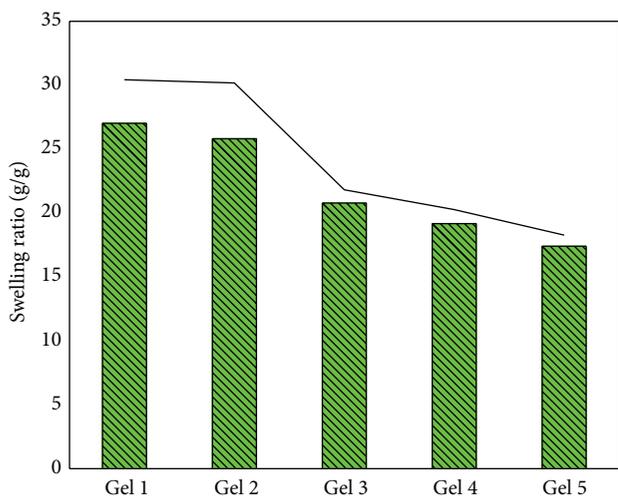


FIGURE 5: Equilibrium swelling ratio of the prepared cellulose/MWCNTs hydrogels after immersing in distilled water for a week, as the function of the composition of MWCNTs and cellulose at 25°C.

that the swelling ratio is dependent significantly on the amount of MWCNTs. This phenomenon could be explained in terms of the internal structure and cross-linking degree

of the hydrogels. It has been reported that the swelling ratio of the hydrogels decreased with the augment of pore size due to the increase in the cross-linking density [27]. In this work, MWCNTs were applied to reproduce the cross-linking function and created a porous internal structure instead of increasing the concentration of the cross-linker. Besides, the swelling ratio of prepared hydrogels was also associated with the cross-linking degree which affected the water absorbency of hydrogels, except for the chemical cross-linking of cellulose by ECH. Physical cross-linking of the polymer chains plays an important role in the swelling ratio of the hydrogels [2]. With increasing MWCNTs concentration, physical cross-linking of the hydrogels was strengthened by more intermolecular hydrogen bonds and chain entanglements between MWCNTs and cellulose, leading to the lower swelling degree with an increment of MWCNTs content. The alternative view is that the MWCNTs themselves in this case played a physical cross-linker role, and the addition of them could enhance cross-linking density through increasing in the cross-linking sites, inducing the decrease in swelling ratio [23].

3.3. Thermal Properties of Cellulose/MWCNTs Hydrogels. The thermal properties of cellulose/MWCNTs composite hydrogels (Gels 1–5) were measured by TGA and TG.

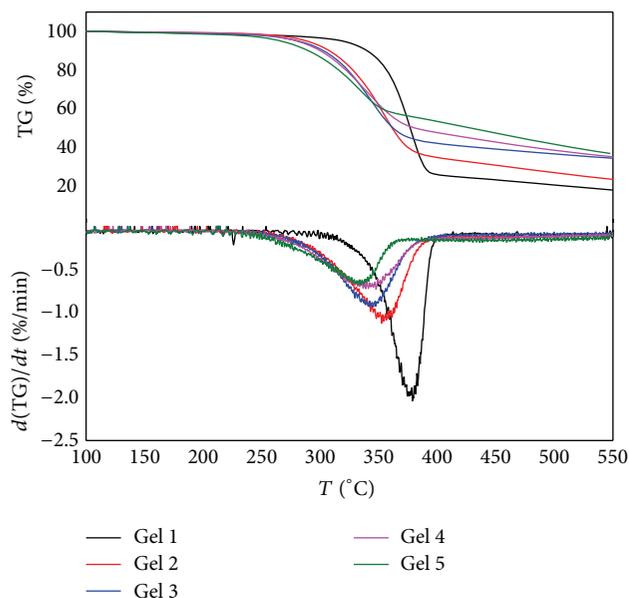


FIGURE 6: TG and DTG curves of the cellulose/MWCNTs hydrogels Gels 1-5.

The DTG curves are exhibited in Figure 6. It is of note that the T_{\max} (the temperature when the rate of weight loss reaches a maximum) and weight loss after being heated to 550°C of the cellulose/MWCNTs hydrogels were basically in order of Gel 5 < Gel 4 < Gel 3 < Gel 2 < Gel 1. Since thermal decomposition of MWCNT started slightly above 600°C [28], the weight loss after heating to 550°C was in accordance with the MWCNTs content. So the investigation into this property would provide important information about the MWCNTs incorporated into the hydrogels. Observed from DTG curves of Gel 1, a peak at 378°C was attributed to the decomposition of cellulose [1]. Notably, the corresponding peaks of Gel 2, Gel 3, Gel 4, and Gel 5 appeared at 352°C, 345°C, 338°C, and 332°C, respectively, demonstrating that the thermal stability slightly decreased with the increase of MWCNTs concentration. Therefore, a conclusion could be drawn that the amount of MWCNTs could result in significant effect on the thermal property of cellulose/MWCNTs hydrogels.

3.4. Mechanical Properties of Cellulose/MWCNTs Hydrogels.

Figure 7 depicts typical stress-strain behavior of Gels 1-5 in the swollen state at different contents of MWCNTs content. It is found that composite hydrogel Gel 5 possessed the highest ultimate compressive strength (83 KPa) and Gel 1 possessed the largest strain (99.98%) among all hydrogels, as seen from stress values at breaking points in Figure 7. This suggested that adding the MWCNTs to the hydrogels matrix is helpful to the improvement of mechanical properties. Simultaneously, it is noticed that ultimate compressive strength of the composite hydrogels indistinctly increased with an increase in MWCNTs concentrations. This dramatic change in compressive modulus indicated that the interactions between cellulose matrix and MWCNTs were strong enough to allow a very efficient load transfer to MWCNTs, providing high mechanical strength.

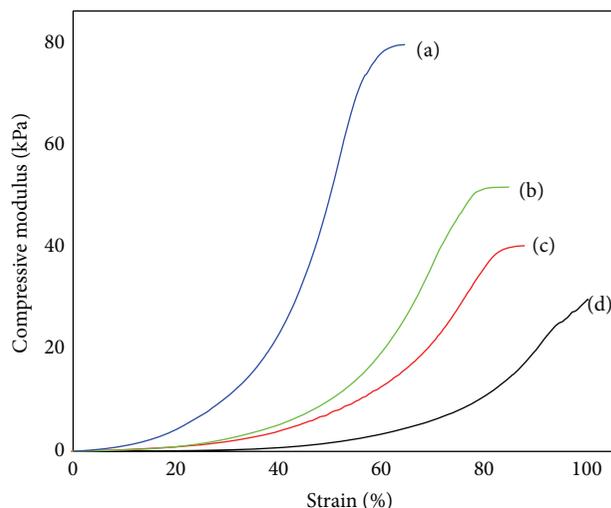


FIGURE 7: Typical compressive modulus-strain curves of cellulose/MWCNTs hydrogels with different weight ratios: (a) Gel 1 (20:1), (b) Gel 2 (10:1), (c) Gel 4 (3:1), and (e) Gel 5 (2:1) at room temperature.

In general, the mechanical properties of MWCNTs-reinforced composites strongly depend on the extent of load transfer between the matrix and MWCNTs. Since the MWCNTs have high aspect ratio, high modulus, and high strength, the loading force could be transferred to the nanotubes. The main mechanisms of load transfer from matrix to filler are micromechanical interlocking, interfacial shear stress, chemical bonding, and van der Waals force [15, 29, 30]. The polymeric grafts along the MWCNTs walls could physically knot and tangle together with those polymer chains of cellulose matrix, leading to very strong interactions between the MWCNTs and the matrix, and MWCNTs thus served as the network centers to transfer local stress evenly to all other polymer chains. Consequently, the overall mechanical properties of the polymer composite were improved [19]. In this research, TEM images of cellulose/MWCNTs hydrogels provided strong proof for this explanation, as shown in Figures 3(c) and 3(d). Hence, the incorporation of MWCNTs into a polymer matrix could potentially be applied for the preparation of structural materials with dramatically improved mechanical property.

4. Conclusions

In summary, we have prepared a cellulose/MWCNTs hydrogel that has excellent mechanical properties as well as enhanced adsorption capacity in NaOH/urea aqueous solution by cross-linking with ECH. HR-TEM and SEM images exhibited the uniformly distributed morphology and macroporous structure of MWCNTs and composite hydrogels. Simultaneously, the compression mechanical tests have revealed that the composite hydrogels display excellent compressive strength. All these results show that the composite hydrogels with an excellent swelling and mechanical performances could be constructed by adjusting or modulating

the concentration of MWCNTs. In conclusion, we believe that MWCNTs could further extend the applicability of cellulose and be widely applied as reinforcements in the mechanical strength of polymer-based hydrogels. It is expected that the as-prepared composite hydrogels possess potential applications in drug controlled release and tissue engineering.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

Acknowledgment

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