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Rheological and mechanical study of regenerated cellulose/multi-walled carbon nanotube composites

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Abstract
Regenerated cellulose (RC)-based composites reinforced with multi-walled carbon nanotubes (MWCNTs) were prepared by a facile casting method. The morphology and microstructure of the fabricated composites were characterized using transmission electron microscopy, Fourier transform infrared spectroscopy (FTIR) and Raman spectroscopy. Thermogravimetry and derivative thermogravimetric analysis were conducted to investigate the effect of MWCNTs on the thermal behaviors of the RC. The results showed that the introduction of MWCNTs enhanced the thermal stability of the RC. Moreover, the effect of the dispersion state of MWCNTs in microcrystalline cellulose/ZnCl₂ solutions with varying MWCNT loadings was studied by rheological tests. The mechanical properties of composite films were remarkably improved compared to those of pure RC film. Specifically, the composite film containing 3 wt% of MWCNTs exhibits a 123% enhancement in tensile strength and a 163% enhancement in the Young’s modulus compared with the pure RC film.

Keywords: regenerated cellulose, rheology, mechanical property, multi-walled carbon nanotubes

1. Introduction
Cellulose, the most abundant natural biopolymer in the world, is renewable in nature [9, 24]. Moreover, it is biocompatible and biodegradable, and could be chemically altered to provide new, environmentally friendly and biocompatible products [32]. Cellulose is very hydrophilic, but is insoluble in water and conventional organic solvents due to its well-developed intermolecular hydrogen bonding network [4]. Therefore, cellulose and its derivatives are commonly used in the manufacture of membranes and fibers both at the laboratory and industry scales [31]. Based on this, regenerated cellulose (RC) is developed. RC, derived from microcrystalline cellulose (MC) through dissolution and regeneration, possesses strong surface activities which are attributed to the presence of its hydrophobic and hydrophilic regions [11]. However, its mechanical and elastic stability need to be improved to widen its applications [31]. A promising strategy has been developed through the incorporation of nanofiller into the RC matrix to achieve enhanced performance. Typical nanofillers could be other polysaccharides [3, 15], ceramics [5, 13, 27], and carbon nanomaterials [10, 12].

Among these nanofillers, carbon nanotubes (CNTs) are considered to be one of the most promising for the reinforcement of the polymer matrix, due to their excellent mechanical and multi-functional properties [28]. This superior nanofiller has been widely studied for modifying a wide range of polymeric composites. CNT-reinforced composites were successfully prepared and exhibited significant mechanical improvement, high electrical conductivity, and superior thermal properties [8]. For example, the incorporation of CNTs can considerably improve the mechanical and thermal properties, and other functions of epoxy composites [20, 25]. However, the overall properties of the fabricated composites
can be affected by the conditions of CNTs incorporation into polymers. In order to achieve the maximum reinforcing effects of CNTs, the CNTs are expected to disperse homogeneously in the composite with good compatibility between the CNTs nanofiller and matrix. Thus, the load could be transferred optimally to the reinforcement CNTs nano particle, resulting in a deterioration of mechanical properties of the final composite [29]. One suitable solution is to functionalize the CNTs to overcome the inherent incompatibility between the nanofillers and polymer matrix. The surface functionalization of CNTs would improve the interfacial adhesion and mechanical properties [8].

The rheological behaviors play a critical role in the processing and manufacturing composites incorporated with fillers, which have been widely studied because they provide insight into their microstructure, physical interactions and gelation [1, 8, 29]. In this study, we report a simple route for preparing a hybrid cellulose–CNT composite with good mechanical properties due to physical cross-linking. First, carboxyl (COOH) functionalized multi-wall carbon nanotubes (MWCNTs) were added to a ZnCl2 solution. Second, MC is dissolved in the MWCNT/ZnCl2 hybrid to form visually homogeneous, viscous aqueous mixtures. The morphology of the prepared cellulose–CNT composites was studied both directly (by microscopy) and indirectly (by rheology). The linear and nonlinear viscoelastic behavior of the cellulose–CNT composite samples was studied. The mechanical property of RC–CNT composite films was also studied.

2. Experimental

2.1. Materials

MC (degree of polymerization up to 350) was purchased from Sinopharm Chemical Reagent Co., Ltd MWCNTs (D 20–30 nm, carboxyl-functional content 1.23 wt%) was purchased from Cheap Tubes Inc., USA. The other chemicals used in the tests were purchased from Sinopharm Chemical Reagent Co., Ltd. All reagents were of analytical grade and used as received without further purifying.

2.2. Preparation of MC–CNT composites

The desired amount of MWCNT powder was added to a 70 wt% ZnCl2 aqueous solution and stirred at room temperature for 30 min, followed by a 30 min ultrasonic treatment to obtain homogenous dispersion. After that, MC was added into the aqeous dispersion to achieve a concentration of 3 wt%. This was heated to 90 °C and stirred vigorously for 2 h. As a result, a series of mixed MC–CNT solutions were obtained. The mass ratios of MWCNTs and MC were 0, 1, 2, 3, 4, 5 and 8 wt%. The mixtures were labeled as MC, MC1, MC2, MC3, MC4, MC5 and MC8, respectively.

2.3. Fabrication of RC–CNT composite films

The RC–CNT composite films were fabricated by a solution casting method. The obtained solution was casted onto glass plate, immersing it into a de-ionized water bath for 30 min, followed by rinsing with de-ionized water. Then RC–CNT composite films were subjected to dialysis for one week to remove ZnCl2. Finally, the composite films were dried at 37 °C for 24 h in a vacuum. The final composite films were named as RC, RC1, RC2, RC3, RC4, RC5 and RC8. The detailed procedure is listed in scheme 1.

2.4. Characterization

Transmission electron microscopy (TEM) images were taken using a JEOL JEM-1400 model instrument (Japan) operated at an accelerating voltage of 100 kV. Fourier transform infrared (FTIR) spectra were recorded on a Spectrum Two Spectrometer (Perkin Elmer, USA) with the wavenumber range of 4000–400 cm−1 at a resolution of 4 cm−1. Raman spectra were recorded on a DXR Smart Raman spectrometer (Thermo Fisher, USA) with 532 nm laser excitation. Thermogravimetric analysis (TG) was carried out by using a TA Instruments model Q5000 TGA. The samples were heated from 20 to 600 °C with a heating rate of 10 °C min−1 under a nitrogen atmosphere.

2.5. Rheological measurements

The dynamic rheological measurement was carried out on a Rotational MARS III Haake Rheometer (Germany) with a plate–plate (P60 Ti L) sensor system. The sample was allowed to equilibrate for 12 h before measurements were taken. In steady shear experiments, 2.9 ml of freshly prepared degassed sample was used and the linear-viscoelastic regime was first determined using a strain sweep from 1 to 100% at 30 °C and a constant frequency of 1 Hz. The value of the strain amplitude was determined to ensure that all measurements made with MC–CNT systems were carried out within...
the linear-viscoelastic regime, where $G'$ and $G''$ are independent of the strain amplitude. Then, the dynamic frequency sweep test at a constant temperature of 30 °C was carried out to study the viscoelastic behavior of MC–CNT solutions over a wide range of angle frequencies (0.1–100 rad s$^{-1}$).

2.6. Mechanical properties

The tensile properties of RC based films were measured by a dynamic mechanical analyzer (CMT4204, Shenzhen SANS Testing Machine Co., Ltd, China). Samples were cut manually by a razor blade into strips 20 mm $\times$ 5 mm $\times$ 12 $\mu$m. The tensile tests were conducted in a ramp displacement mode at a cross-head speed of 1 mm min$^{-1}$. Each sample was measured five times. The average value and the error bars were calculated.

3. Results and discussion

3.1. Structural characterization

The morphology and dispersion of MWCNTs in the MC solution were observed by TEM (figure 1). As shown in figure 1(a), the pristine cellulose solution was clean and smooth which indicated that the solution process was effective to manufacture RC and RC–CNT composite films in this study [16]. For the MC-CNT composite solutions with different MWCNT loadings (figures 1(b)–(c)), MWCNTs display typical nanotubes with a range of diameters and no preferential alignment is noticed. Moreover, MWCNTs were found to disperse uniformly and randomly in the MC matrix, which indicates the good compatibility between MWCNTs and MC. For a MC–CNT composite solution with higher MWCNTs loading (MC$_5$), poorer dispersion of MWCNTs in the cellulose solution was observed which appeared in the form of agglomeration (figure 1(d)).

The optical photographs of the prepared RC film and RC–CNT composite films are shown in figure S1 (see online supporting information). The thicknesses of these films are 12 ± 1 $\mu$m. For pristine RC, the background can be seen very clearly. The transmittance of the blend films decrease with increasing the MWCNT loadings in the composite films, indicating the presence of MWCNTs in the RC matrix.

3.2. FTIR analysis

FTIR measurements were carried out to investigate the interactions between RC and MWCNTs in the composite films (figure 2). For pristine RC, there is a broad absorption band located from 3000 to 3500 cm$^{-1}$ corresponding to the intramolecular hydrogen bond and the hydroxyl group [7, 27]. An absorption located at 2900 cm$^{-1}$ is due to CH$_2$ groups [26]. In the C-O stretching vibration region, the peaks at 1163...
and 1061 cm\(^{-1}\) correspond to the C-O asymmetric bridge stretching and the C-O-C pyranose ring skeletal vibration, respectively [27]. For RC–CNT composite film (RC\(_5\)), a new peak appears at 1720 cm\(^{-1}\) corresponding to the carboxyl groups of MWCNTs which proves the existence of MWCNTs in the RC–CNT composite films.

3.3. Raman spectroscopy

Raman spectroscopy is one of the most powerful and informative techniques to investigate disorder sp\(^2\) carbon material [21]. Raman spectra of RC and RC–CNT composite film (RC\(_5\)) are characterized and displayed in figure 3. There are mainly two regions below 1500 cm\(^{-1}\) and above 2700 cm\(^{-1}\) observed for RC (figure 3(a)). In the 250–550 cm\(^{-1}\) region, bands observed are attributed to C-O, C-C-C, C-O-C, O-C-O and C-C-O deformations, respectively. The vibrational peak located at 900 cm\(^{-1}\) is due to the C-H bending [6]. The peak at 1095 cm\(^{-1}\) represents C-O ring stretching vibrations and C-O-C glycosidic bond stretching [18]. The peaks in the range of 1270 to 1500 cm\(^{-1}\) are assigned to C-C-H, O-C-H, C-O-H, H-C-H and CH\(_2\) bendings, respectively. And there is a strong band at 2900 cm\(^{-1}\) which corresponds to CH\(_2\) stretching vibrations [30]. The spectrum for RC\(_5\) presents essentially the same bands as RC with much weaker intensity (figure 3(b)). Meanwhile, two prominent peaks at 1570 cm\(^{-1}\) and 1320 cm\(^{-1}\) appear in the Raman spectrum of RC\(_5\) which correspond to the G and D bands of MWCNTs, respectively. The G band is caused by inplane vibration of the C-C bonds, and D band is assigned to the disorder induced by defects and curvature in the nanotube lattice [22]. The G and D peaks further confirmed the presence of MWCNTs in the RC\(_5\) composite films.

3.4. Thermal analysis

TG and derivative thermogravimetric (DTG) analysis were conducted to investigate the effect of MWCNTs on the thermal behaviors of RC in a nitrogen atmosphere. The results are displayed in figure 4 and table 1. Two significant weight loss stages below 400 ℃ are observed in the thermal degradation curve of RC (figure 4(a)). The initial weight loss occurred below 100 ℃, which is attributed to the evaporation of absorbed moisture. Physically adsorbed and hydrogen bond-linked water molecules were lost at this first stage. The second weight loss occurred between 250 and 400 ℃, which can be assigned to the thermal degradation and decomposition of RC. For RC–CNT composite films, two significant weight loss stages were also illustrated. However, the weight loss stages slightly shifted to a higher temperature with the addition of MWCNTs. The residues of the composite films manifest the combined effect that the residues of all the composite films are more than the combined residues of the pure RC and the input MWCNTs. For example, the residues of the pure RC and RC\(_5\) are 8.98 wt\% and 17.05 wt\%, respectively. This drastic improvement was attributed to the
strong interaction between MWCNTs and RC, which reduced the mobility of the polymer segments at the interface resulting in an increase of residue of the RC.

The curves of DTG analysis in figure 4(b) show that the temperature at the maximum mass loss rate ($T_{\text{max}}$) of RC is located at 335.5°C. It is also noted from table 1 that $T_{\text{max}}$ values of the composite films with different MWCNT loadings were somewhat higher than those of pristine RC due to the reinforcing effect of thermally stable MWCNT in the RC films.

### 3.5. Rheological properties

The effect of MWCNTs on the rheological properties of MC was studied since microstructures of the composites depend on their rheological properties [23]. Strain amplitude sweep tests were used to determine the linear-viscoelastic regime. The storage modulus $G'$ and loss modulus $G''$ versus dynamic amplitude sweep of pristine MC and MC$_i$ are shown in figure S2 in the online supporting information. It shows that the strain in the range of 1–10% was in the linear-viscoelastic regime. In our study, the strain was set to be 2% in all the dynamic rheological measurements.

The viscoelastic properties of MC containing different contents of MWCNTs were investigated and the results were listed in figures 5(A)–(G). In the case of pristine MC, MC$_1$ and MC$_2$ (figures 5(A)–(C)), $G''$ is larger than $G'$ for the solution over the whole frequency range. Moreover, there is a constant complex viscosity [$\eta^*$] at low frequencies which showed the MC solution was fully relaxed and displayed a typical Newtonian liquid behavior. The increase of MWCNTs changes the rheological property of MC solution. In the case of MC$_3$ (figure 5(D)), $G'$ is close to $G''$ which indicated MWCNTs begin to form very weak networks. On the other hand, when MWCNTs content is more than 4 wt% (figures 5(E)–(G)), $G'$ is higher than $G''$ which shows solid-like flow behavior. In addition, complex viscosity [$\eta^*$] shows a decrease with the increase of angular frequency, indicating MWCNTs–MWCNTs and MC–MWCNTs begin to form physical cross-links. Furthermore, complex viscosity increased rapidly with increasing MWCNT content, showing that the solid-like viscoelastic behavior was enhanced due to the formation of strong network.

The rheological property of solution depends on the interactions between MWCNTs and the MC solution. When MWCNTs were added to the MC solution, the physical interactions between MWCNTs–MC resulted in the increased complex viscosity. However, aggregation of MWCNTs appears with high MWCNT loadings in the MC solution, which is consistent with TEM result, resulting in the decrease of complex viscosity. The relaxation of MC is affected by the presence of MWCNTs, as shown in figures 5(A)–(G). At lower concentration of MWCNTs (figures 5(B)–(C)), the low-frequency rheological properties could be attributed to the effect of the MWCNTs on the polymer chain mobility [17]. At higher concentration (figures 5(D)–(G)), these responses are related to network formation due to MWCNTs–MWCNTs interactions.

### Table 1. The maximum mass loss rate ($T_{\text{max}}$), residues and mechanical properties of RC and its composite films with different MWCNT loadings.

<table>
<thead>
<tr>
<th>Samples</th>
<th>$T_{\text{max}}$ (°C)</th>
<th>Residue (%)</th>
<th>Tensile strength (MPa)</th>
<th>Young’s modulus (MPa)</th>
<th>Elongation at break (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>RC</td>
<td>335.5</td>
<td>9.0</td>
<td>13.7 ± 1.8</td>
<td>730 ± 9</td>
<td>1.4 ± 0.2</td>
</tr>
<tr>
<td>RC$_1$</td>
<td>339.8</td>
<td>12.5</td>
<td>15.5 ± 0.1</td>
<td>100 ± 60</td>
<td>3.1 ± 0.6</td>
</tr>
<tr>
<td>RC$_2$</td>
<td>342.8</td>
<td>13.2</td>
<td>19.2 ± 0.2</td>
<td>1460 ± 93</td>
<td>3.7 ± 0.3</td>
</tr>
<tr>
<td>RC$_3$</td>
<td>345.4</td>
<td>14.9</td>
<td>30.6 ± 0.1</td>
<td>1920 ± 17</td>
<td>5.2 ± 0.2</td>
</tr>
<tr>
<td>RC$_4$</td>
<td>344.8</td>
<td>15.3</td>
<td>26.8 ± 0.2</td>
<td>1269 ± 49</td>
<td>4.7 ± 0.1</td>
</tr>
<tr>
<td>RC$_5$</td>
<td>345.4</td>
<td>17.1</td>
<td>22.4 ± 1.3</td>
<td>1185 ± 37</td>
<td>4.7 ± 0.5</td>
</tr>
<tr>
<td>RC$_8$</td>
<td>343.1</td>
<td>18.5</td>
<td>21.5 ± 2.3</td>
<td>1068 ± 73</td>
<td>4.5 ± 0.1</td>
</tr>
</tbody>
</table>
Figure 5. The storage modulus $G'$, loss modulus $G''$ and complex viscosity $|\eta^*|$ of MC (A), MC$_1$ (B), MC$_2$ (C), MC$_3$ (D), MC$_4$ (E), MC$_5$ (F) and MC$_8$ (G) as a function of angle frequency and (H) tangent loss angle of MC based composites (curves a-g are MC, MC$_1$, MC$_2$, MC$_3$, MC$_4$, MC$_5$ and MC$_8$).
investigated and the typical stress–strain curves are presented in figure 6. As shown, the addition of MWCNTs resulted in an upwards slope of the stress–strain curve. It was found that incorporating MWCNTs into the RC matrix could improve its mechanical properties. The tensile strengths of RC with different contents of MWCNTs are listed in table 1. It is very obvious that the tensile strength of RC–CNT composite films improved with increasing MWCNT loadings. Incorporation of 3 wt% MWCNTs dramatically improved the mechanical properties of RC film. The tensile strength of pristine RC is 13.7 MPa, while its composite film with a loading of 3 wt% MWCNTs exhibited the strength of 30.6 MPa with an improvement of 123%, delivering the largest enhancement of the mechanical property of RC. This is due to the strong interaction between MWCNTs and the polymer matrix, which is favorable to the stress transfer between both components. With increasing MWCNT loading in the composite film, the tensile strength began to decrease slightly. This is due to the high loading of MWCNTs aggregated in the RC matrix, which is consistent with TEM images.

There is a similar trend for the Young’s modulus of RC–CNT composite films (table 1). The Young’s modulus also increased with MWCNT content at first, and then decreased with higher loadings. In the case of RC3, there is an increase of 163% in the Young’s modulus compared to pristine RC film. In addition, the introduction of MWCNTs also improved the elongation at break (table 1). These improvements in mechanical properties are mainly attributed to three aspects: the good compatibility between functionalized MWCNTs and the RC matrix, the homogeneous dispersion of MWCNTs and effective stress transfer between RC matrix and MWCNTs through the strong interfacial interactions. As a result, the introduction of MWCNTs as reinforcement effectively improved the mechanical properties of RC films.

Rheological properties may have significant impacts on the final film product and could be responsible for the potential for mechanical property enhancement [4]. There is an optimum loading value for MWCNTs in this system. Higher or lower loading leads to poorer mechanical properties. There are two intercompetitive factors to explain this phenomenon: (1) increasing MWCNT content can increase of interaction between MWCNTs and MC, which is beneficial to the stability of the network; (2) the increased viscosity can limit the mobility of MC chains, which goes against the cross-linking process [2]. The former effect will feature prominently when a small amount of MWCNTs are added in a system. In comparison, the latter one will become dominant when the MWCNT loading is too much that exceeds the optimum value. Besides this, high loading of MWCNTs would lead to their aggregation within the MC matrix and therefore phase separation.

4. Conclusion

Homogeneous and reinforced MC–CNT composites were fabricated by a simple solution-mixing method and a variety of rheological analyses were conducted in order to determine their properties. TEM images showed good dispersion of MWCNTs in the MC solution when a small amount of MWCNTs were introduced. Aggregation appears with higher MWCNT loading. The dynamic rheological measurement showed an increase of complex viscosity for MC solution with increased MWCNT content. Meanwhile, a 3D network forms due to its loss modulus exceeding storage modulus with higher MWCNT loading. The composite films showed simultaneously enhanced mechanical property. It is expected that the MWCNT-reinforced RC could be used to develop cellulose-based materials with high performances.

Acknowledgments

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References


[18] Li Z, Schulz L, Ackley C and Fenske N 2010 Adsorption of tetracycline on kaolinite with pH-dependent surface charges J. Colloid Interface Sci. 351 254–60


