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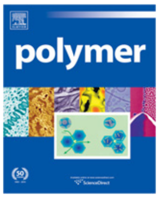

Effects of carbon nanotubes on rheological behavior in cellulose solution dissolved at low temperature

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ABSTRACT

Multi-walled carbon nanotubes (MWNTs) were dispersed, for the first time, in cellulose solution in 9.5 wt% NaOH/4.5 wt% thiourea aqueous system pre-cooled to −5 °C. Dynamic light scattering and transmission electron microscopy results revealed a relatively strong interaction existed between MWNTs and the cellulose macromolecules, leading to a good dispersion of MWNTs in the cellulose solution. Their rheological behaviors, especially the sol–gel transition were investigated by using the advanced rheological expanded system on the basis of Winter and Chambon theory. The gel point and gel concentration of the cellulose/MWNTs solution system were determined, indicating a regularly rheological behavior. The data of loss tangent and relaxation exponent (n) indicated an enhancement in the viscoelasticity of the MWNTs/cellulose system. The results from scaling law before and beyond the sol–gel transition in the MWNTs/cellulose system confirmed that the cluster formation and alteration of the gelation structure occurred at the gel point. Interestingly, the n values calculated by both the Winter and Chambon theory and scaling law were coincident only at relatively low temperature. The predicted gel strength values of the MWNTs/cellulose system were significantly larger than the pure cellulose solution, suggesting a relatively high strength, supported by the mechanical strength of the cellulose/MWNTs material.

1. Introduction

As the most abundant renewable resource, cellulose can be converted into derivatives and regenerated fibers and films, as well as various functional materials [1]. As a result of inter- and intramolecular hydrogen bonds, cellulose is not soluble in common solvent [2]. There are excellent solvents such as *N*-methylmorpholine-*N*-oxide (NMMO) [3], lithium chloride/*N*, *N*-dimethylacetamide (LiCl/DMAc) [4], and 1-butyl-3-methylimidazolium chloride [5], which can dissolve cellulose at high temperature. In our laboratory, a new solvent system including NaOH/thiourea, NaOH/urea and LiOH/urea aqueous solutions has been developed to dissolve cellulose at low temperature (−5 ~ −12 °C) rather than high temperature, creating a new concept and "green" approach for polymer dissolution. In the system a new hydrogen-bonding network structure between solvent molecules and cellulose macromolecules can be created to destroy the inter- and intramolecular hydrogen-bonding in the native cellulose at low temperature, leading to good dissolution [6]. It is worth noting that novel fibers have been spun from the cellulose dopes [7], and a series of functional materials has been created. Thus, the cellulose solution system is an attractive and interesting research on the preparation of nano-materials, especially inorganic nano-particles or carbon nanotubes in the aqueous system.

Carbon nanotubes (CNTs) are known as examples of nanomaterials with high aspect ratio and many exciting properties. These properties lead to a wide variety of possible applications, such as incorporation into composites for high-strength applications, formation of composites with high conductivity, use as field emitters for high-power microwave transmitter applications, low-voltage electromechanical actuators, electrostatic paint and nanoscale probe tips [8]. Nowadays, CNTs hybrids have attracted great attention, by introducing the remarkable properties of CNTs into flexible polymer materials. However, the difficulty of CNTs dispersing in common solvents confines its application and research. It has been reported that CNTs were introduced in cellulose materials to improve their mechanical properties and transport properties [9–11]. However, the dispersion of CNTs in NaOH/thiourea aqueous system has been published scarcely. Recently, we found that cellulose/MWNTs composite could be prepared by dispersing MWNTs in the NaOH/thiourea solvent to enhance the mechanical properties. To create cellulose/MWNTs materials, it is

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important to clarify the influence of MWNTs on the rheological properties and sol–gel transition of cellulose solution to explore the interactions between MWNTs and cellulose chains. In this condition, rheometer is a suitable tool for the investigation of the sol–gel systems [12,13]. In this work, the influences of MWNTs on the rheological behaviors of cellulose solution dissolved in NaOH/thiourea aqueous solution at low temperature were investigated. We hope to provide useful information on the interaction between two components and sol–gel transition behavior of the cellulose containing MWNTs to promote the development of MWNTs/cellulose functional materials. This work can supply a novel pathway and useful data for fabricating cellulose based materials containing MWNTs.

2. Experimental section

2.1. Materials

Cellulose (cotton linter pulps) with a α-cellulose content of more than 95% was supplied by Hubei Chemical Fiber Co. Ltd. (Xiangfan, China). Its weight-average molecular weight (M_w) was determined in 4.6 wt% LiOH/15.0 wt% urea aqueous solution with laser light scattering to be 12.0×10^4 g/mol [14]. The cellulose sample was vacuum-dried at 55 °C for 24 h to remove any moisture before use. NaOH and thiourea of analytical grade (Shanghai Chemical Reagent Co. Ltd., China) were used without further purification. Multi-walled carbon nanotubes (MWNTs, 99.9% purity) with a 10 nm outer diameter, about 3 ~ 5 nm inner diameter and more than several micrometers length were purchased from the Department of Chemical Engineering, Tsinghua University [15–17].

2.2. Preparation of cellulose/MWNTs solution and film

An aqueous solution containing NaOH/thiourea/H_2O at the ratio of 9.5:4.5:86.0 by weight was used as a solvent for cellulose. Desired amount of MWNTs was immersed in the solvent, and the MWNTs suspension was ultrasonically treated in a JY98-3D Ultrasonic Crusher (Ningbo Scientz Biotechnology Co. Ltd). The treated solution was pre-cooled to −5 °C, and desired amount of cellulose was added immediately at an ambient temperature below 25 °C within 5 min with stirring at 3000 rpm. The resultant solutions were centrifuged to degas at 4000 rpm for 10 min. To prevent any transformation of solution state at ambient temperature at long storage time, the prepared solutions were used immediately for viscoelastic tests without delay, coded as a *fresh* solution.

The weight ratio $f = W_{\mathrm{MWNTs}}/W_{\mathrm{cellulose}}$ was defined as a structure parameter. Cellulose/MWNTs solutions with different f values (0.1%, 0.5%, 1.0%, 1.5%, 2.0% and 2.5%) were investigated. For comparison, the cellulose solution without MWNTs was coded as *pure* cellulose solution in this work.

The transparent cellulose solution ($c_{\mathrm{cellulose}} = 4.0$ wt%) and a cellulose/MWNTs solution ($f = 0.5\%$, $c_{\mathrm{cellulose}} = 4.0$ wt%) were immediately cast on a glass plate to give a thickness of 250 mm for a gel sheet, and then immersed into a coagulation bath with 5 wt% H_2SO_4 for 5 min at 25 °C to coagulate and regenerate. The resulting films were washed with running water and then with deionized water. The wet films were fixed on a glass plate to prevent shrinkage, and finally were air-dried at ambient temperature to obtain regenerated cellulose films.

2.3. Characterization

Transmission electron microscope (TEM) observation of the morphology of cellulose solution and MWNTs/cellulose solution was carried out on a JEM-2010 (HT) transmission electron microscope (JEOL TEM, Japan). A thin layer of the dilute cellulose solution was suspended on a holey carbon film, which was supported on a copper grid. The specimen was dried in air at ambient temperature within 10 min and then was imaged on TEM at an accelerating voltage of 200 kV.

Dynamic light scattering (DLS) was used to characterize the molecular size and shape of the dilute cellulose solution in the NaOH/thiourea system. A modified commercial light scattering spectrometer (ALV/SP-125, ALV, Germany) equipped with an ALV-5000/E multi-τ digital time correlator and a He–Ne laser (at $\lambda = 632.8$ nm) was used at a scattering angle θ of 90°. The test solutions were made optically clean by filtration through 0.45 μm Millipore filters. The CONTIN program [18] was used for the analysis of the dynamic light scattering data. The hydrodynamic radius, R_h, was calculated by using the Stokes–Einstein relation as:

$$R_h = k_B T / 6\pi\eta_0 D \tag{1}$$

where k_B is the Boltzmann constant, T is the temperature in units of K, η_0 is the solvent viscosity, and D represents the translational diffusion coefficient.

The dynamic rheology measurement was carried out on an ARES-RFS III rheometer (TA Instruments, U.S.A.). Double-concentric cylinder geometry with a gap of 2 mm was used to measure dynamic viscoelastic parameters such as the storage modulus and loss modulus ($G'(\omega)$ and $G''(\omega)$) as functions of angular frequency (ω), time (t) or temperature (T). The rheometer was equipped with two force transducers allowing the torque measurement in the range from 0.004 to 1000 g cm. The values of the strain amplitude were checked to ensure that all measurements were set as 10%, which is within a linear viscoelastic regime. For each measurement, fresh cellulose solution was prepared, and then was poured into the Couette geometry instrument, which had been kept at each measurement temperature without pre-shearing or oscillating. Temperature control was established by connection with a Julabo FS18 cooling/heating bath kept within ±0.2 °C over an extended time. For the frequency sweep measurements, time $t = 0$ min was defined when the temperature reached the desired value. The sweep of frequency was from 0.01 to 100 rad/s. To reduce testing error, each test was repeated two times, and the differences were all very small and within experimental errors.

The tensile strength (σ_b) and elongation at break (ε_b) of the samples were measured on a universal testing machine (CMT-6503, Shenzhen SANS Test Machine Co. Ltd., China) according to the ISO6239-1986 standard with a strain rate of 1/min (tensile rate of 50 mm/min). Before testing, the films were allowed to rest for one week in 43% RH (saturated K_2CO_3 solution at room temperature). Because the strength data are related to the environmental temperature and humidity, these values were measured under the same conditions. Five parallel measurements were carried out for each sample.

3. Results and discussion

3.1. Interaction between MWNTs and cellulose in the solution

Our previous work [6] has revealed that cellulose forms inclusion complexes (ICs) which easily aggregate, and cellulose exists in NaOH/thiourea mainly as single ICs and sphere-like IC aggregates. To clarify the dispersion of MWNTs in the cellulose solution and the interactions between the two components, DLS and TEM were applied to study the dilute solution. Fig. 1 shows the apparent hydrodynamic radius ($R_{h,app}$) distribution of pure cellulose solution and MWNTs/cellulose solution. There were two peaks of 20 and 157 nm of $R_{h,app}$ in the pure cellulose solution, and 25 and 224 nm of

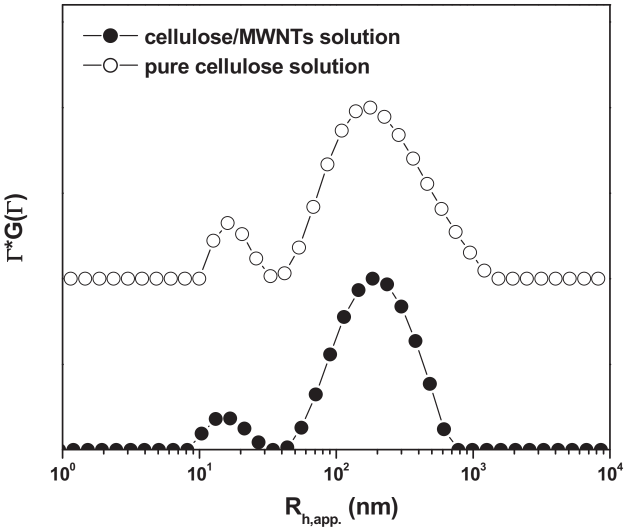

Fig. 1. CONTIN analysis of DLS measurement at an angle of 90° of pure cellulose solution with a 0.04 wt% concentration and a 0.5%(f)–0.04 wt%($c_{cellulose}$) cellulose/MWNTs solution. $\Gamma^*G(\Gamma)$ denotes the fraction of scattered intensity over the line-width range with $R_h = k_BT/(6\pi\eta D)$ and $\Gamma = Dq^2$.

$R_{h,app}$ in the MWNTs/cellulose solution, respectively, corresponding to single chains and IC aggregates of cellulose. However, no new peaks corresponding to MWNTs aggregates appeared in the MWNTs/cellulose solution. The results indicated strong interactions between MWNTs and cellulose, so the MWNTs were encaged in the cellulose IC aggregates, leading to the $R_{h,app}$ of IC aggregates in MWNTs/cellulose solution moving to higher values. Fig. 2 shows the TEM image of the pure cellulose dilute solution and MWNTs/cellulose sample. Sphere-like IC aggregates were observed as expected, rather than MWNTs aggregates. Moreover, the sphere-like aggregates with a diameter of 290 nm occurred in MWNTs/cellulose solution. The IC aggregates in the pure cellulose solution had a smaller dimension than that in the MWNTs/cellulose solution. Moreover, the aggregates in MWNTs/cellulose solution exhibited a smooth surface. In view of the DLS and TEM results, cellulose had a strong interaction with MWNTs and the MWNTs could be encaged in the cellulose IC aggregates, leading to good dispersion.

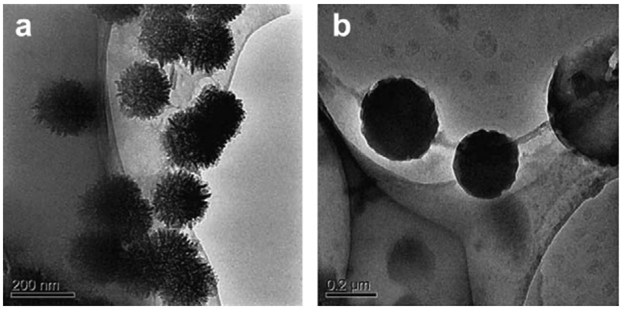

Fig. 2. TEM image of pure cellulose solution with a 0.04 wt% concentration (a), and a 0.5%(f)–0.04 wt%($c_{cellulose}$) cellulose/MWNTs solution (b).

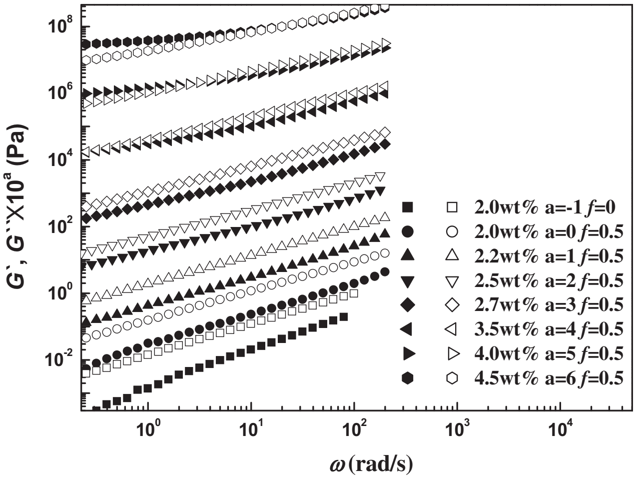

Fig. 3. Angular frequency ω dependence of storage modulus G' (solid symbols) and loss modulus G'' (open symbols) for $f = 0.5\%$ cellulose/MWNTs solution series and the pure cellulose solution. The data have been vertically shifted by 10^a with the given a to avoid overlapping.

3.2. *Rheological behaviors of MWNTs/cellulose solution*

Fig. 3 shows the angular frequency ω dependence of storage modulus (G') and loss modulus (G'') of the MWNTs/cellulose solution series with $f = 0.5\%$ at 25 °C at various cellulose concentrations. The data are vertically shifted by a factor of 10^a to avoid overlapping. It is noted that viscoelasticity enhanced with the addition of MWNTs, indicating the interaction between the MWNTs and cellulose. At low cellulose concentration, $G''(\omega)$ was always higher than $G'(\omega)$ in the whole frequency range without any plateau appearing at $G'(\omega)$ vs ω curves, indicating a liquid behavior. However, at high cellulose concentration, $G'(\omega)$ became higher than $G''(\omega)$ with a plateau appearing at the $G'(\omega)$ vs ω curves in the low-frequency range, suggesting a gel behavior. At a moderate value of cellulose concentration, there was the transition region from fluid to gel, where the curve of $G'(\omega)$ becomes parallel to $G''(\omega)$ on the logarithmic coordinate over a wide frequency range, such as the curve with $c_{cellulose} = 2.2$ wt%. This indicated the occurrence of the sol–gel transition in the MWNTs/cellulose solution.

The most widely used method for confirming gel point is the Winter and Chambon theory [19–21]. They first experimentally established a scaling law of $G'(\omega) = G''(\omega) \sim \omega^{1/2}$ at the gel point, and later generalized it to be

$$G'(\omega) = G''(\omega) \sim \omega^n \quad 0 < n < 1 \tag{2}$$

and

$$G''(\omega)/G'(\omega) = \tan\delta = \tan(n\pi/2) \tag{3}$$

for the gelling system, where tan δ is the loss tangent, and n is the relaxation exponent at the gel point. The frequency independence

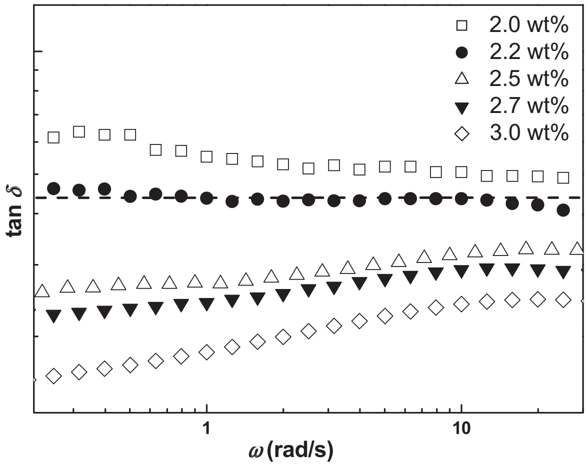

Fig. 4. tan δ as a function of ω for the $f = 0.5\%$ cellulose/MWNTs solutions at various cellulose concentrations at 25 °C.

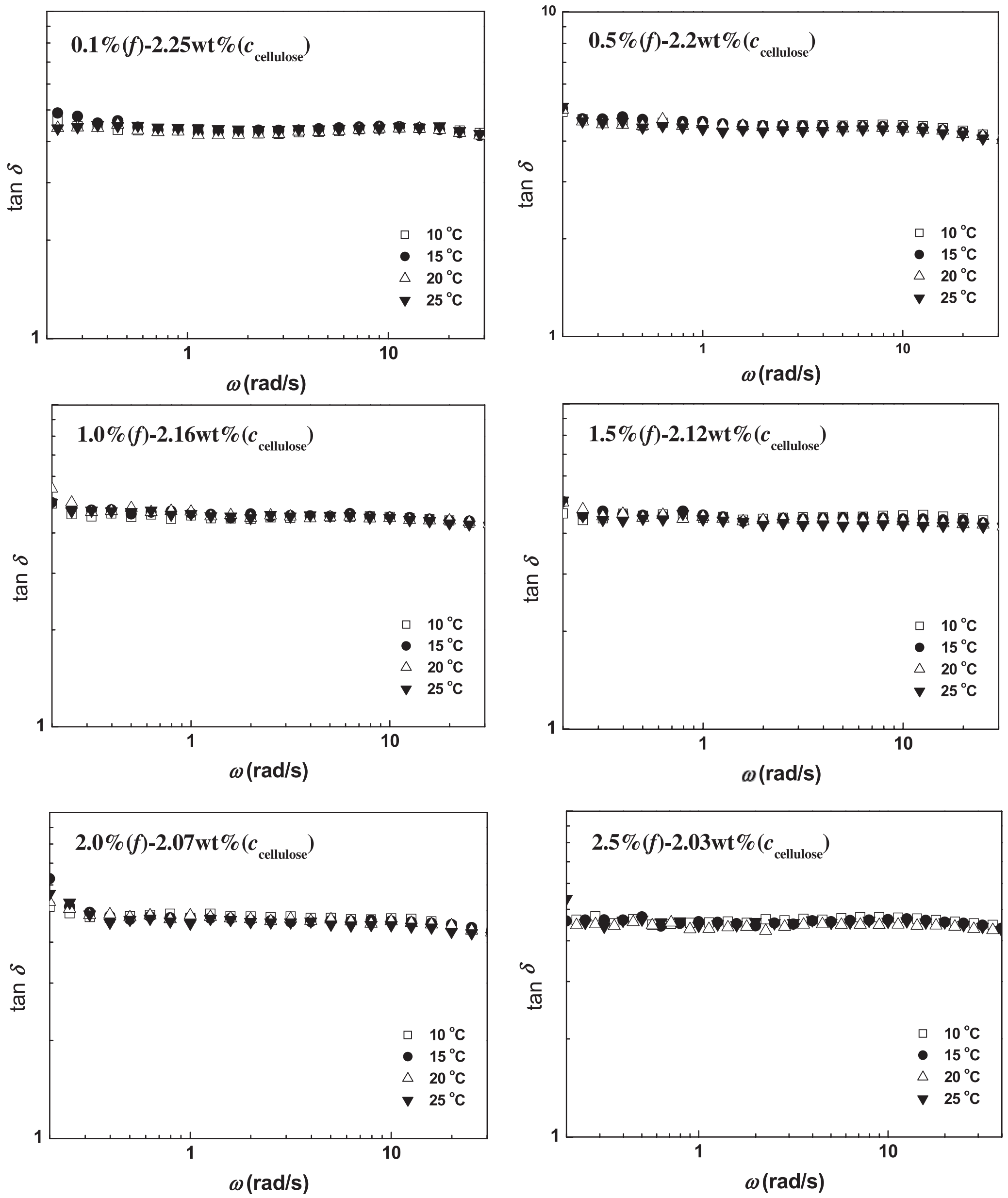

Fig. 5. tan δ as a function of ω for different cellulose solutions coded as 0.5% (f)−2.2 wt%($c_{cellulose}$), 0.1% (f)−2.25 wt%($c_{cellulose}$), 1.0% (f)−2.16 wt%($c_{cellulose}$), 1.5% (f)−2.12 wt%($c_{cellulose}$), 2.0% (f)−2.07 wt%($c_{cellulose}$) and 2.5% (f)−2.03 wt%($c_{cellulose}$) (each solution is at its gel point) at different temperatures.

of tan δ in the vicinity of the gel point has been widely examined for gels [22,23]. Many results have shown that this method is reliable and valid for the determination of the gel point such as the critical gel concentration (c_g) and the critical gel temperature (T_{gel}). Typically, the Winter and Chambon theory has been successfully applied to a fresh solution of cellulose in NaOH/thiourea aqueous system in our previous work [24].

Fig. 4 shows tan δ as a function of ω for $f = 0.5\%$ cellulose/MWNTs solution with different cellulose concentrations at 25 °C. The gel point was determined from plots of tan δ vs frequency, depending on which governs the gelation process [25,26]. The tan δ value for all the curves decreased with an increase of cellulose concentration, indicating an enhancement of elasticity of the cellulose system. The tan δ value of the curve for the cellulose solution with $c_{cellulose} = 2.2$ wt% at 25 °C approached a plateau value of 4.40, indicating frequency independence in the frequency range from 0.2 to 30 rad/s [27]. This obeyed the Winter and Chambon theory [20,21]. Therefore, the gel concentration (c_g) of the $f = 0.5\%$ cellulose/MWNTs solutions at 25 °C was confirmed to be 2.2 wt%. And the relaxation exponent n has been calculated to be 0.858. In general, the n value is related to the physically fractal dimension, and reflects the degree of compactness of the network. Usually, a lower value of n implies the formation of a more highly elastic gel [28–30]. In fact, different values of n have been observed for physical gels, such as 0.77 ~ 0.83 for poly(vinyl chloride) solution [31], 0.34 ~ 0.67 for the polycaprolactone system [32], 0.47 for the waterborne polyurethane system [23], and 0.891 for the pure cellulose solution system [24]. The results revealed a less elastic nature of the cellulose/MWNTs solution at the gel point. By the frequency independence behavior, the gel point of the MWNTs/cellulose solutions with different f values could be determined (not shown).

The gel point of pure cellulose solution is sensitive to temperature: c_g varies from 3.0 wt% to 2.5 wt% as the temperature

Table 1
The experimental values of gelation concentration c_g for the sol–gel transition, tan δ, relaxation exponent n, and gel strength S_g in the MWNTs/cellulose solution with different f values

Sample	T (°C)	c_g (wt%)	tan δ	n	S_g
$f = 0.1\%$	10	2.25	4.34 ± 0.12	0.856 ± 0.004	0.098
	15	2.25	4.36 ± 0.10	0.856 ± 0.003	0.088
	20	2.25	4.30 ± 0.12	0.854 ± 0.004	0.074
	25	2.25	4.40 ± 0.10	0.858 ± 0.003	0.062
Average			4.35 ± 0.12	0.856 ± 0.004	
$f = 0.5\%$	10	2.2	4.49 ± 0.12	0.860 ± 0.004	0.0940
	15	2.2	4.50 ± 0.18	0.860 ± 0.004	0.0784
	20	2.2	4.45 ± 0.14	0.861 ± 0.003	0.0676
	25	2.2	4.40 ± 0.20	0.858 ± 0.006	0.0590
Average			4.46 ± 0.20	0.860 ± 0.006	
$f = 1.0\%$	10	2.16	4.48 ± 0.11	0.860 ± 0.003	0.0719
	15	2.16	4.55 ± 0.16	0.862 ± 0.004	0.0593
	20	2.16	4.53 ± 0.16	0.862 ± 0.004	0.0498
	25	2.16	4.56 ± 0.16	0.862 ± 0.004	0.0443
Average			4.52 ± 0.16	0.862 ± 0.004	
$f = 1.5\%$	10	2.12	4.48 ± 0.11	0.860 ± 0.003	0.0713
	15	2.12	4.48 ± 0.11	0.860 ± 0.003	0.0593
	20	2.12	4.41 ± 0.14	0.858 ± 0.004	0.0510
	25	2.12	4.32 ± 0.11	0.855 ± 0.003	0.0480
Average			4.42 ± 0.14	0.858 ± 0.004	
$f = 2.0\%$	10	2.07	4.77 ± 0.14	0.868 ± 0.001	0.0659
	15	2.07	4.66 ± 0.14	0.865 ± 0.005	0.0547
	20	2.07	4.70 ± 0.16	0.866 ± 0.004	0.0461
	25	2.07	4.60 ± 0.12	0.859 ± 0.007	0.0424
Average			4.68 ± 0.16	0.864 ± 0.007	
$f = 2.5\%$	10	2.03	4.62 ± 0.10	0.864 ± 0.003	0.0476
	15	2.03	4.58 ± 0.15	0.863 ± 0.004	0.0395
	20	2.03	4.44 ± 0.12	0.859 ± 0.003	0.0370
	25	2.03	4.45 ± 0.13	0.859 ± 0.004	0.0291
Average			4.52 ± 0.20	0.861 ± 0.004	
Pure solution [24]	10	3.00	5.70 ± 0.16	0.889 ± 0.003	0.226
	15	2.85	5.84 ± 0.16	0.892 ± 0.003	0.161
	20	2.67	5.78 ± 0.20	0.891 ± 0.004	0.104
	25	2.50	5.72 ± 0.08	0.890 ± 0.002	0.068
Average			5.77 ± 0.20	0.891 ± 0.004	

increases from 10 to 25 °C [24]. However, a different behavior appeared in the cellulose/MWNTs solution. Fig. 5 shows tan δ as a function of frequency ω for MWNTs/cellulose solution at different temperatures in the range from 10 to 25 °C. Take 0.5%(f)–2.2 wt%($c_{\text{cellulose}}$) solution for example; all tan δ curves displayed a constant value of about 4.46, indicating agreement to the Winter and Chambon theory [20,21]. In our findings, the c_g values have been determined to be the same (2.2 wt%), suggesting the gel point is insensitive to the temperature from 10 °C to 25 °C, different from the pure cellulose solution. Obviously, the introduction of MWNTs could alter the gelation properties of the cellulose solution. The results revealed that a more stable structure between cellulose macromolecules, MWNTs and solvent molecules existed in the MWNTs/cellulose solution. Other solutions with different MWNTs contents, coded as 0.1%(f)–2.25 wt%($c_{\text{cellulose}}$), 1.0%(f)–2.16 wt%($c_{\text{cellulose}}$), 1.5%(f)–2.12 wt%($c_{\text{cellulose}}$), 2.0%(f)–2.07 wt%($c_{\text{cellulose}}$) and 2.5%(f)–2.03 wt%($c_{\text{cellulose}}$) (each solution is at its gel point) at different temperatures have a similar behavior. And the temperature insensitive behavior was universal, similar to the $f = 0.5\%$ cellulose/MWNTs solution. This indicated that the MWNTs/cellulose solution properties were a universal phenomenon in the f value range from 0.1% to 2.5%. Interestingly, tan δ values at the gel point of each MWNTs/cellulose solution with different f values were close and in agreement with each other, as listed in Table 1. Compared with the n value of the pure cellulose solution, the MWNTs/cellulose solution had smaller n value, indicating that the pure cellulose solution was still less elastic than MWNTs/cellulose solution. Moreover, the vanishing of temperature dependence with the introduction of MWNTs indicated a more stable solution consisting of cellulose molecules, solvent and MWNTs.

Fig. 6 shows the c_g variation as a function of the f value in the MWNTs/cellulose solution. c_g decreased as f increased, indicating the cellulose solutions form a gel more easily at higher f value. Moreover, the c_g curve was a linear function to f. Therefore, the c_g value for the cellulose solutions was affected significantly by the MWNTs amount in the system, as a result of the interactions between the cellulose molecules and the MWNTs. In view of these results, the Winter and Chambon theory was proved to be applicable to the MWNTs/cellulose solution, which is a complex system.

$G(t)$ is predicted to obey a power law relaxation at the gel point [32]:

$$G(t) = S_g \cdot t^{-n} \tag{4}$$

Here S_g is the gel strength and has an unusual dimension of Pa·s^n, n is also the relaxation exponent that determines the stress relaxation rate at the gel point. To express S_g as $S_g = G(t) \cdot t^n$, a similar expression can be applied to $G'(\omega)$ and $G''(\omega)$ at the gel point as [33]:

$$G'(\omega) = G''(\omega)/\tan\delta = S_g \omega^n \Gamma(1-n)\cos(n\pi/2) \tag{5}$$

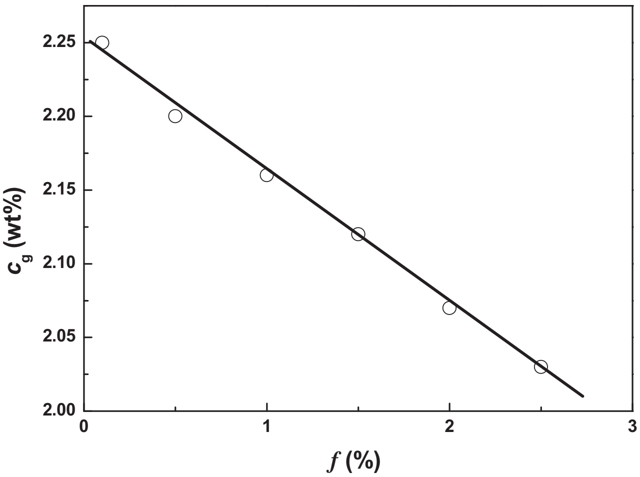

Fig. 6. c_g as a function of the f value of MWNTs/cellulose solution.

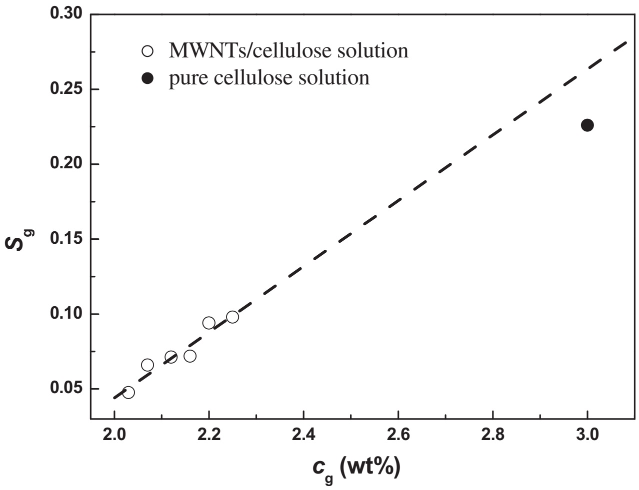

Fig. 7. S_g values at 10 °C of the MWNTs/cellulose solution and pure cellulose solution series as a function of c_g. The dashed line gives the linear fitting for the MWNTs/cellulose solution (open symbols).

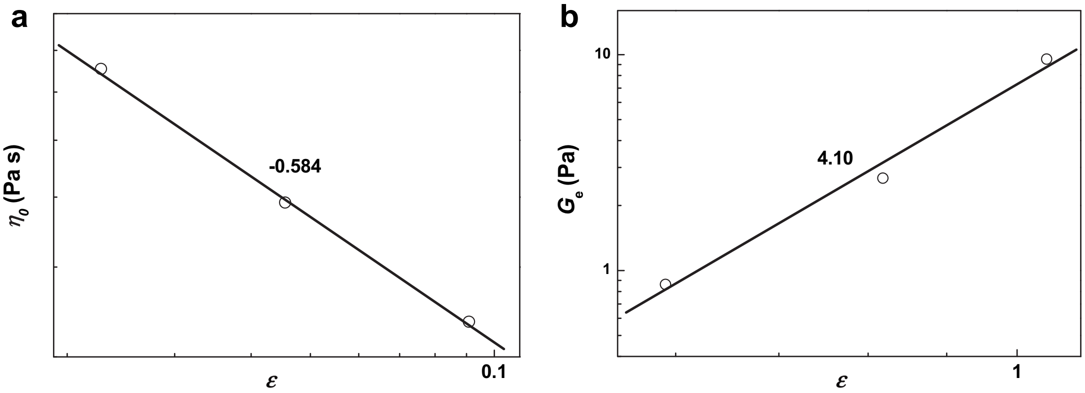

Fig. 8. η_0 (a) and G_e (b) as a function of the relative distance ϵ for the $f = 0.5$ cellulose/MWNTs solution at 10 °C. The linear fittings give solid straight lines, and the values represent the slope of the fitted lines.

Here $\Gamma(1-n)$ is the Γ function. By testing the n value, we can calculate S_g from $G'(\omega)$ and $G''(\omega)$ at the gel point using Eq. (5), and the calculated S_g data are also listed in Table 1. Fig. 7 shows S_g values of MWNTs/cellulose solution and the pure cellulose solution series at 10 °C as a function of c_g. The dashed line displayed the linear fitting to the MWNTs/cellulose solution. There was a linear relationship between S_g and c_g, indicating that S_g was related to the total mass of cellulose in the system. For a constant n, the increase of the cross-link density of a chemical gel usually leads to an increase in S_g [25,32]. In our gelling system, the S_g values were lower than the reported values of poly(vinyl chloride)/bis(2-ethylhexyl) phthalate or polycaprolactone systems [32,33]. It is suggested that the cellulose gels formed in the temperature range from 10 to 25 °C were relatively weak on the whole, which is in agreement with a high n value. Compared with the S_g values of MWNTs/cellulose solution, the solid point of the pure cellulose solution at 3.0 wt% cellulose concentration was lower than the fitted line of MWNTs/cellulose solution. The extrapolated S_g value of MWNTs/cellulose solution was larger than the pure cellulose solution; this further confirmed the strong interactions between cellulose and MWNTs.

3.3. *Scaling law before and beyond sol–gel transition*

The data of $f = 0.5\%$ cellulose/MWNTs solution from the scaling law before and beyond the sol–gel transition were compared with those from the Winter and Chambon theory. Because of the critical nature of the liquid–solid transition, transient rheological properties such as zero-shear viscosity (η_0) measurable before the gel point, and equilibrium modulus (G_e) measurable beyond the gel point, show a distinct scaling behavior in the vicinity of the gel point [34] as

$$\eta_0 \propto \varepsilon^{-\gamma} \quad \text{for } p < p_g, \qquad G_e \propto \varepsilon^{z} \quad \text{for } p > p_g \tag{6}$$

Here $\varepsilon = |p_g - p|/p_g$ indicates the relative distance of a variable p departing from the sol–gel transition point p_g, and p can be the cross-linking degree, gelation time, gelation temperature, gelation concentration and so forth. In Eq. (6), γ is the critical exponent determining the critical characteristics in the vicinity of the sol–gel transition, and γ is a parameter governing the gelation rate. On the other hand, G_e is the quasi-equilibrium modulus, and z is the scaling exponent [35]. Winter et al. [20,26] have proposed a scaling law to describe the relationship between n, z, and γ before and beyond the gel point as

$$n = z/(z+\gamma) \tag{7}$$

where n is the scaling exponent for Eqs. (2 and 3) at the gel point. The same expression has also been derived by Martin et al. [36]. Once we have obtained the c_g of the MWNTs/cellulose solution in NaOH/thiourea system, we can use the cellulose concentration (c) to replace the variable p as $\varepsilon = |c_g - c|/c_g$ to calculate the exponents γ and z. Therefore, γ and z can be directly calculated from the slope of the plots of η_0 and G_e against ϵ in log–log scale.

Table 2
γ, z values measured and the calculated n values by scaling law for $f = 0.5\%$ cellulose solution

T (°C)	c_g (wt%)	γ from scaling law	z from scaling law	n from scaling law	n from Winter theory
10	2.2	0.584	4.10	0.875	0.860 ± 0.004
15	2.2	0.620	5.26	0.894	0.860 ± 0.004
20	2.2	0.516	5.66	0.916	0.861 ± 0.003
25	2.2	0.489	5.74	0.922	0.858 ± 0.006

Fig. 8 shows η_0 (a) and G_e (b) as functions of the relative distance ϵ for the $f = 0.5$ cellulose/MWNTs solution at 10 °C. The curves at the other temperatures showed a similar rule and they were not shown here. The values of the critical exponent γ and z are listed in Table 2. In Fig. 8(a), the zero-shear viscosity was estimated by the extrapolation to zero frequency. The linear fittings exhibited solid straight lines at 10 ~ 25 °C. In the measured concentration range below c_g, a linear fit could be obtained for the cellulose solution at each temperature. The γ value varied with temperature, and as shown in Eq. (6), larger γ indicated a faster gelation rate. In another way, the gelation rate is defined as the increment of η_0 per ϵ. By taking the derivative of η_0 against ϵ and rearranging the equation, the gelation rate: $d\eta_0/d\epsilon = -\gamma\eta_0/\epsilon$ could be calculated. On the basis of this definition of the gelation rate, the gelation rate was faster at relatively low temperature, because the cellulose solution has higher values of η_0 at low temperature [36]. The capability of the gelation was governed not only by the exponent γ but also by η_0 that is a function of temperature [37]. In Fig. 8(b), G_e has been obtained from $G'(\omega)$ in the frequency independent range. For the MWNTs/cellulose solution with the same f and cellulose concentration, G_e also behaved as a function of temperature, and the slopes (z) increased as temperature increased, indicating that the growth rate of the cluster was also influenced by the temperature. z is related to the growth rate of clusters in the gelling system beyond the gel point. Higher z values could be observed at higher temperature, indicating that the growth of the network structure could be accelerated at higher temperature and the temperature had a more obvious effect on the network beyond the gel point. This was different from the pure cellulose solution, in which the z value beyond the gel point is independent of the temperature [24].

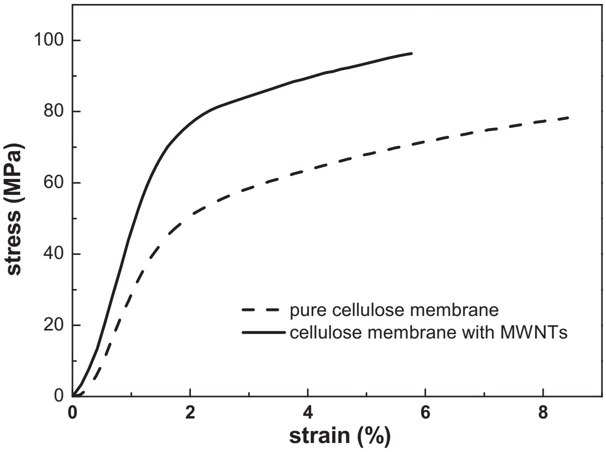

Fig. 9. Stress–strain curves for pure cellulose membrane ($c_{\text{cellulose}} = 4$ wt%) and cellulose membrane with MWNTs ($f = 0.5\%$, $c_{\text{cellulose}} = 4.0$ wt%).

Therefore, the introduction of MWNTs could destroy the cluster structure of the cellulose/solvent. From Table 2, the n values from scaling law and Winter theory coincided with each other only at low temperature (10 °C). The results indicated that the symmetric scaling law before and beyond the gel point was suitable for application to the complex cellulose system at relatively low temperature, similar to the pure cellulose solution. Therefore, the MWNTs/cellulose solution exhibited behaviors similar to the cellulose solution, and can be used to fabricate various fibers, films and beads.

3.4. Mechanical properties of cellulose/MWNTs materials

To further support the conclusion dealing with strong interaction between MWNTs and cellulose in the MWNTs/cellulose system, the mechanical properties of the membrane prepared from the cellulose solution containing MWNTs were measured. The stress–strain curves for the pure cellulose membrane ($c_{\text{cellulose}} = 4.0$ wt%) and the MWNTs/cellulose membrane ($f = 0.5\%$, $c_{\text{cellulose}} = 4.0$ wt%) are shown in Fig. 9. With the addition of MWNTs, the tensile strength of the cellulose membrane and the Young's modulus increased a lot, while the elongation at break decreased slightly. The results indicated that the addition of MWNTs significantly improved the mechanical properties of the cellulose membranes, in accordance with the conclusion drawn by S_g. Therefore, the MWNTs/cellulose solution will be promising for the creation of MWNTs based functional materials.

4. Conclusions

MWNTs have been dispersed in the cellulose solution through mixture in NaOH/thiourea aqueous solution at low temperature. The TEM and DLS results indicated that a strong interaction between MWNTs and cellulose chains led to the bonding between MWNTs and cellulose chains in the cellulose IC aggregates. The MWNTs/cellulose solution could be described by the Winter and Chambon theory from 10 to 25 °C. Furthermore, the scaling law before and beyond the gel point: $n = z/(z+\gamma)$ for the MWNTs/cellulose solution was coincident with the Winter and Chambon theory at relatively low temperature, similar to the pure cellulose solution. The addition of MWNTs reduced the tan δ and n values, indicating a stronger interaction between MWNTs, cellulose macromolecules and solvent molecules existed in the solution. The c_g values in the MWNTs/cellulose solution system decreased linearly with an increase of f, but the temperature dependence of c_g disappeared, different from the pure cellulose solution. The MWNTs/cellulose solution was relatively stable, compared with the pure cellulose solution. There was relatively high gel strength and strong interaction in the MWNTs/cellulose solution system, which were also supported by the fact that the mechanical properties of the cellulose materials could be improved by the addition of MWNTs.

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