Morphological influence of Cellulose Nanoparticles (CNs) from Cottonseed Hulls on Rheological Properties of Polyvinyl Alcohol/CN Suspensions

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Abstract

The present work describes the isolation of cellulose nanoparticles (CNs) with different morphologies and their influence on rheological properties of CN and CN-poly (vinyl alcohol) (PVA) suspensions. Cottonseed hulls were used for the first time to extract three types of CNs, including fibrous cellulose nanofibers, rod-like cellulose nanocrystals and spherical cellulose nanoparticles through mechanical and chemical methods. Rheology results showed that the rheological behavior of the CN suspensions was strongly dependent on CN concentration and particle morphology. For PVA/CN systems, concentration of PVA/CN suspension, morphology of CNs, and weight ratio of CN to PVA were three main factors that influenced their rheology behaviors. This research reveals the importance of CN morphology and composition

concentration on the rheological properties of PVA/CN, providing new insight in preparing high performance hydrogels, fibers and films base on PVA/CN suspension systems.

Keywords: Cottonseed hull, cellulose nanocrystals, morphology, polyvinyl alcohol, rheological behavior

1. Introduction

Cellulose, the most abundant natural biopolymer on earth, is widely used because of its low-cost, biocompatibility, biodegradability, and sustainability (Yue et al., 2012). Cellulose nanoparticles (CNs), including cellulose nanofibers (CNFs), rod-like cellulose nanocrystals (CNCs) and spherical cellulose nanocrystals (SCNCs), can be extracted from various cellulosic sources through mechanical disintegration , controlled sulfuric acid hydrolysis and mixed acid hydrolysis (Wang, Ding & Cheng, 2007), respectively. Because of the large surface area, high aspect ratio, high Young's modulus and lightweight, CNs have been applied as multifunctional agents in many fields, especially in biodegradable composites, biomedicine, packaging film and gels, where green and environmentally friendly materials are highly desirable (Li et al., 2015).

In most of the CN-reinforced composites, the properties are dependent on the type of CNs employed, dispersion microstructure, and processing conditions (Habibi, Lucia & Rojas, 2010). For instance, CNFs exhibit stronger reinforcements in a polymer matrix because of their larger aspect ratio and stronger percolation ability. Colloidal aqueous suspensions of CNCs develop three different phase structures, from isotropic, chiral nematic ordered structure to gel as the concentration increases, resulting in a distinct optical performance (Kim & Song, 2015). SCNCs show extremely uniform size, larger specific area and higher thermal stability than rod-like CNCs (Wang, Ding & Cheng, 2007). Furthermore, the dispersion of CNs in polymer matrix also

strongly effects the mechanical properties of the composites (Kamal & Khoshkava, 2015; Liimatainen et al., 2013). Therefore, understanding the relationships among processing, structure and morphology behavior of various types of CNs and CN-reinforced polymer suspension is of considerable scientific interest and practical significance in the material research of property improvement (Li et al., 2015).

Based on the rheology theory (Mewis & Wagner, 2012), particle shape has significant effects on dispersion rheology that presents in dilute dispersions and polymer-particle suspensions, which can only be partly understood by mapping onto the established behavior of dispersions of spherical particles. Some molecular details like particle size, alignment, inter-particle spacing and their affinity with the surrounding media (hydrophilicity or hydrophobicity), which controls particle-particle and particle-solvent interactions, and greatly affects the system rheology behavior. Rheology behavior can help predict the thermodynamic properties of CNs and reveal the dispersion microstructure of the CN/polymer suspensions. Therefore, rheology measurement is an effective method to study the miscibility and phase morphology of CN/polymer blends, which strongly affect the mechanical properties of the CN-based materials (Yao, Mukuze, Zhang & Wang, 2013). Although extensive studies reported that both CNCs (Kim & Song, 2015; Lu, Hemraz, Khalili & Boluk, 2014; Shafiei-Sabet, Hamad & Hatzikiriakos, 2012) and CNFs (Ishii, Saito & Isogai, 2011; Saarinen, Haavisto, Sorvari, Salmela & Seppälä, 2014) exhibited a typical shear thinning and viscoelastic rheological behavior in aqueous and/or CN/polymer blends (Grüneberger, Künniger, Zimmermann & Arnold, 2014; Li et al., 2016) suspensions, there are few investigations compared the rheological properties between CN suspensions from the same cellulose material and CN-reinforced polymer suspensions. Based on the comparison, we can proposed a detail and reasonable mechanism of how the morphology of CNs effected on the

rheological behavior of polymer system, and then to figure out the general suitable addition amount for different type of CNs, e.g. CNFs, CNCs or SCNCs in polymers based on the rheological principle. Poly(vinyl alcohol), as one of the most used polymers in the film industry, was selected as the representative matrix in our polymer/CN system.

Cottonseed hulls are the outer covering of cottonseeds, which are removed from the cotton kernel before the oil is extracted. They are currently used as roughage in animal feed, as a garden or field mulch, or as a component of the growth media for mushroom production. As cottonseed hulls are a readily available and inexpensive by-product of cotton, it is important to develop their new applications in efforts to promote green and high-value chemistry (Cheng, Dowd, Shogren & Biswas, 2011).

In this work, cottonseed hulls were used for the first time to extract CNCs, SCNCs and CNFs through sulfuric acid hydrolysis, mixed acid hydrolysis and mechanical disintegration, respectively. The rheological behaviors of various CN suspensions and PVA/CN suspensions were studied comprehensively in order to establish the relationships between the CN morphology and rheological behavior of the CN and PVA/CN suspensions. A detail and reasonable mechanism of how the morphology of CNs effected on the rheological behavior of PVA was proposed and the general suitable addition amount for different type of CNs, e.g. CNFs, CNCs or SCNCs in PVA was also estimated based on the rheological results. It is expected that these results will be useful for preparation of high performance CN/PVA and other CN/polymer composites.

2. Experiment and characterization

2.1 Materials and methods

Cottonseed hulls were supplied by Delta Oil Mill, Inc. (Jonestown, Mississippi, U.S.A), which contain cellulose (30.8 wt%), hemicellulose (20.0 wt%), lignin (17.8 wt%) and other components like protein (5.2 wt%), crude fat (2.1 wt%), ash (3.0 wt%) and moisture (11.5 wt%) (Sutivisedsak, Cheng, Dowd, Selling & Biswas, 2012). They were crushed and passed through an 80-mesh sieve to eliminate impurities. Chemical reagents, including sodium chlorite (80 wt%, puriss.p.a), acetic acid (99.7 wt%, ACS reagent), sodium hydroxide (97 wt%, ACS reagent), sulfuric acid (98 wt%, reagent grade) and hydrochloric acid (37 wt%, reagent grade), were all purchased from Sigma-Aldrich Corp. (St. Louis, MO, U.S.A.). All chemicals and deionized water were used as received.

2.2 Isolation of pure cellulose from cottonseed hulls

The procedures for isolating cellulose from cottonseed hulls follow the steps used in our previous work (Zhou, He, Jiang & He, 2015). In brief, the crushed and dried cottonseed hull material was bleached twice with 1% (w/v) sodium chlorite solution (fiber to liquor ratio of 1:35 w/v) at 75°C for 1 h with an acetate buffer to maintain the solution pH<4, in order to remove most of the lignin. The samples were then treated with 10 wt% sodium hydroxide (NaOH) overnight at room temperature, followed by treatment at 90°C for 3 h to remove the hemicelluloses. Finally, the samples were further purified with an acidified sodium chlorite solution at 75 °C for 1 h. The cellulose obtained was washed with distilled water until a neutral pH reached and then dried at 60°C for use.

2.3 Preparation of CNF suspensions

The CNFs were prepared by mechanical disintegration using the wet disk milling and high-pressure homogenization. In brief, water suspension containing 1.5 wt% cottonseed hull

cellulose was disk milled using a Supermasscolloider MKCA6-2 (Masuko Sangyo Co., Ltd., Saitama, Japan) with a disk clearance of 4 μm at a rotational speed of 1000 rpm. The suspension was collected and disk milled repeatedly at the same rotational speed but with a series of disk clearance of 2, 1, 0.5, 0.4, 0.3, 0.2, 0.1 μm successively. After that, the CNF suspension was pumped through a pair of Z-shaped interaction chambers (one 200 μm ceramic and one 87 μm diamond) five times at an operating pressure of 207 MPa by a high-pressure homogenizer (Microfluidizer M-110P, Microfluidics Corp., Newton, MA, U.S.A.). Finally, the obtained CNF suspension was adjusted to the 1.5, 1.0, 0.5 and 0.25 wt%, labeled as CNF-1.5, CNF-1.0, CNF-0.5, and CNF-0.25 for the rheological measurements.

2.4 Preparation of CNC suspensions

The pure cottonseed hull cellulose was treated with 64 wt % sulfuric acid at 45 °C for 50 min under vigorous stirring, in a 1:20 cellulose-to-liquor ratio (g/ml), based on procedure used in previous work(Zhou, He, Jiang & He, 2015). After being diluted using 10-fold deionized water, the suspension was centrifuged twice at 9,000 rpm for 10 min to remove the excess acid. The collected sediment was re-dispersed in fresh deionized water, and placed into the regenerated cellulose dialysis tubes. The dialysis was conducted in deionized water for 2~3 days until neutral pH was reached. Finally, the CNC suspensions were adjusted to 1.5, 1.0, 0.5, and 0.25 wt %, labeled as CNC-1.5, CNC-1.0, CNC-0.5, and CNC-0.25 by slowly evaporating the water or adding the deionized water for the rheological measurements.

2.5 Preparation of SCNC suspensions

The SCNCs were extracted from the pure cellulose using the mixed-acid hydrolysis method (Wang, Ding & Cheng, 2007). In brief, the cottonseed hull cellulose was treated with mixed

acids composed of 30% (v/v) sulfuric acid and 10% (v/v) hydrochloric acid in water for 10 h at 68 °C. The ratio of mixed acid to cellulose was 60 ml/g. The suspension was under ultrasonic treatment and vigorous stirring during the treatment. After hydrolysis, the suspension was centrifuged and dialyzed, following the same steps used for the CNC preparation. The SCNC suspension was also adjusted to the 1.5, 1.0, 0.5 and 0.25 wt%, labeled as SCNC-1.5, SCNC-1.0, SCNC-0.5, and SCNC-0.25 for the rheological measurements.

2.6 Preparation of CN/PVA suspensions

1 g PVA powder was dispersed in a certain amount of deionized water and then the mixture was subjected to vigorous stirring at 80 °C for 1 h and room temperature for 23 h to prepare 5 wt% and 15 wt% concentration of PVA in water. 3 wt%, 6 wt% or 9 wt% amount of CNs (ratio of CNs to PVA) were mixed into the suspensions and stirred at room temperature for 24 h. The well dispersed suspensions were stored in sealed glass containers and placed in a refrigerator at 5 °C prior to the rheological measurements. Sample codes and details of the formulations of each sample are shown in Table 1.

Table.1 Samples codes and details of the formulations of each sample

Sample	PVA (g)	CN (g)	H ₂ O (g)
PVA15/CN3	1.00	0.03	5.67
PVA5/CN3	1.00	0.03	19.0
PVA5/CN6	1.00	0.06	19.0
PVA5/CN9	1.00	0.09	19.0

2.7 Characterization

2.7.1 Chemical structure and surface charge

Fourier transform infrared (FTIR) spectroscopy was employed to analyze the changes in the chemical structure of the cottonseed hulls after chemical treatment and acid hydrolysis. The untreated cottonseed hulls, purified cellulose, freeze-dried CNCs, SCNCs and CNFs were analyzed using a Bruker FTIR spectrometer (Alpha, Bruker Optics Inc., Billerica, MA, USA) in the attenuated total reflectance (ATR) mode. The spectra were recorded from 32 scans between 4000 and 600 cm^{-1} with a spectral resolution of 4 cm^{-1} . The zeta potential values of CNs were tested using a ZetaTrac analyzer (MicroTrac Inc., Largo, FL). Before each run, the concentration of CN suspensions was adjusted to 0.1 wt %. For each sample, ten measurements were carried out, and the average value was calculated.

2.7.2 Morphology

Transmission Electron Microscopy (TEM) was used to analyze the morphology of extracted CNs. A droplet (5 μL) of diluted CN suspension was deposited on a 300-mesh Lacey Carbon Film (LC300-CU-100) and then negatively stained with 2 wt % uranyl acetate solution for about 2 min to enhance the sample contrast. All samples were observed using a transmission electron microscope (JEM 1400, JEOL USA, Inc. Peabody, Massachusetts, U.S.A.) with an accelerating voltage of 120 kV.

2.7.3 Rheological Measurements

Rheological properties of CN and PVA/CN suspensions were measured using a stress controlled rheometer (AR 2000ex, TA Instrument, Inc., New Castle, Delaware, U.S.A.) with a cone and plate geometry (cone angle, 2°; diameter, 40 mm; truncation, 56 μm) at 25 °C. Steady-state viscosity was measured in a wide shear rate range from 0.1 to 1000 s^{-1} . Strain sweep was

conducted to determine the linear viscoelastic region before each frequency sweep within a strain range from 0.01% to 100% at a fixed frequency of 1 Hz. Frequency sweep measurements were carried out over an angular frequency range from 0.1 to 100 rad/s within the linear viscoelastic region based on the results of strain sweep.

3. Results and discussion

3.1 Chemical structure and morphology of CNs

Figure 1 shows the FTIR spectra of raw cottonseed hulls, extracted cellulose and three CNs (CNFs, SCNCs and CNCs). The broad bands at 3400 and around 2900 cm^{-1} correspond to the stretching of -OH groups and the C-H stretching of methyl and methylene groups (in cellulose, hemicellulose and lignin), respectively (Reddy, Guduri & Rajulu, 2009). After alkali and bleaching treatments, the prominent peak of the raw cottonseed hull at 1723 cm^{-1} attributed either to the acetyl and uronic ester groups of the hemicellulose or to the ester linkage of the carboxylic groups of the ferulic and p-coumeric acids of lignin and/or hemicellulose (Alemdar & Sain, 2008), disappeared completely. The peak at 1507 and 1250 cm^{-1} corresponding to the aromatic skeletal vibration of C=C in lignin and the -COO vibration of acetyl groups in hemicellulose, also disappeared in the extracted cellulose. This indicated that most of the hemicellulose and lignin were removed from the raw cottonseed hull during the step-wise chemical treatment (Supporting Information Figure S1 and S2). Other peaks, such as 1061 and 897 cm^{-1} peaks, are associated with the C-O stretching and C1-H deformation vibrations of the glycosidic linkage between the glucose units of cellulose, which appeared in all spectra (Alemdar & Sain, 2008).

No significant differences were observed in the spectra between the extracted cellulose and CNs (i.e., CNFs, SCNCs and CNCs), indicating that the cellulose molecular structure remained unchanged during the mechanical or acid treatment except that a tiny peak at 1205 cm^{-1} related to S=O vibration appeared in the spectra of CNCs due to the esterification reaction which occurred in the surfuric acid hydrolysis process (Lu & Hsieh, 2010). However, XRD results indicated that the cellulose crystal form transformed from type I to type II when NaOH concentration was greater than 10% because of the mercerization (Yue et al., 2015). This conversion occurred more obviously in CNCs than CNFs and SCNCs, evidencing that cellulose II has the more stable structure than cellulose I against the acid and mechanical treatments (S.I. Figure S3).

Fig.1 FTIR spectra of raw cottonseed hulls (a), isolated cellulose (b), and freeze-dried CNFs (c), SCNCs (d) and CNCs (e).

Figures 2a and 2b show the TEM micrographs of CNFs resulting from mechanical treatment (wet disk milling and high-pressure homogenization). Several large cellulose bundles consisting of wire-like nanofibers with nanoscale widths were aggregated and twisted randomly. Although

the aggregated bundles had a wide range of diameters from 20 nm to 100 nm and lengths up to several micrometers, most of the individual nanofibers had a width of 10~100 nm. Thus it was difficult to use single mechanical disintegration method to disrupt the aggregation of nanofibers caused by the remaining strong inter-fiber hydrogen bonding (Chen et al., 2014). However, the observed highly entangled network had a significant influence on the viscoelastic rheological properties of CNF suspensions (to be discussed in the rheological part). The TEM micrographs of SCNC resulting from mixed acid hydrolysis are presented in Figures 2c and 2d. It is clearly observed that most nano-particles were spherical while a few rod-like particles still existed due to insufficiently ultrasonic treatment (Wang, Ding & Cheng, 2007). The diameter of the SCNCs was distributed in the range of 15–35 nm with an average diameter of 25 nm, which was similar to the size of SCNCs from waste cotton fabrics (30 nm) (Xiong, Zhang, Tian, Zhou & Lu, 2012), but much smaller than those from the microcrystalline cellulose (60nm) (Wang, Ding & Cheng, 2007). Figures 2e and 2f show the TEM micrographs of CNCs isolated from sulfuric acid hydrolysis. Individual rod-like CNs were clearly observed, confirming the successful extraction of whiskers from cottonseed hull. However, most of the CNCs appeared as aggregates due to the high specific area and strong hydrogen bonds formed between the nanocrystals (Flauzino Neto, Silvério, Dantas & Pasquini, 2013). The dimensions of CNCs determined by TEM were about 95.91 ± 47.62 nm in length and 8.22 ± 5.94 nm in width. The aspect ratio (L/D) showed an average value of approximately 10, which was considered the minimum value for a good stress transfer agent from the matrix to the fibers for any significant reinforcement to occur (Azeredo et al., 2009). . Considering that CNs are usually used in the freeze-dried form in most of hydrophobic polymers, the morphology of freeze-dried CNs were also characterized (S.I. Figure S4).

Zeta-potential values of the extracted CNs are also shown in Table.2. Generally, a stable colloid has a threshold value of ± 30 mV, whereas a colloid with lower ζ -potential tends to flocculate quickly. CNCs and SCNCs had ζ -potential values of -39.61 ± 1.56 and -30.98 ± 1.08 because of the introduction of negatively charged sulfate groups (S.I. Figure S5), displaying a long time stable dispersion in aqueous suspensions (S.I. Figure S6). However, CNFs with a ζ -potential value of -15.01 ± 0.65 mv flocculated in 1 hour.

Table.2 Physicochemical Characteristics of CNs

samples	Diameter (nm)	Length (nm)	Aspect ratio (L/D)	ζ -potential (mV)
CNFs	38.68 ± 56.43	> 1000	>100	-15.01 ± 0.65
SCNCs	25.11 ± 15.00	N/A	~ 1	-30.98 ± 1.08
CNCs	8.22 ± 5.94	95.91 ± 47.62	$5 \sim 25$	-39.61 ± 1.56

Fig. 2 TEM micrographs of CNFs (a, b), SCNCs (c, d), and CNCs (e, f).

3.2 Steady-Flow and dynamic Rheological Behaviors of CNs aqueous Suspensions

Figure 3 shows steady-state viscosities as a function of the shear rate for various CN suspensions. For CNFs (Fig.3a), it was observed that all suspensions exhibited similar shear-thinning behavior, which was characterized by the decrease of viscosity with increasing shear rate (Grüneberger, Künniger, Zimmermann & Arnold, 2014). Higher concentrations resulted in higher viscosities along the whole curve because the increased concentrations of CNFs facilitated the creation of a more rigid and entangled network among fibrils. Furthermore, each viscosity-shear rate curve can be divided into four characteristic regions. In region I, a linearly shear thinning curve was observed under the low shear rate range because of the slow orientation of chaotic fibrils along

the shear direction under the shear force. In region II, the viscosity stopped decreasing and a Newtonian plateau was observed. Based on Iotti's hypothesis (Iotti, Gregersen, Moe & Lenes, 2010), the reason was proposed that the ultra-long CNFs completed the formation of an entangled network with high specific surface area covered by hydroxyl groups, which could take part in the formation of temporary hydrogen bonds and Van der Waals interactions. The physical entangled network with chemical interaction prohibited the continuous reduction of viscosity, sometimes even resulted in an increase of viscosity. It was worth noting that the start of the plateau region shifted to a lower shear rate (from about 20 s^{-1} to 3 s^{-1}) with decreasing CNF concentrations. It was proposed that the entangled network was organized more easily at lower concentrations, which accelerated the onset of the plateau. In region III, the observed decrease in viscosity was due to the breakdown of entangled network at high shear rates. In region IV, another plateau appeared because most of entangled network was disrupted upon the higher shear rate and a well oriented structure was formed again.

For all SCNC suspensions (Fig.3b), they displayed a typical shear thinning behavior and the viscosity increased with the increased concentration, indicating a typical rheology behavior of CNs. Interestingly, the curves gradually transformed from three shear thinning regions to one shear thinning region when the concentration decreased from 1.5 to 0.25 wt%. The possible reason was that, unlike the rod-like CNC suspensions where the viscosity behavior mainly depended on the formation and destruction of chiral nematic ordered phases (Shafiei-Sabet, Hamad & Hatzikiriakos, 2012), the SCNCs had an isotropic structure regardless of shear rate within the whole shear region. At low concentrations (e.g., 0.25 and 0.5 wt %), the suspensions exhibited a typical shear thinning behavior during the entire shear rate due to the shear destruction. Upon further increase in the concentration, the possibility of the collision in

spherical nanoparticles inhibited the decrease of viscosity, resulting in a flow stability after shear thinning. This phenomenon occurred more frequently at higher concentrations because of the dynamic balance between the shear destruction and hydrogen bond formation combined with the growth of particle collision.

It has been reported that CNC suspensions generally exhibit a Newtonian fluid behavior at low concentrations and a shear thinning behavior at high concentrations (Lu, Hemraz, Khalili & Boluk, 2014). In this work (Fig.3c), the CNC suspensions at high concentrations (>1 wt%) presented a shear thinning behavior when the shear rate was lower than 1 S^{-1} due to the alignment of the chiral nematic liquid crystal domains, and then a Newtonian plateau region at higher shear rates due to the achievement of orientation. That all the suspensions presented the relative lower viscosity than some other researches was possibly due to three reasons. Firstly, the CNC particle dimensions (e.g., length and width) were too small to offer strong resistance against the shear stress, which could not exhibit stable rheology behavior at the selected concentration under our rheometer sensitivity. Secondly, the ultrasound treatment introduced before tests probably severely affected the viscosity of CNC suspensions. Shafiei-Sabet et al (Shafiei-Sabet, Hamad & Hatzikiriakos, 2012) indicated that sonication breaks up the gel structure of high concentration samples, and disperses the individual CNC nanoparticles. Thus, it significantly decreased the viscosity of the samples. Thirdly, the high negatively charged surface also improved the dispersion stability of CNCs. All these results strongly indicated that the steady flow behavior of the CN suspensions was strongly dependent on CN concentration and their morphology.

Fig.3 Steady-state viscosities as a function of the shear rate of CN suspensions: CNFs (a), SCNCs (b), and CNCs (c). At a low concentration (0.25 and 0.5 wt %) and low shear rate region ($<1 \text{ S}^{-1}$), the viscosity of CNCs could not be measured precisely because of the sensitivity of rheometer.

Dynamic frequency sweep results can be used to characterize or classify polymer based solutions (Clark & Ross-Murphy, 1987). The traditional classification commonly defined the solution phase behavior into three categories: the viscoelastic solid, the gel, and the viscous fluid, which can be quantitatively measured by the loss tangent $\tan \delta = G''/G'$. In principle, fluid character is dominant when $\tan \delta > 1$ and solid character is dominant when $\tan \delta < 1$. Hence, a gel point at

which G' is equivalent to G'' can be evaluated from the curve of $\tan \delta$ with respect to angular frequency. (Winter, 1986).

Viscoelastic storage modulus (G'), loss modulus (G''), and loss tangent $\tan \delta$ as a function of angular frequency (ω) of CN suspensions with different concentrations are also shown in Figure 4. For all CNF suspensions (Fig 4a and 4b), they behaved as predominant viscoelastic solid-like materials, where the G' was independent of frequency and higher than G'' ($\tan \delta < 1$) over the entire investigated frequency range. It was due to the network formation caused by the high aspect ratio and strong surface interactions of the fibrous particles, as reported previously (Ishii, Saito & Isogai, 2011; Li et al., 2015). For SCNC suspensions (Fig 4c and 4d), the behavior of the high concentration (1.5 and 1.0 wt%) suspensions was also a typical viscoelastic solid just like the CNF suspensions. When the concentration was decreased to 0.5 wt%, the G' and G'' tended to increase as the angular frequency increased, indicating that the behavior started to shift from solid-like to gel-like. Finally, in the case of 0.25 wt% SCNC suspension, a gel-like behavior was observed, where G' and G'' were strongly dependent upon the angular frequency and overlap over an extended range of frequency ($\tan \delta$ floated around 1). It indicated that suspension concentration had a strong influence on the viscoelastic behavior of spherical particles. For all CNC suspensions (Fig 4e and 4f), both G' and G'' exhibited a strong dependence upon the angular frequency and G' was slightly higher than G'' ($0.1 < \tan \delta < 1$), indicating a weak gel-like behavior. These dynamic rheological behaviors revealed strong dependence of the rheological properties and phase transition of CN suspensions upon the concentration and morphology of CNs, which was in a good agreement with the steady-flow rheological results.

Fig.4 Storage modulus (G'), loss modulus (G''), and loss tangent $\tan \delta$ as a function of angular frequency (ω) of CN suspensions: CNFs (a, b), SCNCs (c, d), and CNCs (e, f).

3.3 Steady-Flow and dynamic Rheological Behaviors of PVA/CN Suspensions

Actually, CNs not only show characteristic rheology behavior in their aqueous solutions, but also have a great influence in PVA/CN systems. To adopt PVA/CN suspensions for industrial

applications, it is important to characterize their rheological properties so as to be able to manufacture various products, such as hydrogels, fibers, and films, with excellent properties. In this work, the concentration of PVA/CN suspension, morphology of CNs, and weight ratio of CNs to PVA was considered to be three main factors influencing their rheology behavior and studied as follows.

Figure 5 shows the steady-flow viscosities against the shear rate and viscosities at shear rate of 1 s^{-1} of PVA15/CN3 and PVA5/CN3 suspensions. All PVA15/CN3 suspensions exhibited higher values of viscosity than PVA5/CN3 over the whole shear rates, indicating that the concentration of suspension dominated the general range of viscosity. Both pure PVA15 and PVA5 suspensions showed Newtonian flow behavior, which transformed into typical shear thinning behavior after adding the CNs. For example, at the concentration of 15 wt%, the viscosity of the aqueous PVA solution at the shear rate of 1 s^{-1} increased from 0.145 to 0.276, 0.386 and 1.897 Pa·S with the addition of CNCs, SCNCs and CNFs, respectively, as shown in fig 5b. The similar results were also reflected in the PVA5/CN3 suspensions except that PVA5/CNC3 exhibited similar Newtonian flow behavior unlike PVA15/CNC3. These results demonstrated that the PVA concentration and CN morphology mainly affected the steady-flow behavior of PVA/CN suspensions.

Fig.5 Steady-flow viscosities against the shear rate (a) and viscosities at a shear rate of 1 s^{-1} (b) of PVA15/CN3 and PVA5/CN3 suspensions.

In order to better understand the differences in the rheological behavior of PVA/CN suspensions, the possible network within PVA/CNF, PVA/SCNC and PVA/CNC suspensions were proposed, as illustrated in Scheme 1. Previous literature (Briscoe, Luckham & Zhu, 2000) has reported that there were two main interactions, i.e., physical entanglements and inter or intra hydrogen bonding existed among CNs and PVA chains, which accounted for the control of rheology behavior. For PVA/CNF, the physical entanglements between CNFs and PVA chains were quite strong due to the large aspect ratio and high flexibility of CNFs. Meanwhile, the entangled network between CNFs and PVA chains was further enhanced by the formation of hydrogen bonds between hydroxyl groups from CNFs and PVA chain. Therefore, a large increase in the viscosity of PVA suspensions was observed. For SCNCs and CNCs, both of them with relatively low aspect ratios and high crystallinity had less flexibility than CNFs, leading to the reduced possibility of formation of physically entangled network between SCNCs/CNCs and PVA chains. Therefore, in the PVA/SCNC and PVA/CNC suspensions, the intensity of network primarily depended on the amount of hydrogen bonds between SCNCs/CNCs and PVAs chains. It was

believed that SCNCs had a larger specific surface area than CNCs, i.e., more hydroxyl groups were exposed on the surface of SCNCs compared to CNCs leading to more effective surface interaction. Besides, the growth of the collision possibility in SCNC particles inhibited the decrease of viscosity, while the orientation of rod-like CNCs promoted the decrease of viscosity. Therefore, it resulted in a higher viscosity in the PVA/SCNC suspension than in PVA/CNC suspension

Scheme.1 Schematic illustrations of the proposed network of (a) PVA/CNF suspension, (b) PVA/SCNC suspension, (c) PVA/CNC suspension.

The weight ratio of CNs to PVA played another important role in affecting the rheology behavior of systems because of the presence of strong hydrogen bonding between CNs and PVA chain. Considering the poor dispersion of CNs in high concentration of PVA aqueous suspensions, the concentration of PVA aqueous solution was fixed as 5 wt%.

Steady-Flow viscosities and dynamic modulus against the shear rate curves of PVA/CN3, PVA/CN6 and PVA/CN9 suspensions are shown in Figure 6. For the PVA5/CNF suspensions

(fig 6a), with increasing CNF contents, more profound shear thinning behavior appeared. It was worth noting that a typical shear fluctuation of CNFs, which resulted from the physical entanglement and hydrogen bonding interaction of CNFs (discussed above), also appeared obviously. It indicated that the PVA molecular chains had participated in the CNFs entangled network through physical and chemical interaction. These results provided good support for our hypothesis discussed previously. The storage modulus (G') and loss modulus (G'') and $\tan \delta$ against shear rate of PVA5/CNF with increased CNF concentration are shown in Fig.7a and Fig.7b, respectively. The PVA/CNF suspensions transformed from a typical viscoelastic solid/gel to fluid-like behavior as the increasing shear rate. The more CNFs were added, the higher transformation ($\tan \delta=1$) angular frequency was shown. The possible reason was that the gel-like behavior of PVA/CN suspensions was mainly caused by the physical entanglement and hydrogen bonding between CNs and PVA chain, according to the steady-flow rheological results. At a low frequency, there was enough time for the disrupted entanglements or hydrogen bonds to recover during the oscillation period, which allowed the systems to keep solid/gel-like behavior. With an increase in frequency, the relaxation time for the re-arrangement of the disrupted physical entanglements and hydrogen bonds was largely shortened, resulting in a higher G'' than G' . Therefore, the incorporation of more CNFs yielded tighter physical entanglements and stronger hydrogen bonds, requiring stronger disruption effect which the higher frequency could offer. The similar rheology behavior transformation occurred in the PVA5/SCNC (Fig 6b, 7c and 7d) suspensions. Unlike the PVA/CNF system, PVA/SCNC suspensions showed lower viscosities and smoother shear thinning behavior, because much weaker physical entanglements existed between SCNCs and PVA chains. The viscoelastic solid/gel and fluid-like transformation occurred at lower frequency than PVA5/CNF at the same CN concentration. It demonstrated that

SCNCs still had strong hydrogen bonding interaction with the PVA molecular as discussed previously. For PVA5/CNC (Fig 6c, 7e and 7f) systems, the Newtonian fluid behavior was well kept even when the CNCs content increased to 9 wt%. It indicated that, for PVA5/CNC systems, the addition of CNCs had little influence on the shear behavior other than what happened at the higher concentration (15 wt%) of PVA (shown in Fig 5). These results evidenced that the concentration of PVA acted as the principal factor influencing the rheological behavior of system.

Fig.6 Steady-Flow viscosities against the shear rate curves of PVA5/CN suspensions: CNF (a), SCNC (d), and CNC (g).

Fig.7 Storage modulus (G'), loss modulus (G''), and loss tangent $\tan \delta$ as a function of angular frequency (ω) of PVA5/CN suspensions: CNF (a, b), SCNC (c,d), and CNC (e, f)

4. Conclusion

Cellulose nanoparticles with fibrous, spherical, and rod-like forms were extracted from cottonseed hulls, resulting the distinct rheological behaviors. The CNF suspensions exhibited shear thinning behavior and rigid solid-like viscoelastic behavior within the whole shear rates studied, due to the formation of highly entangled network. The SCNC suspensions exhibited the similar rheology behavior as CNF suspensions at concentration higher than 0.5wt%, but shifted from solid-like to fluid-like when the concentration was lower than 0.5 wt%. However, the CNC suspensions presented a less obvious shear thinning behavior and fluid-like viscoelastic behavior at lower concentrations. Thus, morphology plays the key role in affecting the rheological behavior of CN aqueous suspensions in various concentrations, CNs with larger size (dimension and length) contributed to the higher viscosity value, more complex state-flow rheological behavior and more solid-like viscoelastic behavior.

The concentration of PVA suspension, morphology of CNs, and weight ratio of CNs to PVA were three main factors that influenced the rheology behavior of system. The concentration of PVA suspension mainly controlled the viscosity range of the system while the addition of CNs resulted in the increasing shear thinning behavior. The ratio of CNs to PVA had a great influence on the viscosity and viscoelastic behavior of both PVA5/CNF and PVA5/SCNCs systems but little impact on the PVA5/CNC system. Physical entanglement and hydrogen bonding interaction between CNs and PVA was taken into account for the distinct rheology behavior. Therefore, the recommended weight ratios of CNFs or SCNCs to PVA were no more than 3% and 6%, respectively when the concentration of PVA solution was fixed at 5 wt%. However, CNCs could

be used at a much higher ratio (up to 9% of PVA) even when the concentration of PVA solution was 15 wt%. It is expected these findings will provide us some fundamental information for the preparation of high performance CN-polymer nanocomposites in both academic and industrial fields.

Acknowledgments

The work is supported by the Science and Technology Project of Guangzhou [201508020090], the USDA National Institute of Food and Agriculture McIntire Stennis project [1000017] and China Scholarship Council (CSC). Mention of trade names or commercial products in this publication is solely for the purpose of providing specific information and does not imply recommendation or endorsement by the U.S. Department of Agriculture. USDA is an equal opportunity provider and employer.

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