



## Cross-linkage effect of cellulose/laponite hybrids in aqueous dispersions and solid films



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### ABSTRACT

Homogenous cellulose/laponite aqueous dispersions and composite films were respectively prepared from the pre-cooling NaOH/urea aqueous systems. Rheological measurements of aqueous dispersions demonstrated a sol-to-gel transition triggered by loading of laponite, reflecting a cross-linkage effect of cellulose/laponite hybrids. Similarly, based on scanning electron microscopy (SEM), Fourier-transform infrared (FTIR) spectroscopy, and X-ray diffraction (XRD) characterizations, as well as mechanical and thermal measurements, the cross-linkage effect of cellulose/laponite hybrids was also found in solid films, which played an important role in improving the tensile strength ( $\sigma_b$ ) of composite films. For instance, the  $\sigma_b$  exhibited a largest enhancement up to 75.7% at a critical laponite content of 0.100 wt%, indicating that the property of composite film was closely related with the dispersion and interaction state of laponite, i.e. its content in cellulose matrix. These results were expected to provide significant information for fabrication and utility of cellulose-based materials.

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### 1. Introduction

Cellulose, as a kind of biodegradable material, has attracted great industrial and academic interest for sustainable development and environmental conservation because of its abundance, low cost, eco-friendly characteristics, and great potential to replace petrochemically derived compounds in many cases (Chen & Zhang, 2006; Cranston & Gray, 2006; Klemm, Heublein, Fink, & Bohn, 2005; Ma, Burger, Hsiao, & Chu, 2011). Generally, there are two obstacles for sufficient utility of cellulose. First, cellulose is difficult to process in solution or as a melt because of its large proportion of intra- and inter-molecular hydrogen bonds, which brings about large difficulties for fabrication of fiber-, film-, and bulk-based cellulose materials by regeneration method. Therefore, a variety of systems have been exploited and found for dissolution of cellulose. Among these systems including N,N-dimethylacetamide (DMAc)/LiCl (Kondo, Togawa, & Brown, 2001), N-methylmorpholine N-oxide (NMMO)/water (Fink, Weigel, Purz, & Ganster, 2001; Kulpinski, 2005), ionic liquid (Wu, Wang, Li, Li, &

Wang, 2009; Zhao et al., 2007), etc., the pre-cooling NaOH/urea aqueous system (Cai & Zhang, 2006; Fukuzumi, Saito, Iwata, Kumamoto, & Isogai, 2008; Li et al., 2010) has attracted most attention because of its high efficiency, low cost, environmental friendliness, and facile procedure. This system, only cheap chemicals of NaOH and urea were used, offered a green and versatile means for machining of cellulose-based materials, which has greatly pushed forward the research process of cellulose-based material field.

Second, the pure cellulose materials usually possess poor mechanical and thermal properties and hence greatly hinder their practical applications. The inclusion of nanometer-scale fillers, such as montmorillonite (Cerruti et al., 2008; Mahmoudian, Wahit, Ismail, & Yussuf, 2012), carbon black (Knite, Teteris, Kiploka, & Kaupuzs, 2004), carbon nanotubes (Cha, Kim, Arshad, Mo, & Hong, 2005; Qi, Liu, Gao, & Mäder, 2013; Zhan, Kuntz, Wan, & Mukherjee, 2003), cellulose nanocrystals or nanowhiskers (Habibi, Lucia, & Rojas, 2010), and graphene oxide (Wang, Lou, Wang, & Hao, 2012), into cellulose matrix has been a common way to resolve the above problem. Wang et al. dissolved microcrystalline cellulose (MCC) in an ionic liquid, 1-butyl-3-methylimidazolium chloride ([Bmim]Cl), and then dispersed graphene oxide nanosheets in this solution, resulting in the reinforcement of the regenerated composite films (Wang et al., 2012). Cerruti et al. reported the preparation of cellulose/montmorillonite nanocomposites with high thermostability

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by a precipitation method. Cellulose composite films were also prepared by blending native cellulose nanowhiskers in cellulose NaOH/urea aqueous solutions (Qi, Chang, & Zhang, 2009). Good comparability and strong interactions between the nanoadditives and cellulose matrix were considered to be the key factors for property performance of cellulose-based composite materials.

Laponite, synthetic layered silicate with high biocompatibility, is readily exfoliated into single two-dimensional (2D) thin nanoplatelets owing to the abundant oxygen-containing groups on its surfaces (Fig. S1). At a suitable concentration, the laponite could lead to gel formation in aqueous systems by electrostatic interactions between negatively charged faces and positively charged edges of the nanoplatelets, imparting these systems outstanding suspension, thixotropy and other unique properties. These features make laponite an ideal waterborne additive to improve the properties of a wide range of industrial products such as cosmetics, food, medicine, and paint (Mourchid & Levitz, 1998; Thompson & Butterworth, 1992; Willenbacher, 1996). However, it is a pity that few researches on cellulose-based materials using laponite as the nanoadditives have been reported.

In this work, laponite was dispersed into cellulose NaOH/urea aqueous solution to form aqueous dispersion. Then cellulose/laponite composite film was also obtained by regenerating from the aqueous dispersion. In order to reveal the dispersion and interaction state of cellulose/laponite hybrids in aqueous dispersions and solid films, rheological, mechanical, and thermal property measurements were conducted except for SEM, FTIR, and XRD characterizations. Meanwhile, based on the experimental results, the relationship between disperse and interaction state of cellulose/laponite hybrids and properties of the aqueous dispersions and composite films was proposed and discussed.

## 2. Experimental

### 2.1. Materials

Cellulose (cotton linter pulp) with a degree of polymerization (DP) of ~525 was supplied by Yinying Chemical Fiber Co. Ltd. (Gaomi, China). NaOH and urea were of analytical reagent grade (Shanghai Chemical Reagent Co. Ltd., China). Laponite with transmittance of over 99% was a gift from Huizhi Fine Chemical Co. Ltd. (Sihong, China). All of them were used as obtained without further purification.

### 2.2. Preparation of cellulose/laponite aqueous dispersions

An aqueous solution containing 7 wt% NaOH and 12 wt% urea was pre-cooled to  $-12^{\circ}\text{C}$ , into which a known amount of cellulose (4 wt%) was added and dispersed at a temperature between 0 and  $4^{\circ}\text{C}$  under stirring. Then the 4 wt% cellulose solution was obtained after degassed by centrifugation at 4000 rpm for 5 min.

Laponite was first dispersed into pure water. Then a known weight of NaOH (7 wt%) and urea (12 wt%) was added under stirring for 30 min at 3000 rpm. Finally, a well dispersed suspension of laponite was obtained.

The two NaOH/urea aqueous systems, containing dissolved cellulose and dispersed laponite, respectively, were completely mixed by stirring, resulting in homogeneous and translucent cellulose/laponite aqueous dispersions with a fixed cellulose concentration (2 wt%) but different contents of laponite ( $w_{\text{laponite}} = 0, 0.033, 0.067, 0.100, 0.133, \text{ and } 0.167 \text{ wt\%}$ , respectively). It is worth noting that the dispersion with higher loading of laponite was not prepared because it became apparently turbid when the laponite content is above 0.167 wt%.

### 2.3. Preparation of cellulose/laponite composite films

The preparation procedures of cellulose/laponite composite films are shown in Fig. S2. Typically, the mold was first coated with a cellulose/laponite aqueous dispersion. Then, a wet film was regenerated by an acetone/water mixed solvent as coagulant and rinsed with pure water to remove NaOH and urea. Finally, the dry cellulose/laponite composite film was gained by a drying process in an oven for 24 h at a constant temperature ( $30^{\circ}\text{C}$ ) and humidity (65%). Here, the adopted volume ratio of acetone to water was 2:1, at which the regenerated films were proved to possess best homogeneity. The as-produced cellulose/laponite composite films were named as F-0, 0.033, 0.067, 0.100, 0.133, 0.167 based on different weight fraction ( $w_{\text{laponite}}$ ).

### 2.4. Rheological experiments

Rheological experiments of cellulose/laponite aqueous dispersions were carried out on a Haake RS6000 rheometer (Germany) with a coaxial cylinder sensor system (Z41 Ti) at different temperatures. The diameters of the rotor and the shear cell are 41.420 and 43.400 mm, respectively. An oscillation amplitude sweep at a fixed frequency of 1 Hz was performed prior to the following oscillation frequency sweep in order to ensure the selected stress was within the linear viscoelastic region of the samples. The samples were allowed to equilibrate in the shear cell for 5 min before each measurement.

### 2.5. Tensile strength measurements

The mechanical strength of the composite films, with a dimension of  $0.4 \text{ cm} \times 5 \text{ cm}$  and a thickness of 38–40  $\mu\text{m}$ , was measured using an universal testing machine (Jinan Tianchen Testing Machine Manufacturing Co. Ltd., China) at a crosshead speed of  $1 \text{ mm min}^{-1}$  and a gauge length of 2 cm. At least five specimens were measured for each type of film to ensure the accuracy and reproducibility.

### 2.6. Other characterizations

The morphologies of the cellulose/laponite composite films were examined by scanning electron microscopy (SEM, JEOL JMS-6700) observation. The composite films were fractured in liquid nitrogen before gold was sputtered for the subsequent SEM observations. Fourier-transform infrared spectroscopy (FTIR) measurements were recorded on a Nexus 670 infrared spectrometer (Thermo-nicolet electron corporation, USA) using a KBr-disk method. X-ray diffraction (XRD) measurements were carried out with an X-ray diffractometer using a Cu  $K\alpha$  target at 40 kV and 30 mA. In FTIR and XRD measurements, the cellulose/laponite composite films were crushed into powders. Thermogravimetric analysis (TGA) was carried out on a TGA/SDTA851<sup>e</sup> system (Mettler-Toledo, Swiss). The temperature was increased from  $40^{\circ}\text{C}$  to  $700^{\circ}\text{C}$  at a rate of  $10^{\circ}\text{C min}^{-1}$  under nitrogen protection.

## 3. Results and discussion

### 3.1. Rheological properties of cellulose/laponite aqueous dispersions

Rheological measurement is one of the most promising means to reveal the characteristics of functional fluids, from which the microstructure of a fluid matrix could be inferred. Fig. 1 shows the elastic modulus ( $G'$ ) of the cellulose/laponite aqueous dispersions as a function of oscillation frequency at various temperatures. The applied shear stress was 0.04 Pa, which has been proved to

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