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Characteristics of concentrated lignocellulosic nanofibrils suspension

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Abstract: Lignocellulosic nanofibrils (LCNF) is usually isolated from biomass with concentration less than 2.0 wt%. The low concentration limited the transportation and end-use application of LCNF. Therefore, the development of concentration process and the characteristics of concentrated LCNF become desirable and important for commercial deployment of LCNF application. In this study, 1.0 wt% LCNF suspension was dewatered to solid concentration of 5.9 wt%, 16.3 wt% and 25.9 wt% by a centrifuge, respectively. The un-concentrated LCNF suspension showed obviously stable translucent and well dispersed in water, while the concentrated LCNF exhibited the gel-like behavior or “solid-like” behavior based on the concentration degree. The bundle-like fibrils were observed in the concentrated LCNF, and average diameter of concentrated LCNF became large but still less than 100 nm. The crystallinity and crystallite size of un-concentrated LCNF and concentrated LCNF were similar, and it was indicated that the morphological structure changes of LCNF mainly occurred in the amorphous region of fibrils. The concentrated LCNF films still had relatively good UV-blocking property, water absorption and oxygen permeability. The increasing basis weight of films was benefit for enhancing the surface smoothness of films and interweaves between fibrils, resulting in the tensile index and specific modulus of films increasing. In sum, the concentration process affected the morphology structure of LCNF, but the concentrated LCNF still kept relatively good properties. Concentration process of LCNF suspension may be a feasible strategy for large-scale LCNF production and storage.

Keywords: lignocellulosic nanofibrils, concentration, film, barrier property, mechanical strength

1. Introduction

Lignocellulosic nanofibrils (LCNF) were new biobased nanomaterials isolated from abundant and renewable biomass resources, and have unique morphologies, characteristics, and functions (Isogai 2020). Extensive LCNF research has promised great potential application areas, such as packaging materials, superabsorbent materials, membranes, biomedicine, energy storage devices, nanocellulose based diagnostic devices (Hoeger, Nair et al. 2013, Wang, Yao et al. 2019, Heidarian, Kaynak et al. 2021). LCNFs are usually produced in diluted aqueous suspensions by mechanical technologies combined chemical pretreatment or enzymatic pretreatment in some cases, and have 4-50nm width and 500-2000nm length in morphological structure. Due to the properties of high surface area, hydrophilic nature, and high water-holding capacity, the LCNF suspension has high thixotropic viscosity and exhibits gel-like behavior even at the concentration of 5~10 wt% solid. Commonly, in the preparation process of LCNF, the solid consistence was controlled less than 2 wt% (Isogai 2020). The low dilute aqueous suspension causes the high costs of shipping problem and affects end-use application requirements (Sinquefield, Ciesielski et al. 2020). Therefore, the development of non-destructive, cost-effective, environmentally friendly concentrating and drying processes is important for the commercial deployment of LCNF applications.

The water adsorbed on the cellulosic fibers includes free water, non-freezing bound water, and freezing bound water. Free water is defined as bulk water, and non-freezing bound water corresponds to the first 1-3 layers of water adjacent to the surface of cellulosic fibers. Freezing bound water is a part of bound water with an undetectable thermal transition. Concentrating LCNF process involves removing the free water from the LCNF suspension to obtain a solids content around 10~30 wt%. While drying process means removing the water completely to obtain “fully dried” fibers. The methods of centrifugation, filtration, and pressing were often introduced for dewatering the LCNF suspension. Centrifugation is a relatively easy process and widely used to separate the solid from suspensions. It has been used to concentrate the LCNF suspension, and the process is similar with the analysis of water retention value in different dewater cellulosic materials. Filtration of LCNF suspension is widely used in lab-scale, but this process takes a long time about 1-4 h (Sethi, Oksman et al. 2018). Sonication-assisted filtration (Sethi, Oksman et al. 2018), electro-assisted filtration

(Wetterling, Jonsson et al. 2017), and modified with cationic electrolyte (Sim, Lee et al. 2015) have been explored to accelerate filtration concentration. Pressing the nanocellulose suspension under high pressure is also proved an effective method for removing water. A plate and frame press were chosen for microfibrillated cellulose dewatering, and the pressed cellulosic cake could achieve 18 wt% solid content (Sinquefield, Ciesielski et al. 2020).

It was worth noting that in the concentrating of LCNF suspension process, besides the concentration changing the morphologies of LCNF may also present to be different. The complex interactions of LCNF with water are largely attributed to its amphiphilic nature. The insolubility of LCNF is generally attributed to the systematic arrays of hydrogen bonds that form in the interiors of LCNF assemblies (Sinquefield, Ciesielski et al. 2020). However, the molecular interactions govern the dewatering which occurred between the LCNF surface and water (Miyamoto, Schnupf et al. 2014). The dominant interaction was the formation of hydrogen bonds attributable to the high number of hydroxyl groups on the surface of LCNF. Hence, the morphologies and properties of concentrated LCNF may be much different compared to un-concentrated LCNF, and this needed to be worthy studied thoroughly. In this study, the 1.0 wt% LCNF will be prepared by mechanical method combined enzymatic pretreatment, and then dewatered them to different concentrations. The characteristics of concentrated LCNF and their films will be investigated, and the properties of the films will be indirectly reflected the combination of nanofibrils. This study will report on a systematic evaluation to elucidate the effect of concentrating on the characteristics of LCNF.

2. Experimental

2.1 Materials

Commercial dried bleached chemi-thermo-mechanical pulp (BCTMP) and endoglucanase (Banzyme 2900, 7.3 IU/ml) were obtained from UPM-kymmene Co., Ltd (Jiangsu, China). Sodium hydroxide, citric acid and glacial acetic acid were purchased from Shanghai Runjie Chemical Reagent Co., Ltd. All other chemicals used were purchased from Macklin Biochemical Co., Ltd (Shanghai, China).

2.2 Preparation process of LCNF

The delignification process of BCTMP was generally followed the procedure

described by Fu et al. until the lignin content of delignified BCTMP reached 11 wt% (Fu, Gao et al. 2020). Then, the delignified BCTMP was treated by endoglucanase according to a previous work (Wang, Gao et al. 2018). Enzymatic pretreatments of delignified BCTMP was carried out at solids consistency of 5.0 % (w/v) in a citrate acid-sodium citrate buffer (pH 5.5) with the enzyme loading of 5 mg/g (substrate). The slurry was incubated at 50°C in an incubator shaker with 200 rpm for 1.5h. After enzymatic treatment, the slurry was placed in 95 °C water bath for 10 min to inactivate the enzyme, and then washed to neutral with deionized water. After that, the enzymatic treated fibers were dispersed to 1.0 wt% for the mechanical homogenizing treatment. The slurry was treated by a grinder (MKCA6-2J Masuko Sangyo Co., LTD, Japan) with the gap of 0 and -20 µm for 5 passes at 1500 rpm, respectively. Then, the slurry was ground with the gap of -50 and -80 µm for 10 passes at 2000 rpm, respectively. After that, the slurry was deeply ground at the gap of -100 µm with 2000 rpm for 15 passes. The obtained suspension was 1.0 wt% LCNF, and labeled LCNF-C0.

2.3 Concentration process of LCNF

The 1.0 wt% suspensions were concentrated to 5.9 wt%, 16.2 wt% and 25.9 wt% by a centrifuge (H2050R Hunan Xiangyi Centrifuge Instrument Co., Ltd., China) with the centrifugal force of 3000g at 5min, 25min and 55min, respectively. In order to compare the characteristics with unconcentrated sample (LCNF-C0), all the concentrated samples were then diluted and dispersed to 1.0 wt% homogeneous suspension by a high-speed disperser machine at 7200 rpm for 10 min before testing in the following. The corresponding concentrated samples were labeled LCNF-C6, LCNF-C16 and LCNF-C26.

2.4 Preparation of films

LCNF-C0 and LCNF-C16 sample were used for fabrication films by vacuum filtration method over a microporous membrane filter (0.22 µm). The basis weight of films was 60, 70, 80, 90 and 100 g/m², respectively. The corresponding samples were labeled LCNF-C0-60, LCNF-C0-70, LCNF-C0-80, LCNF-C0-90, LCNF-C0-100 and LCNF-C16-60, LCNF-C16-70, LCNF-C16-80, LCNF-C16-90, LCNF-C16-100, respectively. After the filtration, the wet membrane was covered with a microporous membrane. Then, the samples were placed on a plate heater and pressed with a weight of about 30 kg at 80 °C for 8 h. The dried films were placed at 22°C with RH 55% for 24 h.

2.5 Characterization of LCNF

Atomic Force Microscopy (AFM, Leica TCSSP5, Germany) was used to analyze the morphology of LCNF. The sample was diluted to 0.1~1.0 wt% suspension, and then ultrasonically dispersed at 15 °C for 5 min. The diameter distribution of LCNF was calculated by nano measurer 1.2 software.

Transmittance of LCNF suspension was measured by an UV spectrophotometer in the wavelength range of 400~800 nm. LCNF suspension was diluted to 0.1 wt% before testing, and deionized water was used as a reference.

Water retention value (WRV) was usually used to reflect the total internal pore and interfibril surface areas. The improved TAPPI standard method (256 method) was used for measurement, as following: 1.0 wt% LCNF suspension was centrifuged at 3000 g for 30 min. The centrifuged sample was weighed, and then dried at 105 °C in an oven for 24 h to constant weight. The WRV was determined as the amount of water held by the LCNF upon centrifugation relative to the oven dried weight of the substrate.

The crystallinity of samples was performed by a Rigaku D/Max-III A X-ray diffraction analyzer (Japan) using CuK α radiation. The samples were scanned at 40 kV and 30 mA in a 2θ range of 5°~60° at 2.0°/min. The crystallinity index (CrI) was calculated as the Eq.(1),

$$CrI = \frac{I_{200} - I_{am}}{I_{200}} \times 100 \quad (1)$$

Where, I_{200} is the diffraction intensity of the 200 lattice plane at 2θ around 22.5°, and I_{am} is the diffraction intensity of amorphous fraction at 2θ around 18°.

The average crystallite size (D_{hkl}) of the crystal in 200 lattice plane was determined by the Scherrer equation Eq.(2),

$$D_{hkl} = \frac{k\lambda}{\beta \cos\theta} \quad (2)$$

Where, k is the Scherrer constant (0.89), and λ is the wavelength of Cu-K α radiation (0.15418 nm). β is the width of half height of the 200- lattice plane in radian, and θ is the Bragg's angle in radian.

The specific surface area (SSA) of LCNF was determined using a Congo red dye adsorption method. LCNF suspensions were treated with certain amounts of Congo red at 60 °C for 24 h, and then centrifuged at 5000 rpm for 20 min. The absorbance of

the supernatant was detected by the UV-Vis spectrophotometer (UV-2600, Shimadzu Instrument) at 495 nm, and the Congo red concentration in the supernatant was calculated according to the standard curve. The SSA A_{cell} (m²/g) was calculated according to the Eq. (3),

$$A_{cell} = 6.024 \times 10^{23} \frac{m_1 A_d}{M} \quad (3)$$

Where A_d is the area of dye permolecule, 1.73 nm². M is the relative molecular weight of dye molecules, 696.68. m_1 is the saturation value of sample adsorption, g/kg.

Zeta potential of LCNF suspension was measured by Zeta potential meter. 200ml LCNF suspension were put into the beaker, and the measurement results will be displayed on the digital display screen.

2.6 Properties of films

The thickness of films was measurement using L&W Micrometer 51 instrument. The result was an average of repeating 10 times testing. The basis weight of films was determined using TAPPI standard T410 (T410 1998), and the density of films was calculated based on the results of the thickness and basis weight. Porosity of the films was calculated by the Eq.(4),

$$\varepsilon = 1 - \frac{\rho_{sample}}{\rho_{cellulose}} \quad (4)$$

Where, ε the porosity of films. ρ_{sample} is the density of films, and the value of $\rho_{cellulose}$ is 1.5 g/cm³.

The microstructure of films was measured by a field emission scanning electron microscope (FE-SEM) (Merlin, Carl Zeiss, Germany). The surface roughness of films was analyzed by an optical profiler (3D surface profilometer, RTEC Instruments, Inc., San Lose, USA).

Water absorption of films was determined by immersing 5×20 mm strips in deionized water for 2 h, and recorded the sample weight after 1.5, 5, 10, 30, 60, and 120 min using an electronic analytical balance. Relative water absorption (RWA) was determined using Eq.(5):

$$RWA = \frac{w_t - w_0}{w_0} \times 100\% \quad (5)$$

Where w_0 and w_t are the weights of the sample before and after immersion in water, respectively.

Water vapor permeability of films was tested using the moisture permeability tester (TSY-TIH, Languang, China) according to the ISO standard 2528-2017. The

191 testing temperature and relative humidity (RH) were $38\pm 2^{\circ}\text{C}$ and $90\pm 2\%$, respectively.
192 The water vapor permeability was calculated by measuring the weight change,
193 expressed as $\text{g}\cdot\text{m}^{-2}\cdot\text{day}^{-1}$. The results of each sample were evaluated as the average of
194 at least three measurements.

195 Oxygen permeability of films were measured by the oxygen permeability test
196 system (Labthink VAC-V1, Langfang, China) at 23°C and 50% RH according to the
197 ISO standard 15105-1-2007. Pure oxygen was used as testing permeation gas, and the
198 partial pressure gradient of permeation gas was set up 1.0 atm. The results were
199 expressed as $\text{cm}^3\cdot\text{m}^{-2}\cdot\text{day}^{-1}\cdot\text{atm}^{-1}$. The results of each sample were evaluated as the
200 average of at least three measurements.

201 The UV barrier performance and transmittance of the film were measured by a
202 UV spectrophotometer at the wavelength of 200~400 nm and 400~800 nm,
203 respectively.

204 Tensile strength and elastic modulus of films were tested at 23°C and 50% RH using
205 a universal testing tester (Instron5565, USA) according to GB/T 1040-2006. The
206 specimen of 8 mm×36 mm was cut from the films. All tests were performed with a
207 cross-head speed of 5 mm/min, and the clamp span was set to 23 mm. The tensile
208 index was obtained by tensile strength and elastic modulus divided by the density of
209 sample, respectively. The results of each sample were evaluated as the average of at
210 least three measurements.

211 3. Results and discussion

212 3.1 Morphological structure of LCNF

213 The 1.0 wt% LCNF suspension (LCNF-C0) was prepared by mechanical
214 homogenizing treatment after enzymatic pretreatment, and showed obviously stable
215 translucent and well dispersed in water (Fig.1, a). This was because that the
216 consequence of strong hydrogen bonding between water and accessible hydroxyl
217 groups (Qing, Sabo et al. 2013). When the LCNF suspension was concentrated to 5.9
218 wt% (LCNF-C6), the sample exhibited the gel-like behavior. Continue to increase the
219 concentration to 16.2 wt% (LCNF-C16) and 25.9 wt% (LCNF-C26), the samples
220 presented “solid-like” behaviors. Therefore, in order to analyze the fibrils properties
221 and compared with the un-concentrated LCNF suspension, all the concentrated
222 samples were dispersed to 1.0 wt% homogeneous suspensions by a high-speed

dispenser machine. The performances of dispersed samples were shown in Fig.1 (a). Visual observation of the samples in Fig.1 (a) revealed the LCNF-C0 and LCNF-C6 had good homogeneity and dispersion, while LCNF-C16 and LCNF-C26 presented settlement and slight stratification. As showed in Fig.1 (b), The LCNF-C0 had relatively high light transmittance in the range of 400-800 nm visible absorption spectrum, which was more than 55% corresponding to the result of Qing et al. (Qing, Sabo et al. 2013). The light transmittance of the concentrated LCNF decreased much compared to un-concentrated LCNF, especially the transmittance of concentrated LCNF-C26 almost reduced to half of that of the unconcentrated LCNF-C0. The results indicated that the concentration degree of LCNF suspension affected the reversible recovery of LCNF morphology resulting in the light transmittance of concentrated LCNF decreasing.

Fig.1 The transmittance of LCNF samples (a) and the performance of LCNF suspensions (b)

Fig.2 The AFM images and diameter distributions of un-concentrated sample LCNF-C0 and concentrated samples LCNF-C6, LCNF-C16 and LCNF-C26

Fig.2 showed the morphology structure and diameter distributions of LCNF. It indicated that the LCNF-C0 had uniform and slender nanofibrils, while concentrated LCNF had non-uniform and “bundle-like” fibrils. Statistical analysis results showed the diameter distribution of LCNF-C0 was narrow mainly in the range of 20~40 nm, and the average diameter of LCNF-C0 was 28 nm, which were similar with the previous reports (Hoeger, Nair et al. 2013, Bian, Dong et al. 2019, Isogai 2020). However, many bundle-like fibrils besides the nano-fibrils were observed in the concentrated LCNF, leading to the average diameters of concentrated LCNF increasing. The width of LCNF-C6, LCNF-C16 and LCNF-C26 were mainly distributed in the range of 20~80 nm, 40~80 nm and 50~150nm, respectively. The interaction between nanofibrils and water was the formation of hydrogen bonds attributable to the high number of hydroxyl groups on the cellulosic fiber surface (Sinquefield, Ciesielski et al. 2020). In the concentration process many intra-molecular and inter-molecular hydrogen bonds formed between the fibrils, and parts of these bonding combinations could not be open again causing the formation of bundle-like fibrils. The phenomenon had much obviously with the concentration degree of LCNF increasing (Fig.2). It was noting that although the average diameters of concentrated LCNF increased, but the size was still in the nano-scale (Fig.2).

Fig.3 The XRD spectrums of un-concentrated and concentrated LCNF samples

Table 1 Comparison of un-concentrated and concentrated LCNF properties

	LCNF-C0	LCNF-C6	LCNF-C16	LCNF-26
Crystallinity (%)	64.70	65.67	66.56	64.64
D_{hkl} (Å)	35.60	35.93	36.42	37.11
WRV (%)	564	554	519	437
SSA (m ² /g)	174	171	162	146
Zeta (mv)	-45.43	-33.80	-27.10	-20.30

The XRD spectrums of LCNF showed that the concentration process hardly affected the crystal structure (Fig.3 and Table 1). The calculated crystallinities of LCNF were about 65%, and they were consistent with the previous research reported by Bian et al. (Bian, Dong et al. 2019), who documented the crystallinities of LCNF prepared from unbleached pulp were approximately 55.5~66.6% (Table 1). The concentration process resulted in the morphological structure changes of LCNF, but these changes only occurred in the amorphous region. The bundle-like fibers were observed in Fig.2 may be because the hydroxyl groups from the amorphous region forming hydrogen bonding combination. The average crystallite size (D_{hkl}) of the crystal in 200 lattice plane was about 36 Å (Table 1), which is similar with the crystallite length of cellulose nanofibrils from bleached eucalyptus pulp (Xiang, Gao et al. 2016). The results of crystallinity and crystallite length proved again that the concentration process of LCNF suspensions mainly led to the microstructure changes of fiber amorphous region rather than the crystallite region. The water retention values (WRV) of LCNF showed the decreasing trend with the dewatering degree increasing (Table 1). The LCNF-C0 with lignin content 10 wt% prepared based on enzymatic pretreatment had WRV value of 564 % lower than LCNF with WRV 687 % prepared by Bian et al. (Bian, Dong et al. 2019). The reason may be the enzymatic pretreatment of LCNF-C0 was only used endoglucase while Bian et al. combined the endoglucase and xylanase accelerating the fibrillations of fibers and producing much hydroxyl groups on the surface of fibrils (Wang, Gao et al. 2018, Bian, Dong et al. 2019). The WRVs of concentrated LCNF decreased obviously, especially the WRV value of LCNF-C26 reduced by about 29% (Table 1). The specific surface area (SSA) values of LCNF had the similar trend with WRV values. The SSA value of LCNF-C0 was 174 m²/g and corresponded to 161 m²/g of LCNF

prepared from unbleached softwood pulp with lignin content of 13.8% (Table 1) (Spence, Venditti et al. 2010). With the concentration degree of LCNF increasing, the SSA values of LCNF decreased (Table 1). The main reason was that the dewatering process caused irreversible hydrogen bindings among fibrils, and reduced the binding area between nanofibrils and water (Fig.2). The important significance of zeta potential was that its value could reflect the stability of colloidal dispersions. As shown in Table 1, LCNF-C0 showed a relatively high zeta potential of -45.43 mv negative charge because of some carboxyl groups derived mainly from cellulose and hemicellulose (Sim, Lee et al. 2015). The absolute value of zeta potential of concentrated LCNF decreased obviously compared to the un-concentrated LCNF (Table 1). The results indicated that the concentrated LCNF system became unstable with the concentration degree increasing. This conclusion was also consistent with the result from Fig.1 (a).

3.2 Microstructure and physical properties of LCNF film

The un-concentrated and concentrated LCNF films were prepared based on different basis weight, and the properties of films were shown in Table 2. The thickness and porosity of LCNF-C0 films were lower than those of LCNF-C16 films at the same basis weight, while the density property of LCNF-C0 was higher. The thickness and porosity of LCNF-C0-60 were lower 1.25 μm and 3.64% compared to those of LCNF-C16-60 (Table 2), and the results were similar with those reported by Spence et al. (Spence, Venditti et al. 2010, Ferrer, Quintana et al. 2012). The density of LCNF films was in the range of 1.05~1.23 g/cm^3 in accordance with the report by Rojio et al. (Rojio, Peresin et al. 2015). Furthermore, the density and porosity of films had been shown to be related to the diameter distribution of nanofibrils, which in turn indicated levels of fibrillation (Spence, Venditti et al. 2011, Qing, Sabo et al. 2013). The bundle-like fibrils appeared in the LCNF-C16 sample, and the average diameter of LCNF-C16 was larger than that of LCNF-C0 (Fig.2). Consequently, the bonding area between fibrils and the interval formed by the interweaving of fibrils became large leading to the density of films slightly decreasing.

Table 2 The physical properties of films with different basis weight prepared by un-concentrated LCNF-C0 and concentrated LCNF-C16

Sample	Thickness (μm)	Density (g/cm^3)	Porosity (%)
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LCNF-C0-60	49.77	1.09	27.51
LCNF-C0-70	56.31	1.19	20.81
LCNF-C0-80	62.07	1.21	19.64
LCNF-C0-90	66.37	1.21	19.32
LCNF-C0-100	75.04	1.23	18.24
LCNF-C16-60	51.02	1.05	30.15
LCNF-C16-70	62.62	1.06	29.45
LCNF-C16-80	66.59	1.11	25.77
LCNF-C16-90	71.59	1.12	25.64
LCNF-C16-100	77.07	1.18	21.15

The basis weight of films also obviously affected the properties of thickness and porosity. With the basis weight of films increasing, the thickness of films enhanced because the loading of LCNF was improved. The SEM analysis of films showed that the basis weight of films was higher, and the surface of films was smoother (Fig. 4). When the basis weight of films increased from 60 g/m² to 100g/m², the roughness of LCNF-C0 and LCNF-C16 films were decreased by 16.5% and 17.6%, respectively. The increasing basis weight of films was benefit for filling the intervals between fibrils, which could also be stated by the porosity of films (Table 2 and Fig. 4).

Fig.4 The 3D topographies and SEM images of LCNF-C0 and LCNF-C16 films with the basis weight of 60 g/m² and 100 g/m²

3.3 Interactions with water and barrier properties of LCNF films

Relative water absorption (RWA) of LCNF films measured after given water immersion times were shown in Fig.5. RWA of films increased with immersion time increasing especially during the first 10 min. For example, RWA of LCNF-C0-60 and

LCNF-C16-60 increased by 21% and 19.5% after immersion in water for 10 min, respectively. After this time, RWA of films was increased moderately whether the un-concentrated LCNF or concentrated LCNF. Similar behavior was observed previously in the reports (Rojo, Peresin et al. 2015, IK and Gardner 2017). Water adsorption is known to be dependent on the pore structure near the surface. Therefore, The RWA of LCNF-C16 films were a little higher than those of LCNF-C0 films, as the LCNF-C16 had some bundle-like fibrils after concentration process and relatively rough surfaces. This was due to the porosity of LCNF-C16 films were slightly higher than that of LCNF-C0, and the intervals of films promoted the water adsorption (Table 2). For all the films, with the basis weight increasing the RWA relatively increased as the loading of LCNF enhanced, which could adsorb more water. The increasing basis weight of films was benefit for producing much smooth surface (Fig.4), resulting in the RWA of films with basis weight of 60g/m^2 much higher than that of 100g/m^2 . For the unconcentrated LCNF-C0, when the basis weight of film was higher than 70g/m^2 , RWA of films were almost remained constant at the same immersion time. While for the concentrated LCNF-C16, the basis weight of films was improved up to greater than 80g/m^2 . This indicated that the concentration process affected the microstructure and properties of LCNF and LCNF-films (Table1 and Fig.4). The water molecules permeation process was affected the porosity and smoothness of films. When the water molecules got into the interior of films, great capillary force was required for the low porosity and high smooth films (Rojo, Peresin et al. 2015).

Fig.5 Relative water adsorption (RWA) of un-concentrated LCNF-C0 films (a) and concentrated LCNF-C16 films (b) with different basis weight

Fig.6 The water vapor permeability (a) and oxygen permeability (b) of un-concentrated LCNF-C0 and concentrated LCNF-C16 films with different basis weight

Barrier properties of LCNF films were evaluated in terms of water vapor and oxygen permeabilities (WVP and OP, respectively), and the results were listed in Fig.6. The basis weight of films evidently affected the WVP and OP of LCNF-C0 and LCNF-C16 films. When the basis weight of films increased from 60g/m² to 100g/m², the WVP of LCNF-C0 and LCNF-C16 films decreased by 31% and 22%, respectively (Fig.6, a). Accordingly, the OP of films reduced by 35% and 30% (Fig.6, b). The WVP of LCNF-C0 was about 450 g/m².day, and was consistent with the result of LCNF film by Huang et al. (Huang, Nair et al. 2019). The combination of cellulose fibrils formed a dense network by inter-fibrillation bonds, and made the film a suitable barrier material. Therefore, the film structure was a very important factor influencing the gas barrier property. The concentrated process producing bundle-like fibrils could hinder partly hydrogen bonding between the cellulosic fibrils and increased the porosity, allowing water molecules and oxygen molecules permeate through the film easily (Rojo, Peresin et al. 2015, Huang, Nair et al. 2019, Thuy, Hao et al. 2021). Combination the results from Table 2 and Fig.4, the change trend of porosity and density of the film was consistent with the barrier performance of WVP and OP. In sum, the concentration process of LCNF produced much bundle-like fibrils and high porosity of LCNF films resulting in the barrier property of films decreasing.

Fig.7 The UV absorption spectrum of un-concentrated LCNF-C0 (a) and concentrated LCNF-C16 (b)

Fig.7 showed both of LCNF-C0 and LCNF-C16 films had good UV-blocking property. The LCNF films could absorb UVC and UVB completely, and that was to say the light with wavelength between 200-400 nm was completely absorbed by the LCNF films (Fig.7). The LCNF films also showed good UVA blocking property, and the light transmittance of films was less than 2%. Fig.7 (a) and (b) indicated that the concentration process hardly affected the UV blocking property of films. With the basis weight of films increasing, film UV-blocking efficiency of films enhanced (Fig.7). When the basis weight of films was higher than 80 g/m², the UV transmittance of films reduced to less than 0.5% (Fig.7). The blocking properties of films were due to the existence of lignin molecules in the fibrils. Lignin was the only biomass rich in aromatic rings in nature, and contained UV-absorbing functional groups such as phenolic, ketone, and other chromophores (Qian, Qiu et al. 2015, Qian, Zhong et al. 2017). Therefore, the concentrated LCNF films could be considered as a natural broad-spectrum UV blocker, and could be used for food package, pharmaceutical, and electronic energy devices.

3.4 Mechanical properties of LCNF films

Besides the barrier property of films, the mechanical strength properties of films were also important for the application. In order to avoid the strength caused by basis weight of films, tensile index and specific modulus were introduced to analyze film strength, and listed in Fig.8. The tensile index and specific modulus of LCNF-C0 and LCNF-C16 films increased with the basis weight increasing from 60g/m² to 80g/m²,

and constantly remained continued to enhance the basis weight to 100g/m² (Fig.8). The strength of films was mainly determined by the structure of films, and the density of films was benefit for the strength to some extent (Table 2 and Fig.4). The strength of concentrated LCNF-C16 films were lower than that of LCNF-C0 at the same basis weight, indicating the concentration process really reduced the bonding strength of fibrils as previous discussion. The tensile index of LCNF-C0 and LCNF-C16 films was in the range of 79.8~101.7 kN • m/kg and 71.5~94.1 kN • m/kg, while the specific elastic modulus of LCNF-C0 and CNF-C16 was in the range of 6.9~8.5 MN • m/kg and 6.8~7.7 MN • m/kg, respectively. These results were similar with the strength parameters of films in the previous reports (Spence, Venditti et al. 2011, Rojo, Peresin et al. 2015, Huang, Nair et al. 2019). The mechanical strength of concentrated LCNF-C16 films was much higher than that of films prepared by dispersed-LCNF from freeze-dried LCNF suspension (Fu, Gao et al. 2020). This result stated that although the concentration process produced the large diameter distribution of LCNF, the LCNF-C16 still had many hydroxyl groups in the surface and formed hydrogen bonding between fibrils after mechanical dispersing again.

Fig.8 The tensile index (a) and specific elastic modulus (b) properties of un-concentrated LCNF-C0 films and concentrated LCNF-C16 films with different basis weight

4. Conclusions

This study exhaustively analyzed the characteristics of LCNF with different solid concentrations. Low concentration of LCNF suspension limited the transportation and

end-use application of LCNF. Therefore, in this work 1.0 wt% LCNF suspension was dewatered to solid concentration of 5.9 wt%, 16.3 wt% and 25.9 wt% by a centrifuge, respectively. The un-concentrated LCNF suspension showed obviously stable translucent and well dispersed in water, while the concentrated LCNF exhibited the gel-like behavior or “solid-like” behavior based on the concentration degree. The bundle-like fibrils were observed in the concentrated LCNF, and average diameter of concentrated LCNF became large but still less than 100 nm. The concentrated LCNF films had relatively low density, tensile index, specific modulus, and high porosity compared to unconcentrated LCNF film, but had good water vapor and oxygen permeabilities. Due to the existence of lignin molecule in the fibrils, all the LCNF films presented very good UV barrier property. The increasing basis weight of films was benefit for enhancing the surface smoothness of films and interweaves between fibrils, resulting in the tensile index and specific modulus of films increasing. In sum, the concentration process affected the morphology structure of LCNF, but the concentrated LCNF still kept relatively good properties. Concentration process of LCNF suspension may be a feasible strategy for large-scale LCNF production and storage.

Conflicts of interest

The authors declare no competing financial interest.

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