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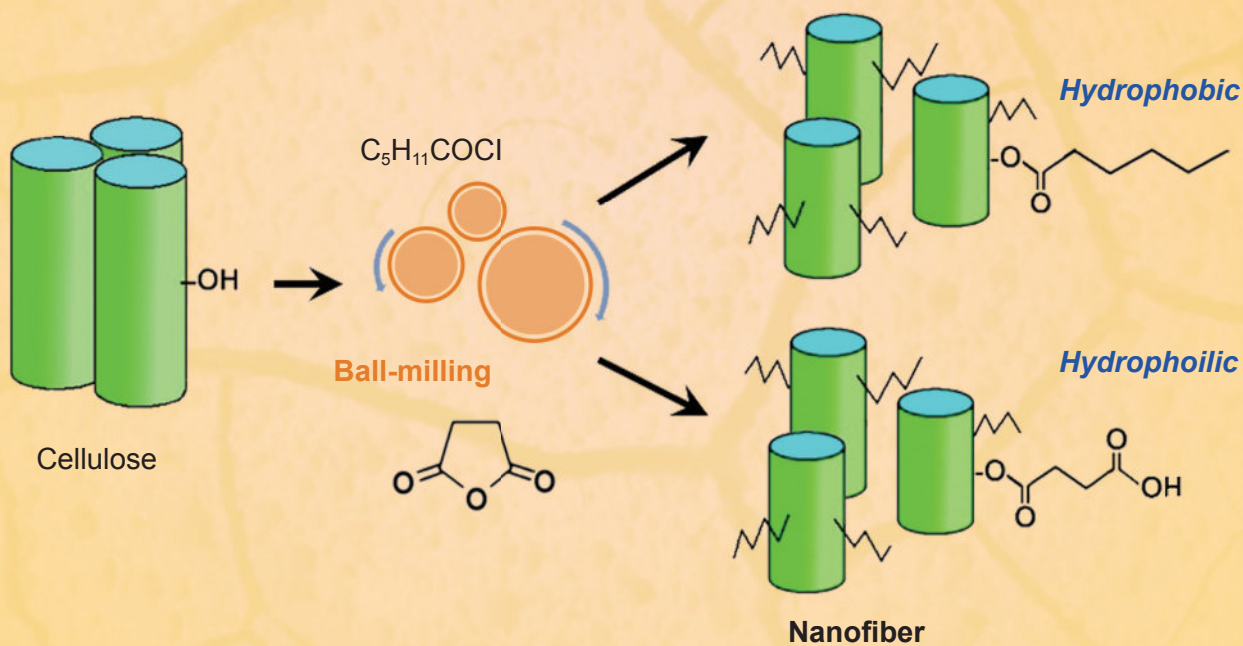
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Simultaneous Extraction of Carboxylated Cellulose Nanocrystals and Nanofibrils via Citric Acid Hydrolysis—A Sustainable Route

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Abstract: In this study, cellulose nanocrystals (CNC) with surface carboxylic groups were prepared from bleached softwood pulp by hydrolysis with concentrated citric acid at concentrations of 60 wt%~80 wt%. The solid residues from acid hydrolysis were collected for producing cellulose nanofibrils (CNF) via post high-pressure homogenization. Citric acid could be easily recovered after hydrolysis reactions through crystallization due to its low water solubility or through precipitation as a calcium salt followed by acidification. Several important properties of CNC and CNF, such as dimension, crystallinity, surface chemistry, thermal stability, were evaluated. Results showed that the obtained CNC and CNF surfaces contained carboxylic acid groups that facilitated functionalization and dispersion in aqueous processing. The recyclability of citric acid and the carboxylated CNC/CNF give the renewable cellulose nanomaterial huge potential for a wide range of industrial applications. Furthermore, the resultant CNC and CNF were used as reinforcing agents to make sodium carboxymethyl cellulose (CMC) films. Both CNC and CNF showed reinforcing effects in CMC composite films. The tensile strength of CMC films increased by 54.3% and 85.7% with 10 wt% inclusion of CNC and CNF, respectively. This study provides detailed information on carboxylated nanocellulose prepared by citric acid hydrolysis; a sustainable approach for the preparation of CNC/CNF is of significant importance for their various uses.

Keywords: cellulose nanocrystals; cellulose nanofibrils; carboxylic acid; cellulose hydrolysis



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1 Introduction

Attention toward exploitation of nanomaterials from renewable sources has increased with the growth of environmental concerns in the past decades. Cellulose is a natural polymer that can be extracted from abundant lignocellulosic biomass. Nanocellulose (NC), isolated from plant cell walls, has great potential to be used for the production of various renewable and functional materials due to its unique mechanical and optical properties^[1]. Therefore, economical and environmentally sustainable production of NC is of critical importance for its industrial application.

NC can be divided into two main categories: cellulose nanocrystals (CNC, “rice-like”) and cellulose nanofibrils (CNF, “noodle-like”), which are different in morphology^[2]. CNC is mainly obtained by hydrolyzing the non-crystalline fraction of cellulose. The production process usually involves strong inorganic acids, such as sulfuric acid or hydrochloric acid, which might increase the cost of acid recovery, create difficulties related to the disposal of large amounts of salt from acid neutralization, or equipment corrosion issues^[3]. Furthermore, the introduction of sulfate groups during sulfuric acid hydrolysis could lower the thermal stability of CNC. Enzymatic hydrolysis combined with post mechanical shearing forces is an environmentally friendly method to produce CNC^[4]. Chemical or mechanical treatment is usually applied prior to enzymatic hydrolysis to increase accessibility of cellulose for CNC production^[5-6]. The extremely long reaction time, poor dispersibility of CNC, and the recovery of enzymes limited its application. The oxidation method can also be used to produce rod-like CNC, but the chemical recovery is not easy to handle, and the toxic reagents, such as TEMPO, ammonium persulfate, and sodium metaperiodate, need to be treated^[7-8]. Currently, it is still a challenge to realize commercial production of CNC. CNF is mainly produced by delaminating inter-fibrillar hydrogen bonding of cellulose microfibrils under intense mechanical forces^[1]. The main hindrance to the commercialization of CNF production is the huge

amount of energy required. Although combining chemical pretreatment with mechanical treatment could reduce energy consumption, the environmentally unfriendly pretreatment procedures (e.g., acid hydrolysis) still hinder the commercial production of CNF^[9].

Pure citric acid (CA) is a white crystalline solid, and it is odorless and of slightly acid taste. It is a weak organic acid commonly found in fruits, especially in citrus^[10]. CA is widely used in food, beverage, and pharmaceutical industries^[11]. It has mild impacts on human health and the environment, and it can be recycled by crystallization or overliming and acidification^[11], which are existing and mature technologies with little technical risk. In addition, CA can be used to produce reducing sugars via hydrolyzing cellulose^[12]. Therefore, it could be a good catalyst for NC production.

In previous work, recoverable acids like phosphotungstic acid^[13], formic acid^[14-17], oxalic acid^[18], maleic acid^[3], and *p*-toluenesulfonic acid^[19], were used to prepare NC. In the present work, a novel and sustainable pathway for the coproduction of CNC and CNF from commercial wood pulp using CA was established. The cellulose was hydrolyzed and modified in one-step hydrolysis with the presence of concentrated CA. Thus, carboxylated CNC was produced through the concurrent acid hydrolysis and acid-catalyzed esterification process. After CA hydrolysis, the precipitated cellulosic solid residue (CSR) was used to produce CNF through the subsequent high-pressure homogenization. Then the isolated CNC and CNF were characterized, and their potential use as reinforcing agents for making CMC composite films was also evaluated.

2 Experimental

2.1 Materials

Bleached softwood pulp was provided by Hengfeng Paper Co., Ltd., China. The commercial pulp had a glucan content of 90.4 wt%, xylan content of 3.5 wt%, and lignin content of 0.1 wt%. Analytical grade CA and

uranyl acetate were purchased from Sinopharm, China.

2.2 CNC and CNF production

Concentrated CA solutions were prepared by heating the desired amount of deionized water in an oil bath to approximately 80°C. Then, an appropriate amount of CA was added to make a solution with the desired concentration by magnetic stirring. Pulp fibers were then added into the acid solution with a concentration of 20 mL/g under stirring. The solution temperature was raised to the desired temperature in a Parr autoclave (USA). At the end of the set time, the reaction was terminated by adding 2-fold deionized water. The resultant suspension was washed, followed by three periods of centrifugation, and then dialyzed against deionized water until the pH value stabilized. After that, the suspension was centrifuged at 3000 r/min for 10 min. The CNC was dispersed into the turbid supernatant and decanted off. The settled CSR was then homogenized by 5 passes at 50 MPa and 0.2 wt% concentration in water to produce CNF. The yields of CNC and CNF were calculated based on the oven dry weight of the starting material.

2.3 Preparation of composite film

CMC and CMC/NC films were prepared using the casting method. Three grams CMC and 0.9 g glycerol (30% of CMC weight) were added to 150 mL of distilled water. The solution was stirred vigorously for about 60 min until complete dissolution. The CMC solution was cast onto a glass plate and dried at 40°C overnight. For the CMC/NC composite film, a certain amount of NC (according to the CMC weight) was mixed in the above-mentioned solution and stirred for 3 h at 23°C. After that, the mixture was cast and dried at 40°C overnight. Before the characterization and test, the prepared films were kept in a humidity chamber under the conditions of 25°C and 50% relative humidity for 24 h.

2.4 Characterization

NC samples produced at 120°C with a CA concentration of 80% were taken for the following analyses. Scanning

electron microscopy (SEM) analyses were conducted on a scanning electron microscope at an accelerating voltage of 3.0 kV; transmission electron microscopy (TEM) images were obtained on a field emission H-7600 electron microscope at an accelerating voltage of 80 kV. After drying, NC samples were stained with a 2% uranyl acetate solution before imaging; Fourier transform infrared spectroscopy (FT-IR) of samples was recorded by a Thermo Nicolet FT-IR spectrometer in the range of 400~4000 cm⁻¹ with a resolution of 4 cm⁻¹; X-ray diffraction analysis (XRD) of the samples was conducted using a Bruker D8 ADVANCE X-ray diffractometer. The data were collected at an angular range of 5°~60° with a scan rate of 4°/min. The crystallinity index (CrI) of cellulose samples was calculated according to Segal's method^[20]; thermal gravimetric analysis (TG) was studied using a thermogravimetric analyzer with a temperature range from room temperature to 600°C at a heating rate of 10°C/min under argon atmosphere (25 mL/min); and tensile strength (TS) of film samples were measured using a Model CMT6503 universal testing machine (MTS Systems Co., Ltd., China). The tensile machine was operated with an initial grip separation of 50 mm and a crosshead speed of 50 mm/min.

3 Results and discussion

3.1 CNC and CNF yields

The schematic flow diagram of NC production process used in this work is presented in Fig.1. The bleached softwood pulp was converted to CSR and CNC functionalized with carboxyl groups through Fischer esterification. CA hydrolysis experiments were carried out at different acid concentrations (60 wt%~80 wt%) and hydrolysis temperatures (100~140°C) with a fixed reaction time of 6 h. The yields of CNC and CSR from these experiments are listed in Table 1. The yields of total solids (CNC+CSR) were negatively correlated with reaction intensity (i.e., temperatures and acid concentrations). No CNC could be obtained under the lowest severity hydrolysis conditions (60%, 100°C), suggesting that more severe reaction conditions

are needed to achieve sufficient hydrolysis for CNC production. CNC yield was still low with the highest yield of approximately 24% due to insufficient hydrolysis, because the acidity of CA was weaker than that of mineral acids such as sulfuric acid. High acid concentrations were used to minimize cellulose crosslinking while enhancing esterification^[3], and therefore higher CNC yields could be obtained at higher acid concentrations. Maximum CNC yields of about 24% were achieved at temperatures of 120 or 140°C with an acid concentration of 80%. This CNC yield was similar to the one obtained using other organic acids, such as oxalic acid^[3], but lower than the one obtained using traditional inorganic acids, such as sulfuric acid^[21].

3.2 Characterization of CNC and CNF

The morphologies of CNC and CNF are revealed by TEM images (Fig.2). The images clearly showed good CNC and CNF dispersion. The diameters and lengths of CNC were approximately (10 ± 4) and (210 ± 80) nm, respectively, as determined by image analyses of a random selection of 50 nano-particles. The CNF had a larger diameter $((15 \pm 8) \text{ nm})$ than the CNC sample. Because the nanofibers and bundles of CNF were long and highly networked, it was not easy to observe the

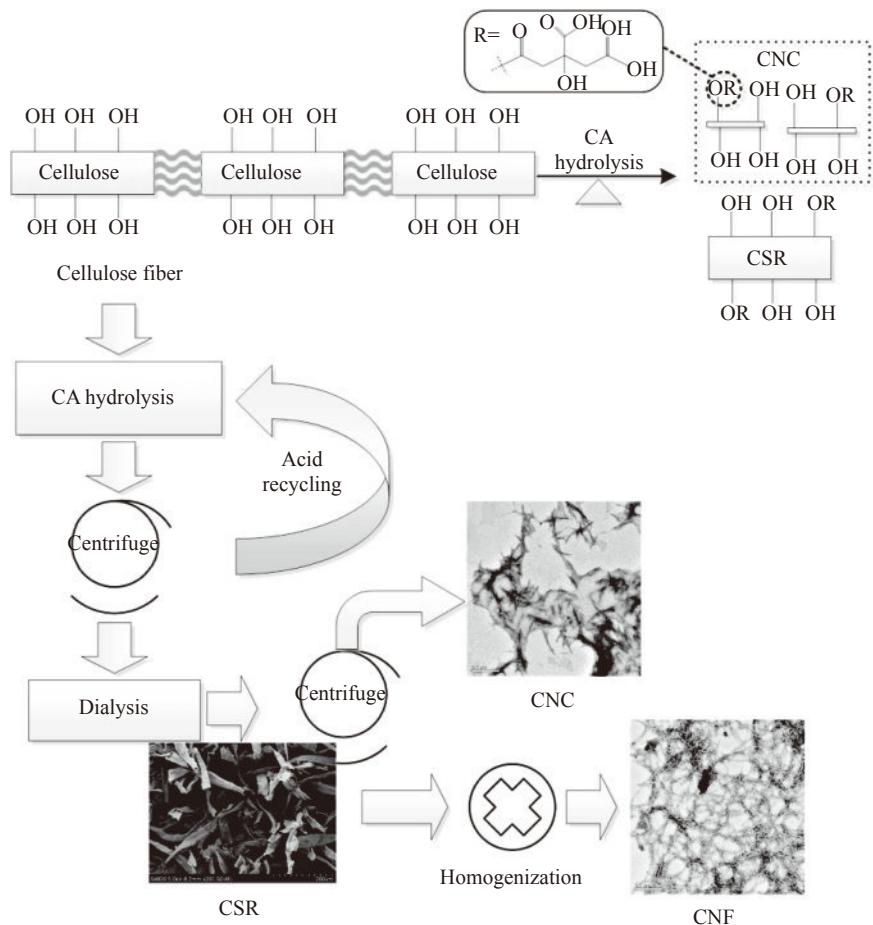


Fig.1 Schematic diagram of cellulose carboxylation, CNC and CNF production

Table 1 Yields of CNC and CSR under various conditions

Concentration /%	Temperature /°C	CNC yield /%	CSR yield /%
60	100	0	98.5
	120	6.3	89.8
	140	21.0	69.9
80	100	18.3	76.7
	120	23.8	66.6
	140	24.2	64.0

Yields are based on original pulp fiber mass.

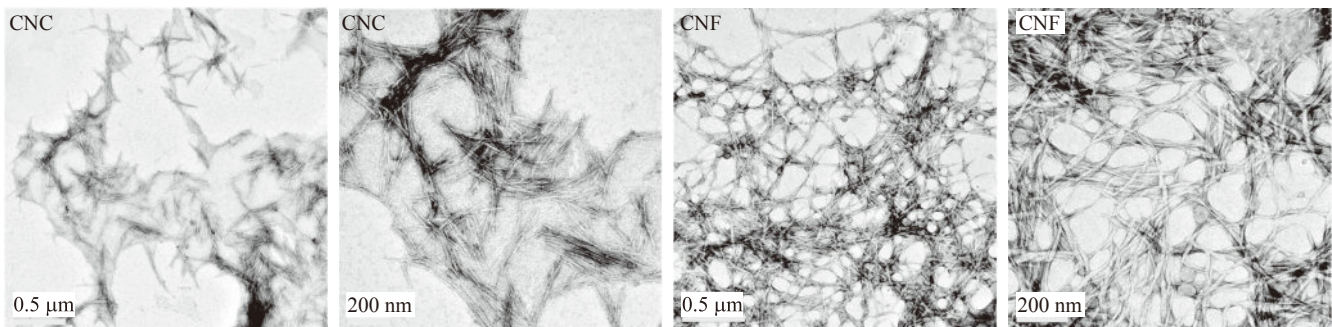


Fig.2 TEM images of CNC and CNF samples

end of an individual nanofiber and measured the exact length.

FT-IR absorption of CNC and CNF samples along with the original pulp fiber were analyzed and the results are shown in Fig.3a. Cellulose esterification by CA is well known for cellulose crosslinking^[22]. The main feature of the NC samples was esterification, as observed from the ester carbonyl groups ($\text{C}=\text{O}$) at 1737 cm^{-1} that did not appear in the original pulp sample. This phenomenon suggests that the carboxyl groups in the CA reacted with cellulose to form ester groups or that the CA was adsorbed onto the surface of cellulose^[23]. To investigate the influence of processing method on the cellulose crystal structure, the changes in XRD curves of the pulp fiber and NC were examined, as shown in Fig.3b. The samples exhibited diffraction peaks at approximately 2θ of 17° and 22.8° , indicating that the native cellulose crystal I structure was preserved. The CrI increased in the following order: $\text{CNC} < \text{pulp fiber} < \text{CNF}$. The CrI of CNC decreased compared to raw pulp fiber, which may be ascribed to the fact that the CA could not only remove the amorphous portion of cellulose but also damage part of

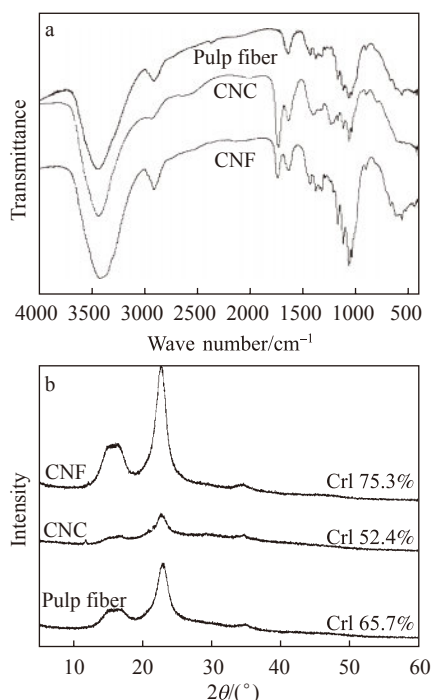


Fig.3 FT-IR spectra (a) of and XRD pattern (b) of pulp fiber and NC samples

the crystalline portion of CNC during the hydrolysis. In contrast, the CrI of CNF increased to 75.3% compared with that of pulp fiber (CrI of 65.7%). The removal of amorphous cellulose and non-crystalline xylan during hydrolysis led to the higher crystallinity. Homogenization did not result in a clear reduction of CrI for CNF samples.

The thermal stabilities of NC were determined to assess its potential use in high-temperature applications. The TG and derivative thermogravimetric (DTG) curves of pulp fiber and NC are illustrated in Fig.4. The TG curves showed a small weight loss before 100°C , corresponding to moisture evaporation. Among the samples, CNC exhibited the lowest thermal stability. The main reason for this might be linked to disruption of its crystalline structure and introduction of surface carboxylic groups during CA hydrolysis and the esterification process. Moreover, smaller fiber dimensions, leading to higher surface areas exposed to heat, also have negative effects on thermal stability^[24]. CNF exhibited slightly lower thermal stability than the pulp fiber, and this may be due to the formation of carboxylate groups on the cellulose surfaces^[25]. In spite of its reduced thermal stability, CNC exhibited

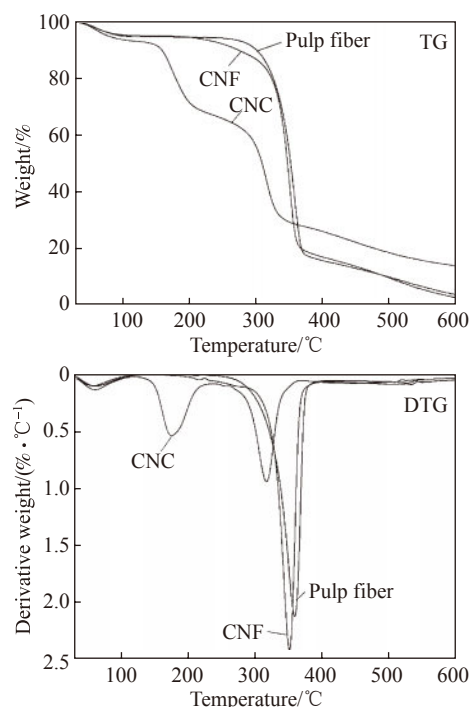


Fig.4 TG and DTG curves of pulp fiber and NC samples

higher yields of char residues than both CNF and the original pulp fiber. This phenomenon was consistent with the outcome of sulfuric acid hydrolysis^[26]. The increased char residues might be due to the dehydration reaction at lower temperatures. The CNC sample exhibited double degradation peaks, possibly because of its wide size distribution and different degrees of esterification^[27].

3.3 CNC/CNF reinforced CMC composite film

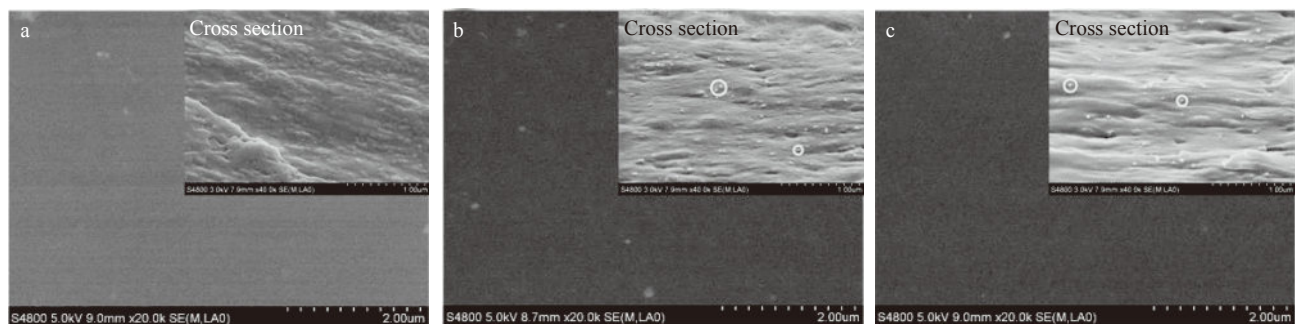
The nanoscale dimensions and high mechanical properties of CNC and CNF make them ideal for polymer reinforcement. Tensile test results of CMC and CMC/NC composite films are shown in Table 2. The TS of CMC film was greatly influenced by mixing with NC, and it was dependent on the content of NC. These mechanical properties increased and then decreased as the NC content increased. The optimal content appeared to be 10% for both CNC and CNF. The composite film containing 10 wt% CNC showed a TS of (61.7 ± 2.1) MPa, which was 54.3% higher than that of pure CMC film. The composite containing 10 wt% CNF exhibited even higher mechanical reinforcement (an increase of 85.7% in TS). The increase in TS was attributed to the high mechanical properties of CNC and CNF, as well as their strong interactions with the CMC matrix. The decrease of TS at a higher NC content (15%) was probably due to agglomeration of NC particles^[28].

Microstructures of the pure CMC film and CMC/NC composite films were observed by SEM imaging, as shown in Fig.5. The degree of distribution of NC particles and the interactions between the NC and CMC

Table 2 Mechanical properties of composite film

Filler	NC Content/%	Tensile strength/MPa
Control	0	40.0 ± 0.8
	1	48.2 ± 0.3
	3	52.3 ± 1.7
	5	57.8 ± 1.9
	10	61.7 ± 2.1
	15	58.8 ± 0.7
CNF	1	50.9 ± 0.5
	3	58.1 ± 2.8
	5	64.1 ± 1.5
	10	74.3 ± 2.2
	15	67.9 ± 2.3

matrix are important to the performance of composite films. Surfaces of all film samples were smooth and homogeneous, and no defect could be observed (Fig. 5). Blending with CNC/CNF did not affect the surface structure of CMC film, indicating that the NC particles were uniformly distributed and compatible with the CMC matrix to form a homogeneous structure. However, after tensile testing, cracked NC could be observed on the images of the cross section of film samples (the marked circles in Fig.5b and Fig.5c). In addition, Fig.6 demonstrates the fracture mechanisms of CMC/NC composite films. The strong interaction between NC particles and CMC matrix as well as bridging formed by NC contributed to the mechanical reinforcing effect^[29]. Due to its longer lengths and higher flexibility, CNF had more interface interactions with the CMC matrix and stronger bridging effects compared with CNC (Fig.6).



CNC/CNF dosage of 5 wt%.

Fig.5 SEM images of surface and cross-section of CMC film (a), CMC/CNC (b) and CMC/CNF (c) composite films

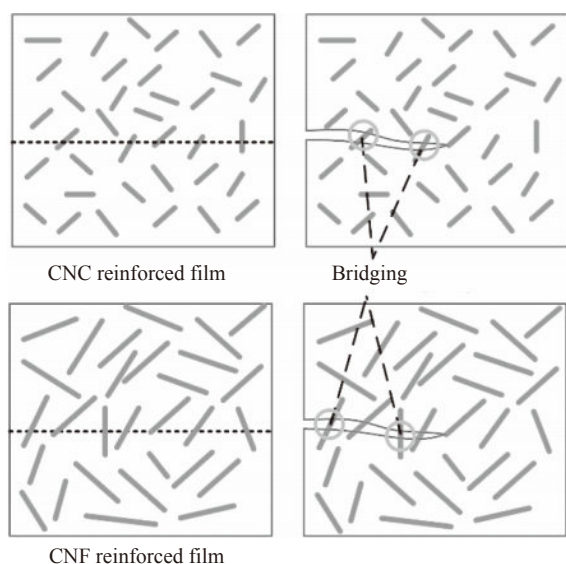


Fig.6 Illustrations of fracture mechanisms of CMC/NC composite film

4 Conclusions

In this study, the concurrent production of cellulose nanocrystals (CNC) and cellulose nanofibrils (CNF) using recyclable citric acid (CA) was investigated. The highest yield of CNC was only 24% due to the insufficient hydrolysis and weak acidity of CA. During the CA hydrolysis, cellulose could be esterified by carboxyl groups of CA, thus generating carboxylated CNC and CNF. This surface modification was important for further functionalization of NC products. Also, both resultant CNC and CNF exhibited lower thermal stabilities than the original pulp fiber due to the disruption of crystalline structures and the formation of carboxylate groups on their surfaces. In addition, owing to strong fiber-matrix interfacial bonding and large aspect ratios of fibers, CNF exhibited a better reinforcing effect to CMC films compared to CNC. This study demonstrated that the CA hydrolysis could be regarded as a green and sustainable method for NC production, although more studies regarding process optimization, recovery rate of CA, and end uses for NC products are needed.

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