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COMPARATIVE STUDY OF CELLULOSE NANOFIBRILS DISINTEGRATED FROM DIFFERENT APPROACHES

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The use of renewable materials has received a great deal of attention over the last several decades due to the environmental impact and finite resources of petroleum and other non-renewable resources. Cellulose nanofibrils are a type of nanomaterial made from natural resources like wood and non-wood plants, and they are considering promising alternative to existing materials in numerous fields (Eichhorn et al., 2010). There are essentially four types of cellulose nanomaterials, including bacterial cellulose nanofibers, electrospun cellulose nanofibers, cellulose nanocrystals, and cellulose nanofibrils (Gardner et al., 2008). Among these fibers, the latter two are extracted from natural fibers chemically and/or mechanically, and are of great potential given the available resources and viability of processing them as well as their performance.

Unlike cellulose nanocrystals (CNCs), cellulose nanofibrils (CNFs) are primarily produced by subjecting pulp fibers to repeated shear and impact to produce materials with unique network structure and high aspect ratio. Since pioneers Herrick and Turbak first produced CNFs in the 1980s, many attempts have been dedicated to seek an efficient approach to disintegrate cellulose fiber to nanofibrils, involving homogenization, ultrafine grinding, refining, microfluidization, intense ultrasonication, cryocrushing in liquid nitrogen, and high-speed blending (Qing et al., 2013). However, the microfibrils in cellulose fiber are laterally combined with rigid hydrogen bonds and highly networked. Though the fibers are initially refined by removing pectin, lignin, and hemicellulose, the individualization and liberation of CNFs are still challenging, especially in terms of larger commercial scale.

To loosen the rigid structure of cellulose with intention of easier defibrillation, several pretreatments including alkaline modification, enzyme hydrolysis, and chemical oxidation have been applied. For instance, Henriksson et al. (2007) proposed that endoglucanase treatment of softwood pulp fibers made it possible to facilitate production of CNFs using a Microfluidizer. Zhu and Sabo (2011) showed that extensive enzymatic treatment of cellulose fibers yielded both sugar streams and hydrolyzed cellulose fibers and that the enzymatic treatment facilitated the production of nanofibrils. Isogai and Saito (2005) reported a chemical treatment involving 2, 2, 6, 6-tetramethylpiperidinyl-1-oxyl (TEMPO) oxidization, which converts hydroxyls of cellulose to carboxyl groups, thus creating repulsive force between individual nanofibrils. The oxidization was found to promote efficient nanofibrillation of cellulose with highly uniform width of 5-10 nm. Liimatainen et al. (2012) reported another oxidization route based on a regioselective and sequential oxidation with periodate and chlorite. However, effects of pretreatments and mechanical disintegration processes on the morphology and properties of CNFs are still not clear. Here, we aim to further understand the effects of pretreatments and mechanical defibrillation on the properties of CNFs and films made from them. Grinding and homogenization, combined with chemical or extensive enzymatic pretreatment, are applied to produce various nanofibrils. The morphology and crystallinity of the CNFs, as well as mechanical and optical properties of their neat films are compared.

Commercially bleached eucalyptus Kraft pulp was blended and mixed with distilled water at 1.5 wt% consistency. The fiber suspension was then mechanically fibrillated in a MKZA6-2 SuperMassColloider (Masuko Sangyo Co., Ltd, Saitama, Japan) at 1500 rpm. Approximately 100 g pulp fibers were ground for 6 h. Before grinding, a commercial grade endoglucanase of FiberCare® from Novozymes (Franklinton, NC, US) was applied to modify the pulp fibers at loading of 3 FPU/g fiber. A portion of the refined pulp was further fibrillated in the Microfluidizer. The fiber suspensions were initially diluted to 1wt% consistency and passed through the 87 μm chamber 15 times at pressure of 150 MPa. The description of specific preparation approaches was shown in Table 1.

Table 1 The preparation approaches and main properties for different species of cellulose nanofibril

Materials	Preparation approaches			Main properties	
	Pretreatment	Refining	Microfluidization	DP	Crystallinity (%)
Pulp fiber	No	No	No	1000	55
R	No	Yes	No	836	47
RM	No	Yes	Yes	664	44
ER	Enzyme hydrolysis	Yes	No	287	60
ERM	Enzyme hydrolysis	Yes	Yes	263	57
TEMPO	TEMPO-oxidization	Yes	Yes	580	34

Figure 1 gives representative scanning electron microscopy images for different types of CNFs. Pulp fibers refined by grinding (Figures 1a, c and g) with or without enzymatic pretreatments still have microfibril bundles intact. However, refining in combination with high-pressure microfluidization produced highly fibrillated nanofibrils, resulting in uniform fiber diameter and excellent network. Unlike mechanical refining, the microfluidization is able to provide intense impact which perhaps accelerates the defibrillation of fibers. A similar finding was proposed in a previous study conducted by Stelte and Sanadi (2009). Interestingly, fibers pretreated with enzymes appear to be short, stiff, and rod-like nanofibrils (Figures 1d and h) compared to the untreated ones (in Figure 1b). Not only did the enzymes reduce the length of course pulp fibers, but qualitatively decrease the networked configuration at different levels. The "ERM" nanofibrils resemble cellulose nanocrystals (Figure 1e) that are acid hydrolyzed from pulp fibers. Because the amorphous regions in cellulose fibers are predominantly removed under strong acid hydrolysis, CNCs are short but stiff (Moon et al., 2011). Due to harsh conditions of acid hydrolysis, the current method may offer an environmentally friendly alternative for producing CNCs. However, further investigation is warranted to fully characterize these CNC-like fibers and to understand how the enzyme influences and attacks the cellulose fibers.

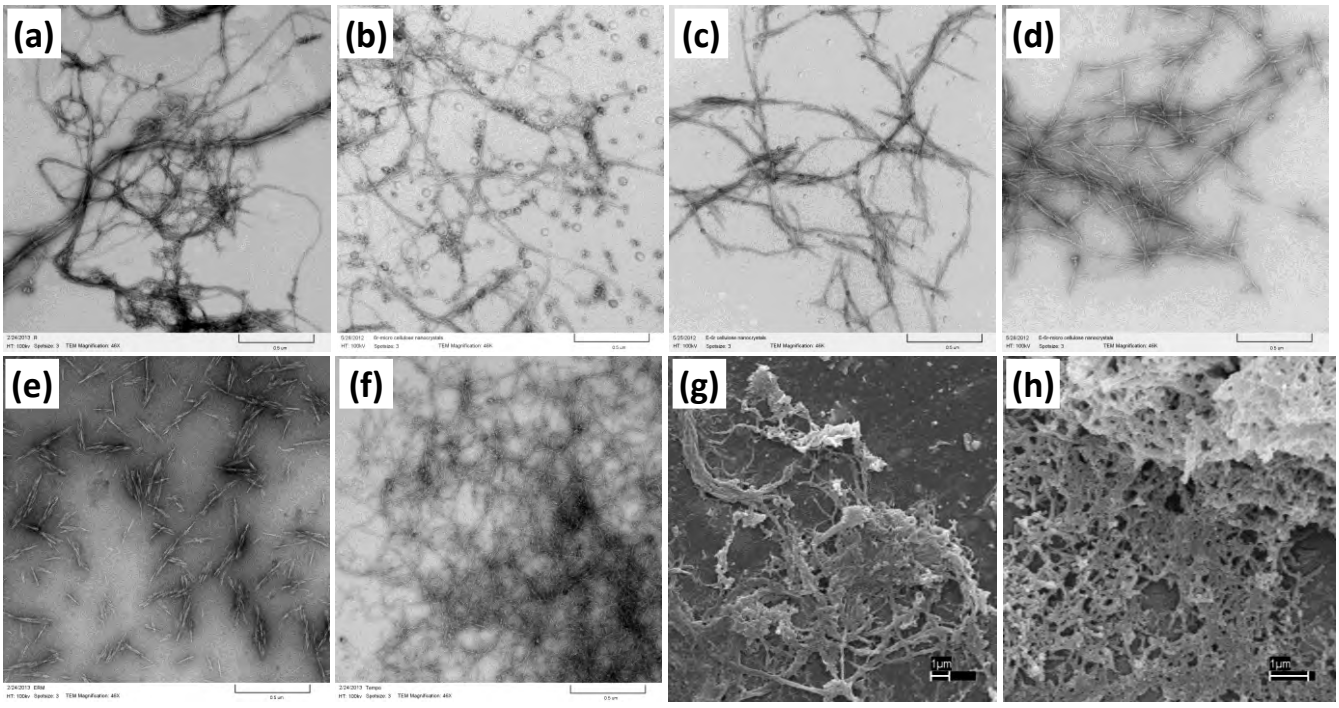

Figure 1 Representative TEM (a-f) and SEM (g and h) images for different types of CNFs. (a): R, (b): RM, (c): ER, (d): ERM, (e): CNCs by acid hydrolysis, (f): TEMPO, (g): R, and (h): ERM. The scale bars are 500 nm (TEM) and 1 μm (SEM) respectively.

The TEMPO-oxidized cellulose nanofibrils were prepared according to the work reported by Saito et al. (2009). As comparison, Figure 1f shows the morphology of TEMPO nanofibrils which have uniform fiber diameter of 5-10nm. The fiber length is more than several micrometers.

Detailed intrinsic properties of CNFs, including degree of polymerization (DP) and crystallinity, are shown in Table 1. The DP value is important parameter to evaluate the length and branching of cellulose molecule chains. Note that both "ER" and "ERM" nanofibers exhibit lower DP than other CNFs prepared here. This result matches well our previous statement that extensive enzymatic hydrolysis contributed to reduce fiber length when pulp fibers underwent fierce fibrillation. Another positive effect of enzymatic pretreatment is enhancement of the possibility that starting fibers passed through high-pressure microfluidization without any clogging. The DP of CNFs after mechanical fibrillation was decreased compared to raw pulp fibers and largely depended on the processing conditions.

The pretreatments and mechanical nanofibrillation have little impact on the crystal structure of cellulose. However, the intensity of diffraction peaks varied significantly among these samples. The crystallinity indexes shown in Table 1 were calculated based on the Segal method. By peeling off the individual microfibrils from cellulose fibers, CNFs often have low crystallinity, and such results are shown elsewhere in the literature. However, the nanofibrils pretreated with enzymatic hydrolysis possess higher crystallinity (nearly 60%) than even raw pulp fibers (55%). This indicates that enzymatic hydrolysis strongly attacks the amorphous region of cellulose. As a result of partial digestion of amorphous regions, the relative crystallinity was increased. This is consistent with above morphological observation that enzymatically pretreated CNFs mostly presented as stiff, rod-shape particles similar to cellulose nanocrystals. The TEMPO CNFs had surprisingly low crystallinity, which may make them undesirable for applications such as polymer reinforcement. This low crystallinity is likely a result of the combined chemical and mechanical treatments, but more work is needed to understand the low crystallinity of TEMPO CNFs.

The morphological properties of the CNFs prepared in this work are summarized as: 1) enzymatic treatment led to reduced length and reduced networking of fibers; 2) refining in a SuperMassCollider grinder resulted in non-uniform fibril bundles; and 3) the high-pressure microfluidizer resulted in a further liberation of the bundles into more uniform fibrils. Although the type of refining process of grinder is more readily scalable and industrially preferred, its implementation in the manner studied here suggests apparent limitations in the ability to fully create highly uniform nanomaterials, although multi-staged or optimization of process conditions may result in more uniform fibers or tailored nanofibril morphologies. However, processing the cellulose to a homogeneous, nano-scale material may not be necessary depending on the application and desired properties of the CNFs.

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