

A Review: Efficiency Of Nanocrystals And Nanofibrils Cellulose As Reinforcing Element In Composite Films Productions

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ABSTRACT

Cellulose nanocrystals and nanofibrils are nano-sized cellulose obtained by top-down approaches such as isolation and extraction both by chemical and physical methods. Due to the abundance, high-strength, and high-stiff properties of nanocrystals and nanofibrils, they can be used as reinforcement for composite films. This review aims to demonstrate the efficiency of cellulose nanocrystals and nanofibrils as reinforcement for composite films based on the mechanical properties, surface wetting, and crystallinity of the resulting composite films. The method used is to find articles related to the use of nanocrystals and nanofibrils as reinforcing elements on online journal website pages, there are 10 articles used that are related in this review. The result of this literature review is that the use of nanocrystals and nanofibrils for composite film reinforcement can be said to be effective. Based on the composite films formed, almost all types of composite films have high mechanical properties, better surface wetting, and higher crystallinity than without the addition of nanocrystals and nanofibrils as reinforcement composite film. Therefore, this paper can provide information on the effectiveness of nanocrystals and nanofibrils as reinforcement in composite films so that these composite films can be further utilized to make good materials.

Keywords: nanocrystals; nanofibrils; composite film; mechanical strength; crystallinity

1. INTRODUCTION

In the 21st century, much research is devoted to the produce of sustainable and environmentally friendly materials due to the increasing concern about environmental pollution. Cellulose is the most abundant biopolymer in the world which is a linear polymer of glucose. Cellulose is a long-chain polysaccharide consisting of a D-glucose ring linked by β -1,4 glycosidic bonds [1]. Cellulose in the form of nano can be called nanocellulose, which has a size of no more than 100 nm and at least one dimension. In other dimensions, the structure of nanocellulose can reach hundreds of nanometers, micrometers, or more [2]. The physical properties, namely the strength and flexibility of nanocellulose, are high, which is determined by the crystal structure [3].

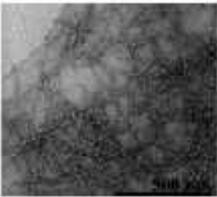
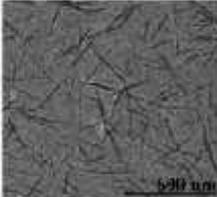
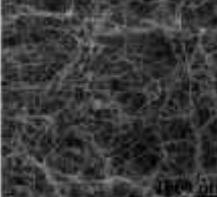
Nanocellulose is divided into three classifications, namely nanofibrillated cellulose (NFCs), nanocrystalline (NCCs), and bacterial nanocellulose (BNCs) [4]. Nanofibrillated cellulose and nanocrystalline cellulose were obtained through top-down approaches such as isolation and extraction by chemical and physical

methods from plants, enzymatic, higher plants such as banana stems, pineapples, rubber, and palm sugar fibers. While bacterial nanocellulose is produced from certain bacteria that are cultivated in culture media [5]. The comparison of the three nanocelluloses is summarized in Table 1.

Nanocellulose can be found in a variety of applications, including biomedical devices, nanocomposite materials, and textiles [6]. Many researchers are currently interested in using cellulose nanocrystals. The advantages of cellulose nanocrystals include a complex network of intermolecular and intramolecular hydrogen bonds that give them good mechanical properties and the capacity to self-assemble into a dense, high-strength, and high-stiff crystal structure [7]. The advantages possessed by cellulose nanocrystals are a complex network of inter- and intramolecular hydrogen bonds that make natural cellulose nanocrystals have good mechanical properties and the ability to self-assemble into a dense, high-strength, and high-stiff crystal structure [7]. One of the uses of

cellulose nanocrystals is to make composite films.

Table 1. Comparison between the three main nanocelluloses [5]

Comparison	Nanofibril Cellulose (NFCs)	Nanocrystalline Cellulose (NCCs)	Bacterial Nanocellulose (BNCs)
Images			
Synonyms	Nanofibril cellulose, nanofibrils dan microfibrils	Nanocrystal cellulose, whiskers, rodlike cellulose microcrystals	Bacterial cellulose, microbial cellulose, bio cellulose
Source	Wood, sugar, potato tuber, hemp, flax	Wood, cotton, flax, wheat straw, ramie, tunicin	Low-molecular-weight sugars and alcohols
Formation Process and Size	<ul style="list-style-type: none">) Delamination of wood pulp by mechanical pressure before and/or after chemical or enzymatic treatment) Diameter: 5–60 nm) Length: several micrometers 	<ul style="list-style-type: none">) Acid hydrolysis of cellulose from many sources) Diameter: 5–70 nm length: 100–250 nm (from plant celluloses); 100 nm to several micrometers (from celluloses of tunicates, algae, bacteria) 	<ul style="list-style-type: none">) Bacterial synthesis) Diameter: 20–100 nm; different types of nanofiber networks

Nanofibrils are cellulose consisting of assembled anhydro glucose ring units consisting of several amorphous and crystalline domains [8]. Cellulose nanofibril (CNF) form composite films with high stiffness and mechanical strength, optical transmittance, low oxygen permeability, and low coefficient of thermal expansion [9].

In a previous review, an analysis of the application of nanocrystalline cellulose as reinforcement for polymeric nanocomposite matrices has been carried out [10]. In this paper, several uses of nanocrystals and nanofibrils as reinforcement in composite films manufacturing applications were studied.

This literature review aims to demonstrate the effectiveness of using nanocrystals and nanofibrils on mechanical properties as reinforcement for the cellulose composite films by reviewing several related articles available in the last 5 years. The result of adding nanocrystals and nanofibrils as reinforcing elements is that they can improve mechanical properties, especially tensile strength, compared to the composite film without the addition of nanocrystals/nanofibrils. Composite films

reinforced by nanocrystals/nanofibrils also showed better surface wetting and higher crystallinity.

2. METODOLOGY

The method used in the literature review is to conduct a literature search in the form of international journal articles available in the last 5 years, namely between 2016-2021 indexed by Scopus. Search literature using online journal sites such as Google Scholar, Science Direct, and ACS Publications. We searched the literature used keywords such as “*Nanocrystals and nanofibrils for composite films cellulose*”, or “*Nanocrystals and nanofibrils as reinforcing elements to composite films*”.

The review identified, studied, and seen its relevance. Ten articles are considered relevant to the use of nanocrystals and nanofibrils in the manufacture of cellulose composite films and their effectiveness. Table 2 shows data from the results of a review of journal articles in the form of the type of nanocrystal or nanofibril used, preparation of composite films, characterization of composite films, and references.

Table 2. The topic, film preparation, characterization, and reference

No	Topic	Film Preparation	Types of Characterization	Reference
1	Cellulose nanocrystal from pea hull waste reinforced carboxymethyl cellulose-based composite films	CMC-based composite films containing various content of CNC were fabricated by solution casting method	Z Morphology Z Mechanical Properties	[11]
2	Cellulose nano whiskers from mulberry pulp (blended with alginate) as reinforcing agent to alginate-based composite film	Alginate/CNW composite were prepared using a solution casting method	Z Mechanical properties	[12]
3	Cellulose nano whiskers from cotton fibers as reinforcing agent in PVA nanocomposite films	PVA/CWs films were prepared by mixing PVA solution and glycerol, then CWs was added to this mixture	Z Mechanical properties	[13]
4	Nanocrystal-nanofibril from wood pulp for composite films	CNC-CNF composite films were made by mixing different ratios of CNC and CNF suspension	Z Surface Wetting	[14]
5	Nanofibril from rice straw cellulose reinforced poly(vinyl alcohol) composite films	Rice straw CNF suspension was added to the PVA powders solution	Z Tensile Property	[15]
6	Cellulose nanofibril from coconut coir reinforced biodegradable composite films	The coir cellulose nanofibrils/PVA composite films were prepared by solution casting	Z Mechanical Property	[16]
7	Modified cellulose nanofibrils as reinforcing agent to prepare starch composite films	Cassava Residue CNF/Cassava Starch composite film were made by mixing CNF modified, cassava starch, glycerol, and distilled water.	Z Crystallinity Z Mechanical Property	[17]
8	Nanofibril cellulose from softwood Kraft pulp reinforced PVA composite film	Nanofibrillated cellulose/PVA composite film were prepared using a solvent casting method	Z Tensile Strength	[18]
9	Cellulose nanofibril from sugarcane bagasse as reinforcing PVA films	Nanofibril cellulose/PVA composite film was prepared by dissolution and solvent casting method	Z Mechanical Properties	[19]
10	Cellulose nanofibers as reinforcement agent for starch-PVA composite film	Thermoplastic starch-PVA composite film were made by solution casting method	Z Crystallinity Z Tensile Strength	[20]

3. RESULT AND DISCUSSION

A. Nanocrystal Cellulose as Reinforcing Elements for Composite Films

One of the nanocelluloses that can be used to reinforce a composite film is nanocrystal. Due to the nature of nanocrystals which have a rather large specific surface area, high modulus of

elasticity, anisotropic particle shape, and low density, nanocrystals can be used as reinforcement for a composite films [21].

As in Li *et al.*'s research [11] using nanocrystals cellulose (CNC) to be reinforced with carboxymethyl cellulose-based (CMC) composite films. Figure 1 is the morphology of the CMC/CNC composite film characterized by

SEM to determine the dispersion of CNC in the CMC matrix.

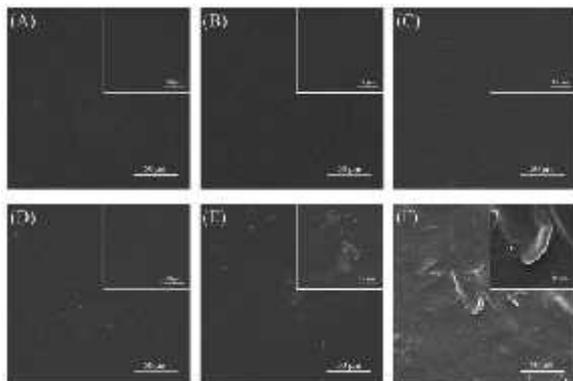


Figure 1. SEM images of (A) 0% CNC; (B) 1% CNC; (C) 3% CNC; (D) 5% CNC; (E) 7% CNC; and (F) 10% CNC composite films [11]

The surface of the composite film without the addition of CNC shows a homogeneous and smooth without any cracks or holes or air bubbles (Figure 1A). Homogeneous and smooth on the surface of the composite film remains visible until the addition of CNC reaches 5 wt.% (Figure 1B-D). These observations indicate that the CNC is well distributed in the continuous CMC matrix and has good compatibility with CMC. However, some agglomeration appeared on the surface of the composite film when the CNC addition reached 7% (Figure 1E-F), this was because the CNC dispersion was not homogeneous in the CMC matrix when the content was higher.

A.1 Mechanical properties of composite films

Li *et al.* [11] explain that mechanical properties of CMC/CNC composite films such as tensile strength, and modulus of elasticity have been identified. Tensile strength increased when CNC was added significantly. Tensile strength increase was up to 50.80% when 5% weight of CNC was added, but it decreased at higher CNC content. However, when compared to pure CMC, there was an increase in tensile strength of 14.5% in CMC/CNC with the addition of 10 wt.% of CNC.

Another study conducted by Wang *et al.* [12] that used cellulose fiber (CF) and cellulose nano whisker (CNW) as reinforcement in alginate-based films. The mechanical strength and stiffness of the alginate films were evaluated by their tensile strength and modulus of elasticity, respectively, decreased when added by cellulose fiber, but increased when added by cellulose nano whisker. The result is shown in Table 3. This is due to the large surface area of the cellulose nano whisker, the free hydroxyl groups available to interact with the alginate polymer matrix.

Table 3. Tensile properties and modulus of elasticity of alginate and alginate-based composite films [12]

Film	Tensile Strength (MPa)	Modulus of Elasticity (GPa)
Alginate	45.6 ± 4.1 ^c	1.58 ± 0.25 ^c
Alginate/CF 2%	36.8 ± 2.7 ^a	0.72 ± 0.07 ^a
Alginate/CF 4%	38.3 ± 2.6 ^{ab}	0.74 ± 0.07 ^a
Alginate/CF 6%	40.4 ± 3.5 ^b	0.70 ± 0.09 ^a
Alginate/CNW 2%	50.9 ± 6.9 ^d	1.62 ± 0.24 ^c
Alginate/CNW 4%	54.9 ± 4.0 ^e	1.79 ± 0.21 ^d
Alginate/CNW 6%	47.0 ± 3.5 ^c	1.45 ± 0.11 ^b

Improved mechanical properties due to the use of cellulose nanocrystals were also obtained from the research of Spagnol *et al.* [13]. In this study, cellulose nano whiskers were used as reinforcing agents for polyvinyl alcohol composite films. Cellulose nano whiskers (CWs) extracted from cotton fibers. The addition of specific amounts of modified-CWs increase up the mechanical properties such as tensile strength and elastic modulus.

There are several modifications of the cellulose nano whisker, namely cellulose nano whisker-maleic anhydride (CWMA), cellulose nano whisker-succinic anhydride (CWSA), cellulose nano whisker-acetic anhydride (CWAA), and cellulose nano whisker-phthalic anhydride (CWPA).

The results of the characterization related to tensile strength and elastic modulus are shown in Figure 2. Only PVA88 (88% of hydroxyl groups) composite films containing CW, CWSA, and CWPA (3, 6, 9, wt.%) exhibits a linear behavior profile for tensile strength. The highest increase rate is obtained when PVA88 is added with 6 wt.% of CWMA. But overall, all kinds of modified-CWs increased tensile strength.

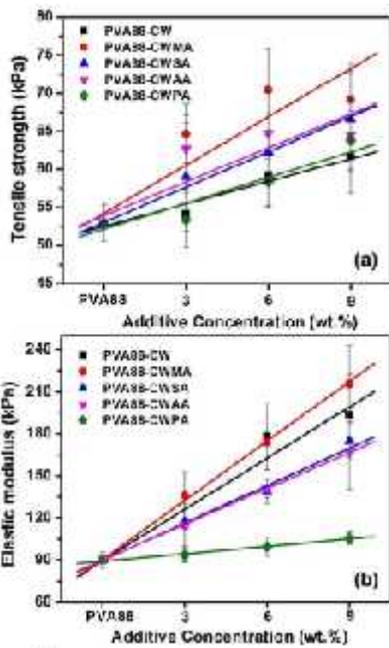


Figure 2. (a) Tensile strength and (b) elastic modulus of PVA88 nanocomposite films containing specific amount of CW, CWMA, CWSA, CWAA, or CWPA additives (3, 6, and 9 wt.%) [13]

Likewise, for the value of the elastic modulus. All nanocomposite films presented a linear model profile of elastic modulus value (Figure 3b). The addition of modified-CWs to PVA88 resulted in a nanocomposite film with a high elastic modulus and with more rigid features.

A.2 Surface wetting of composite films

In contrast to the research discussed previously, research by Sun *et al.* [14] discussed the surface wetting behavior of nanocellulose-based composites. In this study, nanocellulose-based composite films were made with nanocrystalline cellulose (CNCs), nanocellulose fibers (CNFs), and Zn(2-methylimidazole anion)₂ (ZM) modified by CNFs. Compared with a commercial polypropylene-polyethylene-polypropylene (PEP) battery separator film, the CNC-CNF and ZM-CNF films composite had a better wettability. This is because the wettability of the surface of the film is affected by the structure of the film and the functional groups of the surface of the material.

B. Nanofibrils Cellulose as Reinforcing Elements for Composite Films

Among various types of nanocellulose materials, cellulose nanofibrils are the ideal nanocellulose for use as composite reinforcement due to its abundance, renewability, biodegradability, good mechanical properties, low thermal expansion, environmental benefits, and low cost [18].

B.1 Mechanical properties of composite films

Wang *et al.* [15] in their research used cellulose nanofibrils (CNFs) obtained from rice straw as reinforcement in PVA composite films. CNF/PVA composite films were compared with the rice straw cellulose microfibrils (CMFs) reinforced PVA composite films. Figure 3 shows tensile strength of rice straw cellulose fibers reinforced PVA composite films. From the figure 3, information was obtained that the addition of rice straw CNF into the matrix can significantly increase the tensile strength. The maximum tensile strength occurs at cellulose fiber concentration of 3% for the rice straw CNFs/PVA composite film, but 1% for the rice straw CMFs/PVA composite film. Therefore, the reinforcement efficiency of the rice straw CNFs is much higher than that of rice straw CMFs.

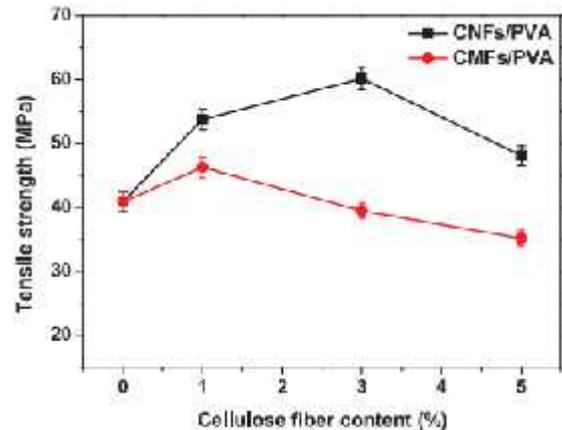


Figure 3. Tensile property of rice straw cellulose fibers reinforced PVA composite films [15]

Wu *et al.* [16] used cellulose nanofibrils from coconut coir fiber (CCNFs) as reinforcement in biodegradable composite films. Tensile strength and elongation of PVA film and CCNF/PVA film were shown in Figure 4. At the addition of CCNF which is lower than 3%, the tensile strength of the composite film continues to increase and then start to decrease after reaching the highest point (CCNF addition = 3%). The same applies to elongation, the elongation at break of PVA film was significantly enhanced up to 545% when the composite film was incorporated by 3% of CCNF.

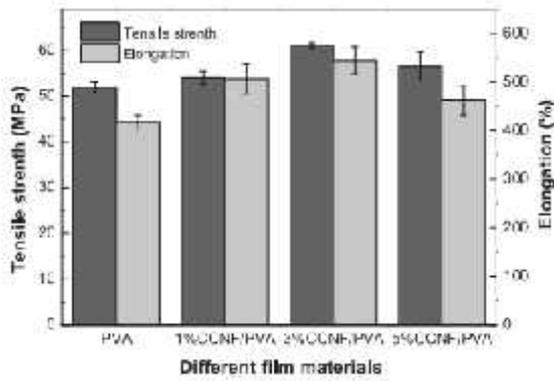


Figure 4. Mechanical properties of PVA film and CCNF/PVA composite film [16]

Huang *et al.* [17] used cellulose nanofibril from cassava residue to reinforce cassava starch composite films. The tensile strength of the composite increase with the increase in CNF content (Figure 5). The highest peak is obtained when the addition of CNF amount is 3-4%, especially, Z-CNF composite film has the highest value of tensile strength. Overall, the tensile strength value increase until it finally decreases after reaching the highest point.

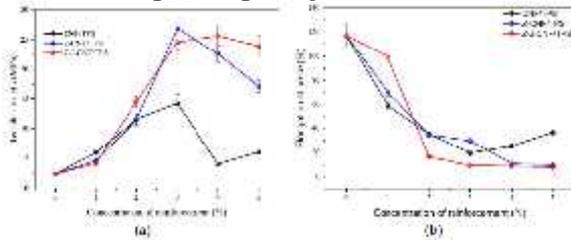


Figure 5. Tensile strength (a) and (b) elongation break of CNF, Z-CNF, and Z-J-CNF composite film [17]

Kord *et al.* [18] used different loadings of cellulose nanofibrils for reinforcement polyvinyl alcohol composite films. Figure 6 shows the tensile strength of neat PVA and various types of PVA/NFC nanocomposite films. As the content of NFC increases, the tensile strength of PVA composite films increases, too. This is due to the intermolecular forces between the NFC and the PVA matrix which can increase the tensile strength of the PVA composite films. This force keeps the tensile strength intact and results in an increase in the tensile strength of the film.

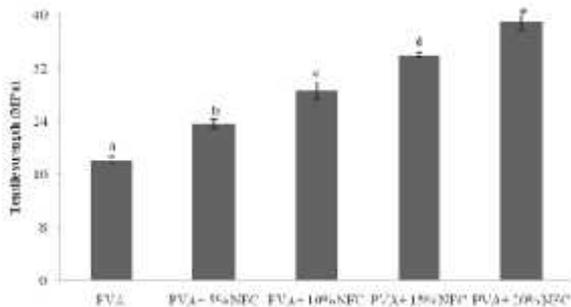


Figure 6. Tensile strength of neat PVA and various types of PVA/NFC nanocomposite films [18]

Otenda *et al.* [19] used cellulose nanofibril from sugarcane bagasse as a reinforcing element in polyvinyl alcohol composite film. The tensile strength obtained in this study showed an increase in yield as the percentage of CNF in the PVA matrix increases as shown in Table 4.

Table 4. Tensile strength of TEMPO oxidation-PVA films [19]

%CNF	Tensile Strength (kPa)
0	1.1 ± 0.2
10	1.2 ± 0.3
20	5.4 ± 2.2
40	5.6 ± 1.1
30	6.6 ± 2.2
50	3.4 ± 0.7

Similar to the research of Wang *et al.* [15], Wu *et al.* [16], and Huang *et al.* [17], in this study [19] the tensile strength increased then decreased after reaching the highest point. One of the causes that occurs is the excess concentration of CNF which cause inadequate CNF dispersion and cause CNF aggregation in the PVA matrix without forming an effective hydrogen bond network [16].

B.2 Crystallinity

In the study of Huang *et al.* [17], cellulose nanofibrils obtained from cassava residue were added to cassava starch as a reinforcing agent to form a composite film, where the cellulose nanofibrils were modified by adding malic acid and silane coupling agent KH-550. L-malic acid and silane coupling agent KH-550 were used for esterification (Z-CNF), cross-linking (J-CNF), cross-linking followed by esterification (J-Z-CNF), and esterification followed by cross-linking (Z-J-CNF). These different modification methods give different results, such as in their crystallinity.

The crystallinity of pure CNF and modified CNF are shown in Table 5. This table shows the crystallinity before and after modification of CNF. The results showed that the crystallinity of the modified CNF is lower than that of the unmodified CNF. The crystallinity of CNF after modification decreases because the addition of a coupling agent destroys the original hydrogen bonds of CNF and replaces them with new hydrogen bonds, which resulting in a decrease in the crystallinity of CNF.

However, overall, the CNF modification process did not significantly reduce the crystallinity, so that although the crystallinity was reduced, CNF still maintained its crystallinity. Therefore, the reinforcement effect of CNF on materials preserved.

Table 5. Crystallinity index (Cr_i) of CNF and modified CNF [17]

Sample	Crystallinity (%)
CNF	57.5 ± 2.0
J-CNF (cross-linking)	53.2 ± 4.2
Z-CNF (esterification)	55.4 ± 4.3
J-Z-CNF (cross-linking followed by esterification)	53.1 ± 2.8
Z-J-CNF (esterification followed by cross-linking)	50.3 ± 3.1

Fahma *et al.* [20] used cellulose nanofibers from oil palm empty fruit bunches as reinforcement agent for thermoplastic cassava starch-PVA composite films. Crystallinity of the nanocomposite films are shown in Table 6.

Table 6. Crystallinity of TPS/PVA cellulose nanocomposite films [20]

Sample	Crystallinity
SPG0NF0	26.3
SPG0NF1	28.2
SPG0NF3	32.7
SPG0NF5	37.8
SPG25NF0	21.8
SPG25NF1	27.8
SPG25NF3	30.5
SPG25NF5	35.3

A series of cellulose nanocomposites TPS/PVA was written with SPG-a-NF-b, where SP is starch and PVA, G is for glycerol, a is for percentage of glycerol, NF is for nanofibers, and b is for percentage of nanofibers content.

Composite films without the addition of glycerol have a higher degree of crystallinity than the addition of glycerol. It was explained that the final crystallinity of a material was dependent on the ability of the chains to form crystals and the mobility of the chains. The presence of glycerol decreased the crystallinity of the starch film due to the decrease in intra- and intermolecular interactions in the starch-starch chain. Meanwhile, adding cellulose nanofibers to the

TPS/PVA composite film enhanced its crystallinity.

The crystallinity of the nanocomposite itself can increase the crystallinity of the TPS/PVA nanocomposite films. A higher percentage of crystallinity in nanocomposite films can make the film stronger, because of its compact and regular structure.

4. CONCLUSIONS

Cellulose nanocrystals and nanofibrils have many uses, one of which is used in the manufacture of composite films. Ten articles identified the use of cellulose nanocrystals and nanofibrils as reinforcement in various composite films showed good effectiveness. The resulting composite film has good mechanical properties, including high tensile strength, good surface water, and crystallinity, resulting in a compact and ordered composite film structure. As a result, adding nanocrystals or nanofibrils to a composite film is an effective method or choice for reinforcing it, and it can be further treated to make valuable materials.

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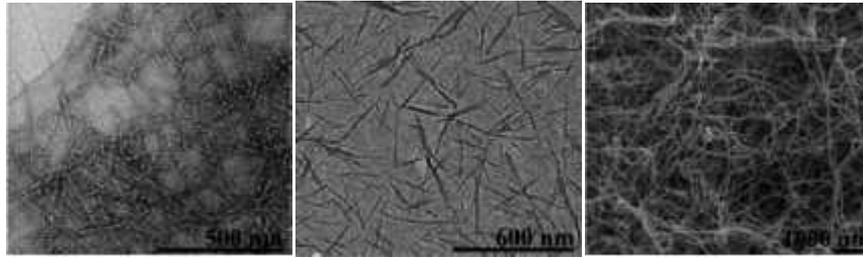


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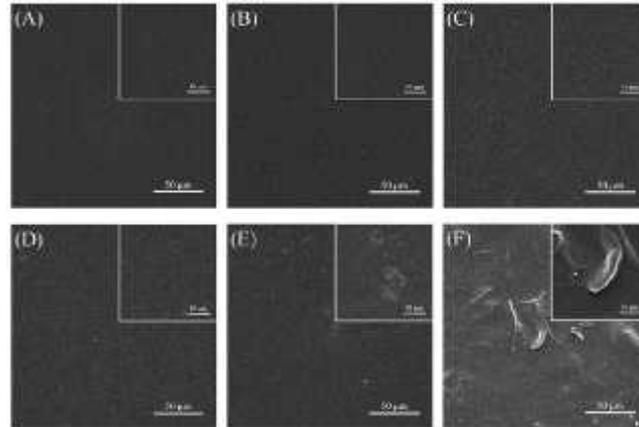


Figure 1. SEM images of (A) 0% CNC; (B) 1% CNC; (C) 3% CNC; (D) 5% CNC; (E) 7% CNC; and (F) 10% CNC composite films [11]

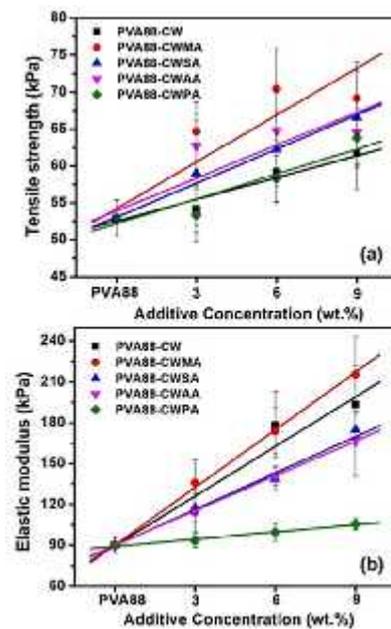


Figure 2. (a) Tensile strength and (b) elastic modulus of PVA88 nanocomposite films containing specific amount of CW, CWMA, CWSA, CWAA, or CWPA additives (3, 6, and 9 wt%) [13]

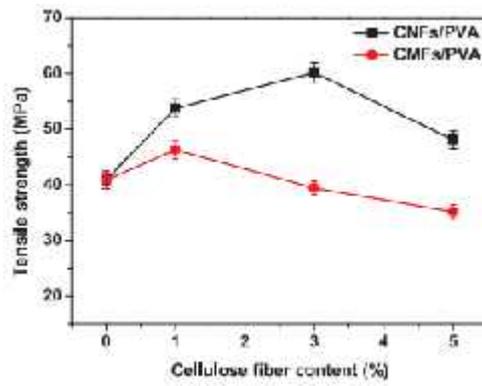


Figure 3. Tensile property of rice straw cellulose fibers reinforced PVA composite films [15]

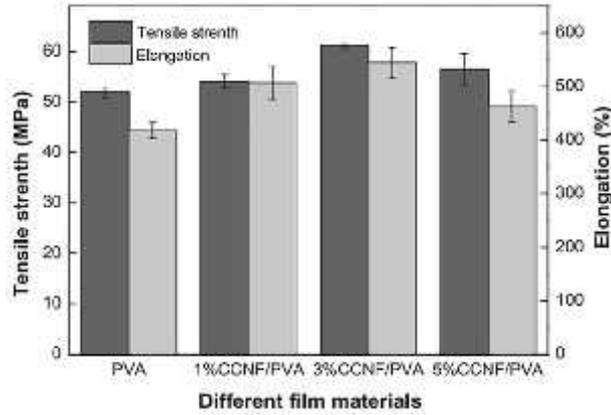


Figure 4. Mechanical properties of PVA film and CCNF/PVA composite film [16]

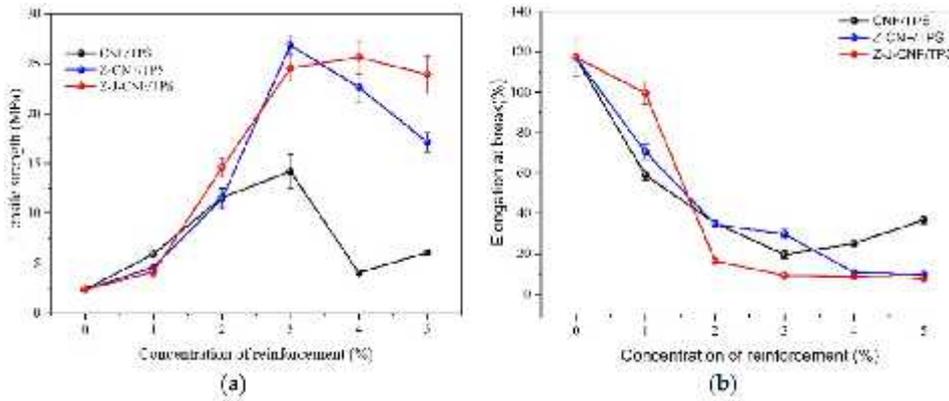


Figure 5. Tensile strength (a) and (b) elongation break of CNF, Z-CNF, and Z-J-CNF composite film [17]

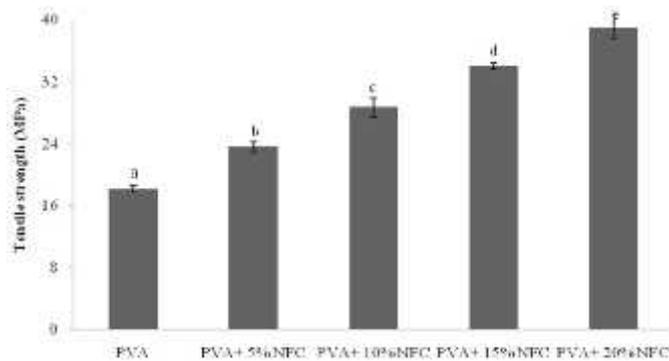


Figure 6. Tensile strength of neat PVA and various types of PVA/NFC nanocomposite films

[18]

Table 1. Comparison between the three main nanocelluloses [5]

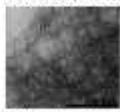
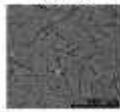
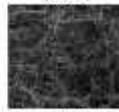
Comparison	Nanofibrillated Cellulose (NFCs)	Nanocrystalline Cellulose (NCCs)	Bacterial Nanocellulose (BNCs)
Images			
Synonyms	Microfibrillated cellulose, nanofibrils and microfibrils	Nanocrystals cellulose, whiskers, rodlike cellulose microcrystals	Bacterial cellulose, microbial cellulose, biocellulose
Source	Wood, sawd, potato fiber, hemp, flax	Wood, cotton, flax, wheat straw, ramie, wood, tunicin	Low-molecular-weight sugars and alcohols
Formation Process and Size	<ul style="list-style-type: none"> Delamination of wood pulp by mechanical pressure before and/or after chemical or enzymatic treatment Diameter: 5-60 nm Length: several micrometers 	<ul style="list-style-type: none"> Acid hydrolysis of cellulose fibers from various sources Diameter: 5-70 nm; length: 100-350 nm (from plant celluloses); 100 nm to several micrometers (from celluloses of tunicates, algae, bacteria) 	<ul style="list-style-type: none"> Bacterial synthesis Diameter: 20-100 nm; different types of similar networks

Table 2. The topic, film preparation, characterization, and reference

No	Topic	Film Preparation	Characterization	Reference
1	Cellulose nanocrystal from pea hull waste reinforced carboxymethyl cellulose-based composite films	CNC based composite films containing various content of CNC were fabricated by solution casting method	- Morphology - Mechanical Properties	[11]
2	Cellulose nanocrystals from mulberry pulp (loaded with alginate) as reinforcing agent in alginate-based composite film	Alginate/CNW composite were prepared using a solution casting method	- Mechanical properties	[12]
3	Cellulose nanocrystals from cotton fibers as reinforcing agent in PVA nanocomposite films	PVA/CNFs films were prepared by mixing PVA, sodium and glycerol, then CNFs were added in this mixture	Mechanical properties	[13]
4	Nanocrystal/nanofibril from wood pulp for composite films	CNC-CNF composite films were made by mixing different ratios of CNC and CNF suspension	- Surface Weting	[14]
5	Nanofibril from rice straw cellulose reinforced poly(vinyl alcohol) composite films	Rice straw CNF suspension was added to the PVA powder solution	Tensile Property	[15]
6	Cellulose nanofibril from cocoon silk reinforced biodegradable composite films	The silk cellulose nanofibrils/PVA composite films were prepared by solution casting	- Mechanical Property	[16]
7	Modified cellulose nanofibrils as reinforcing agent to prepare starch composite films	Control, Cassava, CNF/Cassava Starch composite film were made by mixing CNF modified cassava starch, glycerol and distilled water	- Crystallinity - Mechanical Property	[17]
8	Nanofibril cellulose from softwood Kraft pulp reinforced PVA composite film	Nanofibrillated cellulose/PVA composite film were prepared using a solution casting method	- Tensile Strength	[18]
9	Cellulose nanofibril from sugarcane bagasse as reinforcing PVA films	Nanofibril cellulose/PVA composite film was prepared by dissolution and solution casting method	Mechanical Properties	[19]
10	Cellulose nanofibrils as reinforcing agent for starch/PVA composite film	Thermoplastic starch/PVA composite film were made by solution casting method	- Crystallinity - Tensile Strength	[20]

Table 3. Tensile properties and modulus of elasticity of alginate and alginate-based composite films [12]

Film	Tensile Strength (MPa)	Modulus of Elasticity (GPa)
Alginate	45.6 ± 4.1 ^a	1.58 ± 0.25 ^c
Alginate/CF 2%	36.8 ± 2.7 ^a	0.72 ± 0.07 ^a
Alginate/CF 4%	38.3 ± 2.6 ^{ab}	0.74 ± 0.07 ^a
Alginate/CF 6%	40.4 ± 3.5 ^b	0.70 ± 0.09 ^a
Alginate/CNW 2%	50.9 ± 6.9 ^d	1.62 ± 0.24 ^c
Alginate/CNW 4%	54.9 ± 4.0 ^c	1.79 ± 0.21 ^d
Alginate/CNW 6%	47.0 ± 3.5 ^c	1.45 ± 0.11 ^b

Table 4. Tensile strength of TEMPO oxidation-PVA films [19]

%CNF	Tensile Strength (kPa)
0	1.1 ± 0.2
10	1.2 ± 0.3
20	5.4 ± 2.2
40	5.6 ± 1.1
30	6.6 ± 2.2
50	3.4 ± 0.7

Table 5. Crystallinity index (C_r) of CNF and modified CNF [17]

Sample	Crystallinity (%)
CNF	57.5 ± 2.0
J-CNF (cross-linking)	53.2 ± 4.2
Z-CNF (esterification)	55.4 ± 4.3
J-Z-CNF (cross-linking followed by esterification)	53.1 ± 2.8
Z-J-CNF (esterification followed by cross-linking)	50.3 ± 3.1

Table 6. Crystallinity of TPS/PVA cellulose nanocomposite films [20]

Sample	Crystallinity
SPG0NF0	26.3
SPG0NF1	28.2
SPG0NF3	32.7
SPG0NF5	37.8
SPG25NF0	21.8
SPG25NF1	27.8
SPG25NF3	30.5
SPG25NF5	35.3