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REVIEW

Thermal properties of nanocellulose-reinforced composites: A review

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ABSTRACT: Nanocellulose has received increasing attention in science and industry in recent years as a nanoscale material for the reinforcement of polymer matrix composites due to its superior mechanical properties, renewability, and biodegradability. New nanocellulose sources, modifications, and treatments are under development to reduce the high energy required during production and to create a more suitable industrial-scale production process. Thus, this paper reviews plant-based nanocellulose composites and their properties, with a focus on their thermal-related characteristics. The purpose of this review is to establish for readers the impact of the incorporation of nanocellulose on the thermal and dynamic mechanical properties of nanocellulose composites. Understanding of the thermal properties is important for researchers to assess the suitability of the nanocomposites for a variety of applications in response to new and evolving societal requirements. © 2019 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2020**, *137*, 48544.

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INTRODUCTION

Cellulose can be considered as one of the most illimitable renewable biopolymers on the Earth. It is an almost inexhaustible source of raw material to supply the growing demand for the production of environmental-friendly materials. The annual worldwide production of lignocellulosic biomass is estimated to be approximately 1.3×10^{10} metric tons, which can be considered as one of the most abundant biopolymers available for the reinforcement of composites.[1] Among natural renewable reinforcing materials, cellulose has attracted a great deal of interest due to its biodegradability, availability, high strength-to-weight ratio, low cost, and low density.[2] Cellulose fibers can act as a reinforcement in polymer matrix composites to improve their physical and mechanical properties. However, some drawbacks such as high moisture absorption and poor compatibility with the hydrophobic polymer matrix have significantly reduced the potential for cellulosic materials to be used as a reinforcing agent in polymer matrices, especially for microscale materials.[3] Therefore, nanoscopic cellulosic materials known as nanocellulose are under development in order to address the limitation and incompatibility issues of cellulose. With the nanosize, the cellulose has a higher surface area and lead to a better interfacial adhesion between fiber/fiber and fiber/matrix, which reduces the water uptake and the swelling of composite.[4] Besides, contrary to traditional cellulose filler, which requires higher loading to improve the mechanical properties of composites, a low content of well-dispersed nanofillers is capable to achieve a similar improvement. In other words, nanocellulose can be considered an excellent material for the development of high-performance nanocomposites.

Nanocellulose can be produced from plants or synthesized by bacteria. Plant-based nanocellulose can be classified into (1) elongated fibrils, usually known as microfibrillated cellulose or nanofibrillated cellulose (NFC) and (2) rod-like nanoparticles, typically referred to as nanocrystalline cellulose (NCC) or nanowhiskers.[5] Cellulose produced by aerobic bacteria and hydrolyzed by chemical treatments is referred to bacterial nanocellulose (BNC). Figure 1 shows the electron microscopic images of the three different types of nanocellulose. NFC is a micrometer-long entangled cellulose with a diameter less than 100 nm, which consisting of both amorphous and crystalline parts. NCC is a highly crystalline rod-like nanocellulose commonly produced through acid hydrolysis by the removal of amorphous regions from native cellulose with a diameter of between 5 to 40 nm.[6] BNC is obtained through bottom-up approach and is produced by bacteria that exhibit higher purity, biocompatibility, and crystallinity than plant-source cellulose.[7]

The first NFC was produced from wood by using high-pressure homogenization without any pretreatment.[11,12] However, this method is a very energy-intensive process. Therefore, chemical treatments such as 2,2,6,6-tetramethylpiperidine-1-oxyl radical (TEMPO) oxidation combined with mechanical and chemical

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treatments have recently been developed for the production of NFC to minimize the intensity of mechanical treatment.[13] In addition to TEMPO oxidation, enzymatic hydrolysis combined with mechanical shearing and high-pressure homogenization has also been introduced as a method for the production of NFC.[14] Due to its high effectiveness and eco-friendly nature, enzymatic

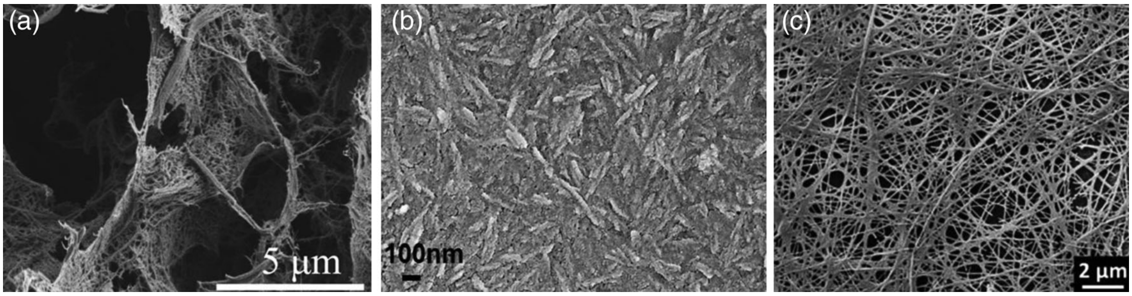

Figure 1. Representative micrographs of the three different types of nanocellulose: (a) NFC (reproduced from ref. 8, Copyright (2018) with permission from Elsevier), (b) NCC (reproduced from ref. 9, with permission from Elsevier), and (c) BNC (reproduced from ref. 10, with permission from The Royal Society of Chemistry).

Table I. Nanocellulose from Various Plant-Based Sources

Formation and size	Cellulose source	Treatment	Features of obtained nanocellulose	Reference
Nanofibrillated cellulose	*Citrullus colocynthis* seeds	Sulfuric acid (40%, 4 h and room temperature)	Diameter less than 100 nm	38
	Birch pulp	Deep eutectic solvent, which made up of aminoguanidine hydrochloride and glycerol (70–100 °C and 5–60 min) and mechanical disintegration	Diameter = 4.6 ± 1.1 nm	39
	Citrus residue	Enzymatic hydrolysis (45 °C. 90 rpm and 48 h)	Length = 458 ± 115 nm Diameter = 10 ± 3 nm	40
	Orange bagasse	Sulfuric acid (5–10 v/v% and 30 min)	Diameter = 18.4–20.5 nm	41
	Microcrystalline cellulose	Sulfuric acid (64 wt %, 60 min and 45 °C)	Length = 200–300 nm Diameter = 40–50 nm	33
	Banana peels	Enzymatic hydrolysis (35 °C. 150 rpm and 24 h) and homogenization	Diameter = 3.3–3.5 nm	42
	Lotus leaf stalk	Chemical pretreatment combined with high-intensity ultrasonication	Length = several micron scale Diameter = 20 ± 5 nm	43
	Bleached bagasse pulp	TEMPO-oxidation with high-shear homogenization	Diameter = 4–5 nm	31
	Bleached eucalyptus wood pulp	High-pressure homogenization	Length = 100–300 nm Diameter = 5–10 nm	44
Nanocrystalline cellulose	Sweet potato residue	Sulfuric acid (65 wt %, 120 min and 55 °C)	Diameter = 20–40 nm	45
	Bleached banana pseudostem fibers	Sulfuric acid (62 wt %, 70 min and 45 °C)	Length = 135 ± 12 nm Diameter = 7.2 ± 1.9 nm	46
	Discarded cigarette filters	Sulfuric acid (55 wt %, 45 min and 45 °C)	Length = 143 nm Diameter = 8 nm	47
	Oil palm empty fruit bunches	Hydrochloric acid (3 M, 2 h and 80 °C)	Length = 190–301 nm Diameter = 10–13 nm	48
	Empty fruit bunch	Sulfuric acid (62 wt %, 60 min and 45 °C)	Diameter less than 50 nm	49
	Wood chips	AVAP biorefinery	Length = 222 ± 139 nm Diameter = 4.5 ± 1.5 nm	25
	Corn husk	Sulfuric acid (55 wt %, 1.5 h and 45 °C)	Diameter = 26.9 ± 3.35 nm	50
	Alpha cellulose	Sulfuric acid (0.8 M, 1 h and 82.2 °C)	Diameter = 18.36 ± 7.34 nm	51
	Sugarcane bagasse	Sulfuric acid (50 wt %, 10 min and 40 °C)	Diameter = 95.9 nm	52

hydrolysis has emerged as a new and efficient method for NFC preparation.

NCC is mainly produced by acid hydrolysis with sulfuric acid (the most commonly utilized solvent)[15] or hydrochloric acid hydrolysis,[16,17] ultrasonication,[18] acidic deep eutectic solvent,[19] or ionic liquid usage.[20,21] The production of NCC involved the extraction of crystalline parts and the removal of amorphous regions from native cellulose fibers.[22] Isolation of NCC from renewable sources has earned increasing interest lately due to its excellent mechanical properties (high specific strength and modulus), large specific surface area, and high aspect ratio.[19]

Whereas bacterial cellulose is an extracellular cellulose produced by several microorganisms, particularly *Acetobacter xylinus* (*A. xylinus*), which is chemically the same as plant cellulose and features a distinctive three-dimensional structure consisting of an ultrafine network of cellulose nanofibers (CNFs).[7] It does not require any pretreatment to remove the noncellulosic components as the cellulose synthesized has a distinct superior purity and crystallinity. Besides, BNC also exhibits an excellent water retention ability, tensile strength, and biocompatibility.[23] Despite its excellent properties, the use of BNC has its own disadvantages as the production cost is very high yet the yield of BNC is extremely low. Therefore, in this review, we focused mainly on the properties of nanocomposites produced from plant-based nanocellulose. The nanocellulose materials obtained from different plant-based resources through different treatments are summarized in Table I. The dimensions of the nanocellulose are usually dependent not only on the type of treatment, time, concentration, and temperature of the reaction but also on the different sources of cellulose.

The concept of using nanocellulose as a reinforcement material in the polymer matrix has attracted the attention of researchers. Due to the presence of nanosize filler, nanocomposite possesses outstanding properties in numerous ways, which could not be achieved by microcomposites. Nanocellulose-reinforced composites are a promising material for replacing the conventional synthetic polymer composites. The wide availability, light weight, superior mechanical strength, and high stiffness of nanocellulose make it an ideal reinforcing material to be utilized in the new biopolymer composites field.[24] With its superior modulus of elasticity (up to 150 GPa), high aspect ratio (up to 640), large specific surface area (several hundred m^2/g), and low thermal expansion coefficient (0.01 ppm/K), nanocellulose has proven to be a significant reinforcement, even at low filler loading levels.[25] Properties of nanocomposites depend on few factors such as the properties of polymer matrix, characteristics of nanocellulose, dispersion of nanocellulose in matrix, and interfacial interaction between filler and polymer matrix.[26–28] Nanocellulose has motivated researchers to explore on biodegradable plastics by developing fully bio-based nanocomposites without counteracting their superiority of biodegradability instead solving its defects. However, the low thermal stability of nanocellulose may restrict the product designing and manufacturing process especially at high temperature. Hence, a clear understanding of the thermal characteristics is important for investigating the maximum processing temperature of nanocellulose-based composites.

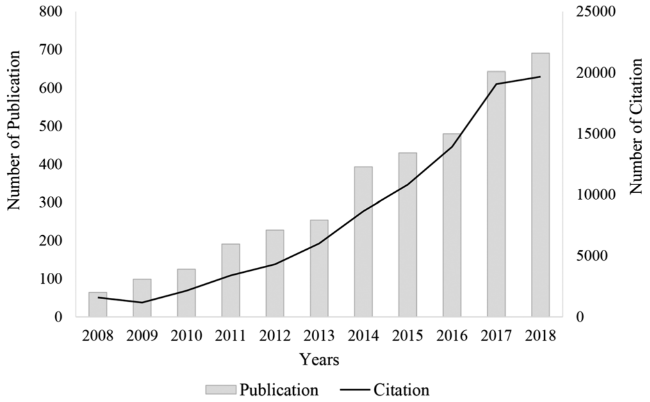

Figure 2. Number of publications and citations regarding cellulose nanocomposites from 2008 to 2018. A title–abstract–keywords search was performed on Scopus using the terms "cellulose nanocomposite or nanocellulose composite."

Researchers have put significant effort into the production and manufacturing of high-performance composites based on nanocellulose.[8,29–37] This particular research field has garnered a great level of interest in the materials science community that does not appear to be relenting, proven by the increasing number of scientific contributions in the field as shown in Figure 2. Therefore, in order to meet the requirements of the materials for diverse applications, the properties of nanocellulose-reinforced composites are essential to be understood especially those involved in thermal properties. The understanding of the thermal properties of nanocomposites is very important in developing the future nanocellulose composites with desirable properties and preventing from repeating the similar problems in former times by improving the techniques or processing methods in the near future. Therefore, this particular review emphasizes on the undiscovered review on the thermal-related properties of nanocellulose composites. This review provides an overview of the scientific literature from the last 10 years regarding the effect of nanocellulose incorporation on the thermal properties. It summarizes the effect of the incorporation of nanocellulose on the thermal properties including thermal stability, thermal behavior, dynamic mechanical properties, and thermal conductivity of hydrophilic and hydrophobic nanocomposites. The potential factors affecting the thermal-related properties are also reviewed.

THERMAL PROPERTIES OF NANOCELLULOSE COMPOSITES

Thermal Stability

Thermal stability is an essential parameter to be considered when determining the potential uses of nanocomposites in various industries such as packaging and the biomedical field.[53] The study of degradation behavior allowed researchers to optimize the designing and processing conditions of composites as well as develop the excellent performance polymers with enhanced thermal stability.[54] It is also important to understand the thermal behavior of nanocellulose during the compounding and extrusion of nanocellulose and thermoplastic composites. The decomposition temperature of nanocellulose is approximately 200–300 °C; thus, the compounding temperature has to be controlled at approximately 200 °C during the manufacturing process in order to prevent the degradation of nanocellulose.[55,56] Differences in the source of nanocellulose, types of matrices, processing techniques, and the drying process could affect the thermal stability of the nanocomposites. Therefore, this review investigates the effect of nanocellulose incorporation on the thermal stability of nanocomposites. The thermal stability of nanocellulose composites is summarized in Table II.

Thermal degradation of polymeric composites normally involves two main stages, which are the elimination of volatile matter or evaporation of water and depolymerization process, respectively.[57] The first step of thermal degradation usually involves the evaporation of low-molecular-weight compounds such as water vapor. The water absorbed by hydrophilic nanocellulose could induce polymer degradation through hydrolysis, which could lead to a decline in thermal stability.[58] The thermal stability of nanocellulose is influenced by numerous factors, including the cellulose source, the processing methods used to isolate the nanocellulose, the sulfate content, and the crystallinity of

Table II. Thermal Stability of Different Nanocellulose Composites

Type of nanocellulose	Type of matrix	T_{ONSET} of neat matrix (°C)	T_{MAX} of neat matrix (°C)	T_{ONSET} of nanocomposites (°C)	T_{MAX} of nanocomposites (°C)	References
Nanocrystalline cellulose (NCC) Decomposition temperature: 257-333 °C[72]	Polyvinyl alcohol	253.5	272.5	235.0-271.5	273.0-339.0	66
	Poly(lactic) acid	270	332	-	313-329	73
	Nitrile butadiene rubber	411	451	386-416	410-465	74
	Sulfonated poly(aryl ether ketone)	326.24	371.65	259.83-306.75	324.35-357.20	75
	Natural rubber	295	450	272	450	76
	Polyvinyl alcohol and chitosan	194	-	240-253	-	77
Nanofibrillated cellulose (NFC) Decomposition temperature: 190—225 °C[66,78]	Epoxy	170.1	362.1	161.5-169.5	347.4-350.7	79
	Starch and chitosan	235	304-313	216-224	302-311	80
	Poly(methyl methacrylate)	331.3	371.4	332.3-342.5	370.2-376.2	81
	Poly(lactic) acid	270	320	282-298	325-337	82

nanocellulose, which can have profound effects on the thermal properties. The increase in sulfate groups after sulfuric acid digestion and the reduction in the crystallinity of nanocellulose could decrease the thermal stability of nanocomposites.[59] Hence, improving the thermal stability of nanocellulose, especially NCC obtained by acid hydrolysis, remains a challenge that requires further study.

The second degradation step accounts for the largest weight loss and can be considered as the most significant indication for the thermal stability of polymer composites. Two different degradation mechanisms were proposed by Kilzer and Broido,[60] cellulose dehydration (an endothermic process to produce "dehydrocellulose"), and the depolymerization of cellulose in competition with dehydration. Dehydrocellulose formed by the first mechanism will decompose into gases and char residue. The thermal stability of composites is strongly influenced by the intermolecular bonding between the nanocellulose and the polymer matrix. Strong intermolecular bonding could enhance the bond dissociation energy needed for chain cleavage of macromolecules.[61] Hence, well-dispersed nanocellulose and good interfacial adhesion between nanocellulose and polymer matrix are required for the improvement of the thermal stability.

Determination of the fundamental properties such as morphology and dimensions of CNF and cellulose nanocrystal (CNC) is a prerequisite for improving the structure–property and structure-processing relationships through a wide range of applications. Martelli-Tosi *et al.*[62] have made a comparison between the thermal stability of the CNF and CNC-incorporated soy protein isolate nanocomposites. The thermal decomposition temperatures of CNF and CNC were 200 and 220 °C, respectively. The study showed that the composites with the incorporation of CNF presented a better thermal stability than the CNC/soy protein isolate nanocomposites. The lower thermal stability of CNC-incorporated composites could be attributed to the high surface area of CNC, which led to a larger exposure to heat and the partial disruption in the cellulose crystal structure.[63]

According to Mandal and Chakrabarty,[64] the addition of NCC greatly improved the thermal stability of nanocomposites by enhancing the filler–PVOH matrix interaction through hydrogen bonding. The strong interaction between filler and matrix increased the thermal energy required for cleavage of crosslinked PVOH nanocomposites and thus improved the resistance to decomposition. A similar study in NCC/gelatine bionanocomposites was also recently reported by Mondragon *et al.*[65] They found that the incorporation of NCC in the gelatine matrix improved the thermal stability by increasing the degradation temperature by 7–9 °C. A significant increase in thermal stability in CNF/PVOH nanocomposites was also reported by Cheikh *et al.*[66] With the addition of 10% CNF, the thermal decomposition temperature of composites increased from 272.5 to 339 °C compared with pristine PVOH. Generally, the addition of nanocellulose into hydrophilic composites improved the thermal properties of the composites.

However, a different thermal behavior was reported by Nagalakshmaiah *et al.*,[67] who observed a slight decline in thermal stability in hydrophilic CNC/PVOH nanocomposites. This reduction in thermal stability was due to the surface sulfation of CNC resulting from the sulfuric acid treatment. This result was in agreement with Neto *et al.*,[68] who showed that the thermal stability decreased after acid hydrolysis treatment of cellulose. As the hydrolysis time increased, the sulfation area increased, and thus the thermal stability declined significantly. Char residue also increased as the acid hydrolysis period was lengthened. This could be due to the increased sulfation area and the sulfate group's flame-retardant activity. Roman and Winter[59] have conducted research on the effect of the sulfate group from sulfuric acid hydrolysis on the thermal degradation behavior of bacterial cellulose. They found that the sulfate content increased with acid concentration, acid-to-cellulose ratio, and hydrolysis time. As the sulfate content increased, the decomposition temperature started at a lower temperature and occurred over a wider range. The hydrolysis treatment of cellulose with sulfuric acid resulted in the introduction of sulfate esters at the cellulose surface. The highly sulfated amorphous regions of cellulose would be degraded before the decomposition of unsulfated crystal interior at higher temperature. However, under extreme hydrolysis conditions, sulfation might not only take place at amorphous domains but also have an effect on cellulose chains at the ends of the crystals.[59] The higher the sulfation area, the more accessible the cellulose to degradation, hence the lower the decomposition temperature. The effect of the sulfate content of sulfated and desulfated nanocellulose on thermal stability was also compared by Lin and Dufresne.[53] Strong experimental results showed that the replacement of hydroxyl groups by sulfate groups during acid hydrolysis could decrease the heat resistance of nanocellulose. The sulfated-nanocellulose showed a lower decomposition temperature than desulfated-nanocellulose. The presence of sulfate group on the outer surface of nanocellulose is easily broken down when the temperature increased to 200 °C. Additionally, sulfate group also acts as a catalyst in degrading the nanocellulose, and hence led to a lower thermal stability.[69]

Due to the hydrophilic nature of nanocellulose, the nanocellulose has an inherent incompatibility issue with hydrophobic matrix [such as poly(lactic acid) (PLA), rubber, and polyethylene) due to the lack of similar functional groups for reaction. When a hydrophobic polymer matrix is employed, the significant difference in the surface energy to the nanocellulose combined with their intrinsic tendency to agglomeration will lead to the poor interfacial adhesion and inhomogeneous dispersion of nanocellulose in polymer matrix.[70] Nagalakshmaiah *et al.*[67] reported that the addition of hydrophilic CNC has led to an obvious decrease in thermal stability in hydrophobic cariflex-isoprene rubber latex. Therefore, many researchers have performed a variety of physical adsorption or chemical modifications on nanocellulose to improve its compatibility with various matrices especially hydrophobic matrices. The CNC was modified to graft either poly(L-lactic acid) (PLLA) or poly(ε-caprolactone) (PCL) chains *via* polymer functionalization in order to improve the dispersion and enhance the compatibility issue of nanocellulose in hydrophobic and nonpolar PLA/PCL composites.[71] PCL-modified CNC/PLA/PCL composites exhibited a better thermal stability than unmodified and PLLA-modified CNC composites. This was due to the homogeneous dispersion of PCL-modified CNC in the matrix, which resulted in the good interfacial adhesion between fillers and matrix. On the other hand, Qian and Sheng[28] improved the hydrophobicity of bamboo cellulose nanowhisker (CNW) with PLA matrix by using different concentrations of silane as a coupling agent and found the thermal stability of composites with 4 wt % silane-modified CNW increased slightly as shown in Figure 3. The onset temperature and maximum degradation temperature were increased from 359.0 and 383.0 °C to 361.2 and 389.1 °C, respectively. The better thermal stability of 4 wt % silane-modified CNW/PLA composites was attributed to the enhanced interfacial reaction between fillers and matrix, and hence, higher activation energy was needed to break down the interactions. Furthermore, excess amount of silane could result in self-condensation, which interrupts the interaction between CNW and PLA and declined the thermal stability.

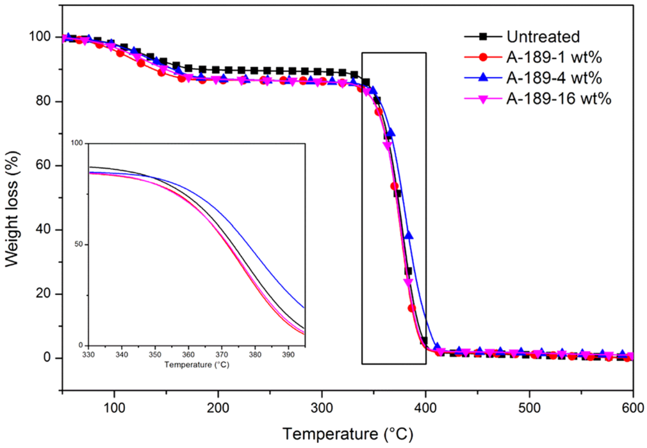

Figure 3. TGA curve of the CNW/PLA composites (reproduced from ref. 28, with permission from Elsevier). [Color figure can be viewed at wileyonlinelibrary.com]

Thomas *et al.*[24] reported the thermal degradation properties of NFC and natural rubber composites in the presence of crosslinking agents. The degradation temperature of all composites decreased except at a low filler concentration (1% NFC). It could be attributed to the NFC, which has a lower thermal stability than natural rubber. However, at lower filler concentration, a hydrogen-bonding network was formed between the crosslinkers, NFC, and natural rubber and contributed to the enhancement in thermal stability. The decline in decomposition temperature at higher filler loading was due to the critical volume fraction and the percolation threshold. Agglomeration at high NFC concentration also contributed to the reduction in degradation temperature.

The nanocellulose preparation process has an important influence on the thermal properties of nanocellulose-filled composites. Hence, the use of a new solvent such as acidified deep eutectic solvent can be considered as an alternative to isolate NCC instead of using conventional acid.[19] However, the usability and applicability of this preparation process still need to be studied further. Note also that the enhancement of the thermal stability properties of the nanocomposite is strongly dependent on the level of dispersion and the final morphology of the nanocomposites.

Thermal Behaviors

Differential scanning calorimetry (DSC) is a popular analytical technique to investigate the thermal properties of the nanocomposite. Thermal characteristics such as glass transition temperature (T_g), melting temperature (T_m), crystallization temperature (T_c), heat of fusion (ΔH_f), and degree of crystallinity (X_c) can be determined using DSC.

Researchers have investigated the thermal characteristics of nanocomposites with various sources of nanocellulose, different matrices, and different nanocellulose preparation techniques. The thermal characteristics of the nanocomposites might vary based on the source of the nanocellulose. Table III summarizes the

Table III. Thermal Characteristics of Nanocomposites

Matrix	Sources of nanocellulose	Process methods	Thermal characteristics of neat matrix	Glass transition temperature (°C)	Melting temperature (°C)	Crystallization temperature (°C)	Degree of crystallinity (%)	References
Polyvinyl alcohol	*Phormium tenax*	Acid hydrolysis (64% sulfuric acid, 45 °C and 30 min)	T_g: 76.63°C T_m: 217.28 °C T_c: 188.94 °C X_c: 29.98%	76.70-78.59	211.96-215.51	187.87-191.77	30.52-32.42	98
	Technical Flax	Acid hydrolysis (64% sulfuric acid, 45 °C and 30 min)	T_g: 76.63 °C T_m: 217.28 °C T_c: 188.94 °C X_c: 29.98%	76.68-77.10	214.59-219.12	191.7-197.20	30.48-31.01	98
	Alfa grass	Acid hydrolysis (50% sulfuric acid, 70 °C and 30 min)	T_g: 73.5 °C T_m: 225.9 °C X_c: 47.9%	73.2-78.6	219.4-224.1	-	34.3-40.7	66
	Commercial crystalline nanocellulose	-	T_g: 68.9 °C T_m: 235.1 °C T_c: 118.8°C	61.8-72.1	233.9-235.3	146.5-189.5	-	99
	Bleached birch kraft pulp	High-pressure fluidization	T_g: 70.6 °C T_m: 184.2 °C T_c: 139.6 °C X_c: 12.9%	70.8-72.0	176.8-184.8	128.5-145.6	13.9-19.1	100
Poly(lactic acid)	*Phormium tenax*	Alkaline treatment and acid treatment	T_g: 58.2 °C T_m: 151.5 °C T_c: 112.6 °C	59.3-59.6	146.0-151.9	102.5-108.9	6.2-6.6	97
	Phormium tenax (without limonene)	Alkaline treatment and acid treatment	T_g: 58.2 °C T_m: 151.5 °C T_c: 112.6 °C	31.6-33.8	143.2-151.5	92.6-99.4	10.0-10.6	97
	CNF gel	Acetylation	T_g: 57.5 °C T_m: 156.3 °C T_c: 82.7 °C X_c: 39.3%	58.3-58.9	150.6-154.2	81.9-88.1	34.0-38.9	101
	Microcrystalline cellulose	Acid hydrolysis and ultrasonication	T_g: 59.8 °C T_m: 165.2 °C T_c: 131.5 °C X_c: 16.7%	59.7	165.1	131.2-131.5	23.3-24.9	102
	Posidonia oceanica waste	Acid hydrolysis and surface modification	T_g: 52.2 °C T_m: 163.1 °C T_c: 89.1 °C	40.6-54.3	157.1-164.1	84.0-92.7	-	73

(Continues)

Table III. Continued

Matrix	Sources of nanocellulose	Process methods	Thermal characteristics of neat matrix	Glass transition temperature (°C)	Melting temperature (°C)	Crystallization temperature (°C)	Degree of crystallinity (%)	References
Poly(L-lactide)	Softwood bleached kraft pulp	TEMPO-oxidation, grafting and ultrasonication	T_g: 58.3 °C T_m: 160.0 °C T_c: 134.0 °C	50.5–51.9	155.5–157.5	111.3–120	-	103
Polycaprolactone	Filter paper	Acid hydrolysis (64% sulfuric acid, 45 °C and 45 min)	T_m: 56.7 °C T_c: 32.2 °C X_c: 49.1%	-	59.0–63.4	31.7–34.5	42.7–52.8	104
	Luffa cylindrica	Alkaline treatment, bleaching, acid hydrolysis, and homogenization	T_g: −62.0 °C T_m: 63.4 °C T_c: 82.7 °C X_c: 51.0%	−59.2 to −57.3	64.9–66.0	-	55.0–64.0	105
Polypropylene-polystyrene	Sisal leaves	Alkaline treatment, bleaching, and steam explosion	T_m: 158.4 °C T_c: 111.9 °C	-	154.9–159.9	111.9–115.9	-	84

thermal characteristics of nanocomposites prepared from different sources of nanocellulose with different matrices and various preparation methods. As seen from Table III, PLA and PVOH are the most common matrices used to prepare nanocomposites. This could be due to their attractive mechanical properties, good renewability, and biodegradability and relatively low cost, which make them popular choices for composite preparation.[83]

Fortunati *et al.*[9] isolated CNC from barley straw and husk by using different pretreatments (chemical and enzymatic pretreatment) and examined their effects on the thermal properties in combination with PVOH/chitosan blends. They found out that the T_g and X_c of CNC/PVOH/chitosan composites improved significantly regardless of the source of CNC and the types of pretreatment. The increase in crystallinity proved that the CNC acted as nucleating agent and promoted the crystallization of the polymer matrices. However, a decrease in T_c was observed after the addition of CNC except for the CNC treated with enzymatic treatment. This suggested that the CNC treated with enzymatic pretreatment has a higher tendency in promoting the nucleation. Similar results were observed by Krishnan *et al.*[84] and Frone *et al.*[85] For high-crystallinity polymeric composites, a higher energy was required to break down the polymer chain than low crystallinity material. Besides, tighter packing and increased intermolecular bonding also contributed to a higher melting point of nanocomposites.[86]

The rigid rod-shaped CNC and flexible CNF were incorporated into the poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV) matrix to develop the nanocomposites. The addition of CNC and CNF induced an increase in the T_c and T_m of PHBV composites. The addition of cellulose nanoparticle promoted the nucleation in the crystallization of PHBV matrix, which in turn leads to a reduction in the X_c. However, CNF/PHBV composite exhibited a higher crystallinity than CNC/PHBV composites. It could be due to the higher surface area of CNC accessible promoting the nucleation of PHBV.[87] The crystallinity of the polymers is mostly affected by the nucleation and confinement by fillers. Hence, depending on the filler concentration, cooling rate, and T_c, the crystallinity and crystallization rate could be influenced by the combined effects of nucleation and confinement.[88]

T_g is an important parameter in thermal analysis. It is mainly influenced by chain mobility, intermolecular reaction, branching, and crosslinking degree.[85] In most studies, the T_g of nanocomposites exhibits no significant changes with the addition of nanocellulose, with examples including epoxy[79] and gluten composites.[89] Furthermore, Niazi *et al.*[90] have observed the downward trend of T_g in nanocellulose fibrils/PVOH composite. They attributed the drop of T_g of the nanocellulose composites to the increased mobility of soft domains in polymer matrix. The incorporation of nanocellulose into PVOH matrix interrupted the original interaction between rigid and soft segments, which led to a higher microphase separation in the polymer matrix and, hence, a decrease in T_g. Nevertheless, a few authors have observed an improvement in the T_g of the host polymer when adding nanocellulose from sugar palm,[91] sugar beet,[92] microcrystalline cellulose,[93] sugarcane bagasse,[94] and empty fruit bunch.[95] A great enhancement in T_g was reported by Ilyas *et al.*[91] The addition of 1 wt % NCC increased the T_g drastically from 37.91 to 49.15 °C. It could be attributed to the restriction imposed by the intermolecular bonding between the filler and the matrix, which limited the flexibility and mobility of starch chains and led to an improvement in T_g. Strong hydrogen bonding between the filler and the polymer matrices also lead to an improvement in T_g.[92]

Surface modification of nanocellulose can also lead to good thermal properties especially with hydrophobic polymer matrices. According to Cao *et al.*,[96] the introduction of carboxyl groups into CNC could produce a nanocomposite with enhanced thermal characteristics. The reinforcement of modified CNC enhanced the T_g notably. The strong interfacial reaction between carboxyl groups in CNC and epoxy groups in epoxidized natural rubber formed the covalent crosslinking network, which inhibited the polymer chain motion and led to a higher T_g than neat epoxidized natural rubber.

Recently, the thermal behaviors of PLA/NCC composites with or without the addition of limonene as a plasticizer were reported by Fortunati *et al.*[97] The incorporation of NCC had no significant effect on the T_g of the nanocomposites as shown in Figure 4. The limonene acted as a plasticizer disturbed the pristine intermolecular reaction of polymer chains and increased the PLA chain mobility, which led to a lower T_g. Well-dispersed NCC in the PLA matrix favored crystallization at a lower temperature. The introduction of limonene also decreased the crystallinity of the nanocomposites. However, the incorporation of NCC as a nucleating agent had a beneficial impact on the crystallinity of the nanocomposites. The overall crystallinity of the nanocomposites increased remarkably, especially for the PLA/limonene/NCC composites. The crystallinity of the PLA/limonene composites almost doubled with the addition of NCC. The incorporation of NCC increased the nucleation sites in amorphous domains, which led to the shorter nucleation induction period and better crystallization kinetics.

The incorporation of nanocellulose improved the thermal characteristics of the composites, with particular improvements noted in its crystallinity and T_m. The incorporation of nanocellulose as a nucleating agent could improve the crystallization rate and increase the overall crystallinity of nanocomposites, in turn enhancing the thermal properties of nanocellulose composites. However, the poor dispersion and agglomeration of nanocellulose, especially at high concentration, affected the thermal properties of nanocomposites. Layer-by-layer deposition can improve the distribution of nanocellulose and enhance the interaction of nanocellulose with the surrounding matrix, in a way that reduces agglomeration and significantly improves the properties of the composites.

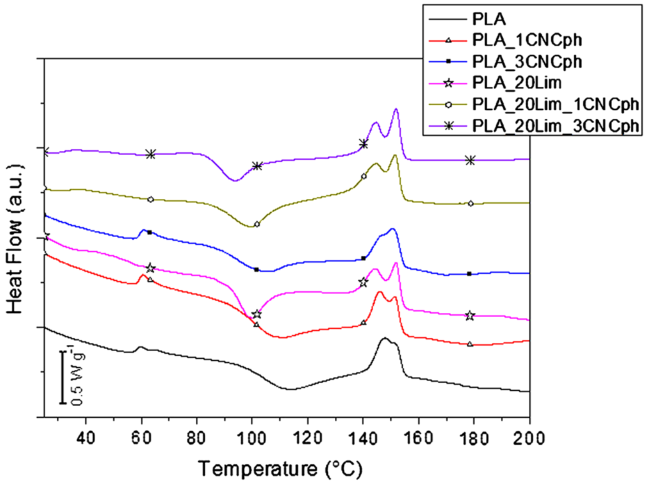

Figure 4. DSC thermogram for PLA and PLA bio-nanocomposites (reproduced from ref. 97, with permission from Elsevier). [Color figure can be viewed at wileyonlinelibrary.com]

Dynamic Mechanical Properties

The thermomechanical properties of nanocomposites can be determined by dynamic mechanical analysis (DMA) and thermomechanical analysis (TMA). Nevertheless, as few thermomechanical studies in the literature use TMA, this review focuses on the thermomechanical properties determined using DMA instead of TMA. DMA is frequently used in nanocomposite characterization, since it allows for the study of the viscoelastic properties of a material over a broad range of temperature. DMA also provides the reinforcement efficiency of the NC on the viscoelastic properties of materials in a wide range of temperatures.

Niazi *et al.*[90] observed a decline in the dynamic mechanical properties of PVOH composites upon the addition of CNF at 0% relative humidity. The intensity of tan δ decreased with the addition of CNF. This result was attributed to the constraint imposed by the CNF against the mobility of PVOH matrix, which caused a more elastic response in the polymer. However, at a higher humidity, the storage modulus was directly proportional to the CNF loading in the composites. The observed results were in good agreement with other research study where the incorporation of CNC has decreased tan δ and increased the storage modulus notably compared with pure PVOH composites.[99] This evidenced that the addition of CNF provided good reinforcement and limited the polymeric chain mobility at the filler and matrix interface level.

The reinforcing effects of NCC and NFC in polyethylene-oxide (PEO) polymer composites were compared.[106] The presence of NCC and NFC in composites increased the T_g and reduced the intensity of tan δ. This was due to the enhanced interfacial adhesion between nanocellulose and PEO polymer. In addition, larger changes in T_g and tan δ were noticed in NFC nanocomposites compared with NCC nanocomposites due to the greater confinement effect and the stronger interfacial adhesion between the fibers and the matrix. The ability of NFC to form entangled and interconnected network or web-like structure might need more energy to achieve the chain segment movement in the composites. Therefore, there is greater change in T_g and tan δ than that for NCC.[107]

In hot pressing process, the process parameters such as temperature, time, and pressure are essential in determining the properties and interfacial characteristics of the nanocellulose composites, since a high temperature and pressure could lead to the degradation of polymer. Salehpour *et al.*[108] investigated the influence of CNF loading and molding process on the storage modulus and tan δ of the PVOH nanocomposites. The addition of CNF had a negative impact on the storage modulus of PVOH composites regardless the conditions of the molding process. It could be due to the poor dispersion of CNF in PVOH composites. The tan δ showed a decline as the molding temperature, time, and pressure decrease; however, the addition of CNF improved the tan δ significantly.

The interaction of nanocellulose and hydrophobic polymers was investigated by numerous researchers. The positive reinforcing effect of CNF could be evidenced in Figure 5 through the strong dependence of storage modulus values on the cellulose concentration.[109] The addition of CNF restricted the mobility of epoxy polymer chains, which in turn to increase the stiffness of the epoxy nanocomposites. The incorporation of 0.75% NFC has led to the highest storage modulus compared with other CNF content. This could be explained by the reinforcing effect and homogeneous dispersion of CNF.[67] The addition of CNF enhanced the intermolecular hydrogen bonds that enable the formation of rigid networks, which in turn increase the storage modulus of the composite. However, the addition of CNF at higher loading has resulted in the agglomeration and formation of voids in the polymer network, which increased the mobility of polymer chains. Other DMA data also showed remarkable improvements in the storage modulus over a wide range of temperature for a large number of polymer nanocomposites with nanocellulose, such as poly(styrene-co-butyl acrylate),[110] unsaturated polyester,[111] poly(butylene succinate),[34] nanoclay,[3] poly(vinyl acetate),[112] PLA,[82] and natural rubber.[113]

The dynamic mechanical properties of microcellulose and NCC/polyester composites were investigated by Bastiurea *et al.*[114] The incorporation of NCC into a polyester matrix resulted in a more significant strengthening effect compared with microcellulose in terms of the storage modulus and loss modulus. The reason for this was due to the strong interfacial adhesion and hydrogen bonding between NCC and the polyester matrix. The nanoscale of NCC increased the mobility and introduced a large amount of interfacial area then allowed a better reaction with the polymeric matrix chains, hence provided a more significant effect in the overall dynamic mechanical properties of composites compared to microcellulose.[115]

Due to hydrophilic nature of nanocellulose, it is always a challenge for the nanocellulose to disperse and distribute in the hydrophobic polymer matrices. Various surface modification of nanocellulose through grafting to enhance the interaction between nanocellulose and hydrophobic matrices has been reported. The enhancement in storage modulus of epoxy composites with the addition of non-modified CNC and modified CNC (grafting of fatty acid to CNC) was observed, indicating the effective stress transfer between filler and matrix.[26] The incorporation of modified-CNC at a degree of substitution of 0.2 displayed highest values of storage modulus and loss modulus. This could be due to the addition of CNC hindered the polymer chain mobility and formed a strong interaction with epoxy matrix, hence improved the dynamic mechanical properties remarkably.

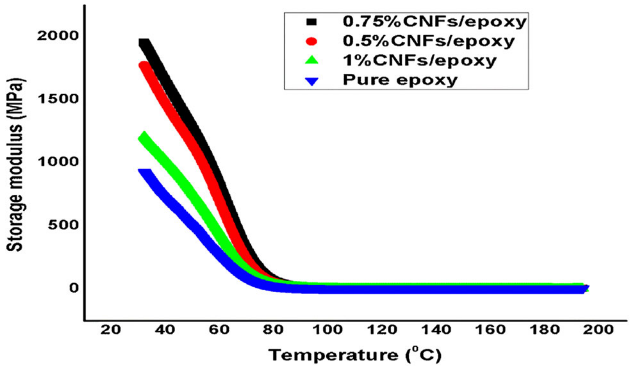

Figure 5. Storage modulus of NFC/epoxy composites (reproduced from ref. 109, with permission from Elsevier). [Color figure can be viewed at wileyonlinelibrary.com]

In conclusion, the addition of nanocellulose improved the dynamic mechanical properties of composites, supporting a wide range of potential industrial applications. However, the dynamic mechanical properties of nanocomposites did not show any improvement at low nanocellulose loading.

Thermal Conductivity

Thermal conductivity is important in materials science, research, electronics, building insulation and related fields, especially where a high operating temperature is required. A good understanding of thermal conductivity is critical, as it allows researchers to develop and design better products by selecting appropriate materials for thermal conduction or insulation purposes.

Uetani, Okada, and Oyama[116] investigated the factors that influence the thermal conductance properties of nanocellulose sheets made from different nanocellulose sources (tunicate NCC, tunicate NFC, cotton NCC, bacterial NFC, Sugi NFC, Sugi NCC, and TEMPO-oxidized Sugi NFC). The results indicated that the crystallite width and cross-sectional area, the orientation of the nanocellulose, the pore size and the thermal resistance between the nanocellulose surfaces will affect the thermal conductivity of the nanocellulose sheets. The thermal conductivity of nanocellulose sheets along the surface was practically the same for all nanocellulose sheets. However, the thermal conductivity in the in-plane direction exhibited a wide variation. Among the nanocellulose sheets, the tunicate NCC sheet showed the highest thermal conductance at 2.5 W/m K, which is 3–5 times that of other common plastic films applied in electronic devices.

The study of thermal conductivity is important in order to prevent the materials from overheating when it is applied in electronic devices. The grafting of polyethylenimine onto CNF showed a 35.01% improvement of thermal conductivity compared to neat epoxy composite.[117] This could be explained by the phonon propagation of NFC, which enhanced the thermal conductivity of the nanocomposites.

Electrospinning can be considered as one of the most promising technology in synthesizing ultrafine fiber. It has been widely applied in various areas such as wound dressing, scaffolding, filtration and protective clothing due to their biocompatibility and biodegradability. Recent studies reported that the use of electrospun PVOH nanofibers as polymer matrix to develop the nanocomposites consisting of CNC as reinforcing filler.[118] The electrospun PVOH nanofiber has a higher thermal conductivity compared to bulk PVOH due to the increase in crystallinity during electrospinning. The addition of CNC had a negative effect on the thermal conductivity of the composites, which suggested that the molecular chain crystallinity has a larger impact on thermal conductivity than the incorporation of CNC. However, the PVOH nanofiber reinforced with 5% CNC has a slightly higher thermal conductivity, which suggested that the thermal conductivity of the PVOH/CNC was probably enhanced by the reinforcement of the backbone rigidity.

Film thermal conductivities were significantly influenced by the degree of NCC alignment and the direction of heat flow relative to the NCC chain axis. The thermal conductivity of self-organized and shear-organized NCC films was studied by Diaz *et al.*[119] Shear-organized NCC films exhibited a higher thermal conductivity compared to self-organized films. As the shear direction increased to 0.76, the thermal conductivity of the shear-organized film doubled to 0.53 m/m K compared to the self-organized NCC film, which was approximately 0.25 m/m K. This could be due to the enhancement in phonon propagation caused by the random interfacial contact.

The study of thermal conductivity in nanocellulose composites has not generally been focused on the effect of nanocellulose incorporation into composites. Therefore, the influence of filler dispersion, processing type, filler size and aspect ratio on thermal conductivity should be further investigated.

CONCLUSION AND FUTURE OUTLOOK

Nanocellulose and its application as a reinforcing material in nanocomposites is a rather new field that has attracted researchers' interest over the past decade due to its environmentally friendly nature, excellent biodegradability and remarkable mechanical reinforcement properties. With the emergence of nanocellulose, it is now possible to achieve the nanoscale engineering of renewable materials for a wide variety of applications including absorbents, printing and biomedical field.

The incorporation of nanocellulose has generally improved thermal and thermomechanical of nanocomposites. However, the efficiency of the composites can also be affected by the morphological and surface properties of nanocellulose and polymer matrices. Hence, to obtain nanocomposites with outstanding properties, these parameters must be controlled in order to enhance the filler and matrix interaction. It is important to understand the thermal behavior of nanocellulose, especially during the processing of nanocellulose and polymer composites. As nanocellulose has a decomposition temperature at approximately 200–300 °C, the processing temperature should be controlled at approximately 200 °C to avoid the degradation of nanocellulose. The composites with the incorporation of NCC usually have a low decomposition temperature compared to NFC due to the presence of sulfate groups on the surface of the NCC as a result of the use of sulfuric acid during the preparation. However, the thermal stability can be enhanced by the desulfation of nanocellulose and other physical or chemical modifications.

Although nanocellulose has excellent material characteristics, the practical transition from laboratory to industrial scale is very difficult and requires the development of technology and engineering to reduce the production cost and energy needed for nanocellulose production. The disintegration of cellulose to nanoscale dimensions and the compatibility with other polymeric materials are still the main problems facing nowadays. Mechanical disintegration consumes a high energy for the production of nanocellulose. Whereas, the separation of nanoparticles through chemical treatments such as acid hydrolysis is time consuming, tedious, hazardous, and requires corrosion resistant reactors. These drawbacks become the strong driving force in developing a more efficient technology to produce nanocellulose. Efforts to overcome poor compatibility between the filler and the polymer matrix have been studied, such as surface modification, use of hydrophilic matrices and the addition of crosslinking agents. Furthermore, pre-treatments such as enzymatic pre-treatment and oxidation pre-treatment have been developed, and the positive results obtained have proven that these pre-treatments are able to reduce the energy required for disintegration by mechanical treatment.

Nanocellulose-reinforced polymer composites are expected to garner increased interest from industry, targeting applications in the packaging and biomedical industries. Continued research and advancement with the strategies proposed here to enhance the performance of the bionanocomposites will contribute to sustainable developments. The application of nanocellulose to industrial technology requires a balance between the performance of the nanocomposite and the cost required for production. Therefore, the implementation of composites that are based on nanocellulose materials still requires some enhancement and discoveries to achieve a nanocomposite that can fulfill both environmental and societal requirements.

ABBREVIATIONS

PLA	poly(lactic acid)
NFC	nanofibrillated cellulose
NCC	nanocrystalline cellulose
BNC	bacterial nanocellulose
TEMPO	2,2,6,6-tetramethylpiperidine-1-oxyl radical
CNF	cellulose nanofiber
CNC	cellulose nanocrystal
PLLA	poly(L-lactic acid)
PCL	poly(ε-caprolactone)
CNW	cellulose nanowhisker
DSC	differential scanning calorimetry
T_g	glass transition temperature
T_m	melting temperature
T_c	crystallization temperature
ΔH_f	heat of fusion
X_c	degree of crystallinity
PHBV	poly(3-hydroxybutyrate-co-3-hydroxyvalerate)
DMA	dynamic mechanical analysis
TMA	thermomechanical analysis
PEO	polyethylene oxide

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REFERENCES

1. Saratale, G.; Oh, S. *African J. Biotechnol.* **2014**, *11*, 1002.
2. Mat Zubir, N. H.; Sam, S. T.; Santiagoo, R.; Zulkepli, N. N.; Wang, J.; Noimam, N. Z.; Wang, J. *Adv. Mater. Res.* **2015**, *1133*, 598.

3. Gabr, M. H.; Phong, N. T.; Abdelkareem, M. A.; Okubo, K.; Uzawa, K.; Kimpara, I.; Fujii, T. *Cellulose*. **2013**, *20*, 819.
4. Soykeabkaew, N.; Laosat, N.; Ngaokla, A.; Yodsuwan, N.; Tunkasiri, T. *Compos. Sci. Technol.* **2012**, *72*, 845.
5. Abdul Khalil, H. P. S.; Bhat, A. H.; Ireana Yusra, A. F. *Carbohydr. Polym.* **2012**, *87*, 963.
6. Abdul Khalil, H. P. S.; Davoudpour, Y.; Islam, M. N.; Mustapha, A.; Sudesh, K.; Dungani, R.; Jawaid, M. *Carbohydr. Polym.* **2014**, *99*, 649.
7. Kirdponpattara, S.; Khamkeaw, A.; Sanchavanakit, N.; Pavasant, P.; Phisalaphong, M. *Carbohydr. Polym.* **2015**, *132*, 146.
8. Suzuki, A.; Sasaki, C.; Asada, C.; Nakamura, Y. *Carbohydr. Polym.* **2018**, *194*, 303.
9. Fortunati, E.; Benincasa, P.; Balestra, G. M.; Luzi, F.; Mazzaglia, A.; Del Buono, D.; Puglia, D.; Torre, L. *Ind. Crops Prod.* **2016**, *92*, 201.
10. Müller, A.; Zink, M.; Hessler, N.; Wesarg, F.; Müller, F. A.; Kralisch, D.; Fischer, D. *RSC Adv.* **2014**, *4*, 57173.
11. Herrick, F. W.; Casebier, R. L.; Hamilton, J. K.; Sandberg, K. R. *J. Appl. Polym. Sci.* **1983**, *37*, 797.
12. Turbak, A. F.; Snyder, F. W.; Sandberg, K. R. *J. Appl. Polym. Sci.* **1985**, *37*, 815.
13. Antti, J.; Hasa, T.; Ahola, J.; Liimatainen, H.; Niinimäki, J. *Carbohydr. Polym.* **2015**, *133*, 524.
14. Yao, X.; Qi, X.; He, Y.; Tan, D.; Chen, F.; Fu, Q. *ACS Appl. Mater. Interfaces*. **2014**, *6*, 2497.
15. Atef, M.; Rezaei, M.; Behrooz, R. *Int. J. Biol. Macromol.* **2014**, *70*, 537.
16. Herrera, M. A.; Mathew, A. P.; Oksman, K. *Carbohydr. Polym.* **2014**, *112*, 494.
17. Huntley, C. J.; Crews, K. D.; Abdalla, M. A.; Russell, A. E.; Curry, M. L. *Int. J. Chem. Eng.* **2015**, *2015*, 1.
18. Li, W.; Yue, J.; Liu, S. *Ultrason. Sonochem.* **2012**, *19*, 479.
19. Sirviö, J. A.; Visanko, M.; Liimatainen, H. *Biomacromolecules*. **2016**, *17*, 3025.
20. Xiao, Y. T.; Chin, W. L.; Abd Hamid, S. B. *Adv. Mater. Res.* **2015**, *1087*, 106.
21. Vinogradova, Y. S.; Chen, J. Y. *J. Text. Inst.* **2016**, *107*, 472.
22. Shanmugarajah, B.; Loo, P.; Mei, I.; Chew, L.; Yaw, S.; Tan, K. W. *Chem. Eng. Trans.* **2015**, *45*, 1705.
23. Dayal, M. S.; Catchmark, J. M. *Carbohydr. Polym.* **2016**, *144*, 447.
24. Thomas, M. G.; Abraham, E.; Jyotishkumar, P.; Maria, H. J.; Pothen, L. A.; Thomas, S. *Int. J. Biol. Macromol.* **2015**, *81*, 768.
25. Kyle, S.; Jessop, Z. M.; Al-Sabah, A.; Hawkins, K.; Lewis, A.; Maffeis, T.; Charbonneau, C.; Gazze, A.; Francis, L. W.; Iakovlev, M.; Nelson, K.; Eichhorn, S. J.; Whitaker, I. S. *Carbohydr. Polym.* **2018**, *198*, 270.
26. Trinh, B. M.; Mekonnen, T. *Polymer (Guildf).* **2018**, *155*, 64.
27. Sabaruddin, F. A.; Paridah, M. T. *IOP Conf. Ser. Mater. Sci. Eng.* **2018**, *368*, 012039.
28. Qian, S.; Sheng, K. *Compos. Sci. Technol.* **2017**, *148*, 59.
29. Velásquez-Cock, J.; Serpa, A.; Vélez, L.; Gañán, P.; Gómez Hoyos, C.; Castro, C.; Duizer, L.; Goff, H. D.; Zuluaga, R. *Food Hydrocoll.* **2019**, *87*, 204.
30. Chen, C.; Li, D.; Abe, K.; Yano, H. *Cellulose*. **2018**, *25*, 5089.
31. Abdel-karim, A. M.; Salama, A. H.; Hassan, M. L. *J. Phys. Org. Chem.* **2018**, *31*, 1.
32. Bideau, B.; Loranger, E.; Daneault, C. *Prog. Org. Coat.* **2018**, *123*, 128.
33. Sampath, U. G. T. M.; Ching, Y. C.; Chuah, C. H.; Singh, R.; Lin, P. C. *Cellulose*. **2017**, *24*, 2215.
34. Joy, J.; Jose, C.; Yu, X.; Mathew, L.; Thomas, S.; Pilla, S. *Cellulose*. **2017**, *24*, 4313.
35. Shah, P.; Pandey, K. *Am. J. Polym. Sci. Technol.* **2017**, *3*, 97.
36. Fortea-Verdejo, M.; Lee, K. Y.; Zimmermann, T.; Bismarck, A. *Compos. Part A Appl. Sci. Manuf.* **2016**, *83*, 63.
37. Zhu, B.; Merindol, R.; Benitez, A. J.; Wang, B.; Walther, A. *ACS Appl. Mater. Interfaces*. **2016**, *8*, 11031.
38. Kouadri, I.; Satha, H. *Ind. Crops Prod.* **2018**, *124*, 787.
39. Li, P.; Sirviö, J. A.; Asante, B.; Liimatainen, H. *Carbohydr. Polym.* **2018**, *199*, 219.
40. da Mariño, M.; Silva, L. L.; Durán, N.; Tasic, L. *Molecules*. **2015**, *20*, 5908.
41. Mariño, M. A.; Rezende, C. A.; Tasic, L. *Cellulose*. **2018**, *25*, 5739.
42. Costa, A. L. R.; Gomes, A.; Tibolla, H.; Menegalli, F. C.; Cunha, R. L. *Carbohydr. Polym.* **2018**, *194*, 122.
43. Chen, Y.; Wu, Q.; Huang, B.; Huang, M.; Ai, X. *BioResources*. **2015**, *10*, 684.
44. Tian, C.; Yi, J.; Wu, Y.; Wu, Q.; Qing, Y.; Wang, L. *Carbohydr. Polym.* **2016**, *136*, 485.
45. Lu, H.; Gui, Y.; Zheng, L.; Liu, X. *Food Res. Int.* **2013**, *50*, 121.
46. Pereira, A. L. S.; Nascimento, D. M. D.; Souza Filho, M. D. S. M.; Morais, J. P. S.; Vasconcelos, N. F.; Feitosa, J. P. A.; Brígida, A. I. S.; Rosa, M. D. F. *Carbohydr. Polym.* **2014**, *112*, 165.
47. Ogundare, S. A.; Moodley, V.; van Zyl, W. E. *Carbohydr. Polym.* **2017**, *175*, 273.
48. Hastuti, N.; Kanomata, K.; Kitaoka, T. *J. Polym. Environ.* **2018**, *26*, 3698.
49. Gan, P. G. P. G.; Sam, S. T. S. T.; Bin Abdullah, M. F. M. F.; bin Zulkepli, N. N. N. N.; Yeong, Y. F. Y. F. *Solid State Phenom.* **2017**, *264*, 9.
50. Yang, X.; Han, F.; Xu, C.; Jiang, S.; Huang, L.; Liu, L.; Xia, Z. *Ind. Crops Prod.* **2017**, *109*, 241.
51. Chen, Y. W.; Lee, H. V.; Abd Hamid, S. B. *BioResources*. **2016**, *11*, 4645.
52. Wulandari, W. T.; Rochliadi, A.; Arcana, I. M. *IOP Conf. Ser. Mater. Sci. Eng.* **2016**, *107*, 012045.

53. Lin, N.; Dufresne, A. *Nanoscale*. **2014**, *6*, 5384.
54. Li, W.; Wu, Q.; Zhao, X.; Huang, Z.; Cao, J.; Li, J.; Liu, S. *Carbohydr. Polym.* **2014**, *113*, 403.
55. dos Santos, R. M.; Flauzino Neto, W. P.; Silvério, H. A.; Martins, D. F.; Dantas, N. O.; Pasquini, D. *Ind. Crops Prod.* **2013**, *50*, 707.
56. Nepomuceno, N. C.; Santos, A. S. F.; Oliveira, J. E.; Glenn, G. M.; Medeiros, E. S. *Cellulose*. **2017**, *24*, 119.
57. Lizundia, E.; Vilas, J. L.; León, L. M. *Carbohydr. Polym.* **2015**, *123*, 256.
58. Srithep, Y.; Ellingham, T.; Peng, J.; Sabo, R.; Clemons, C.; Turng, L. S.; Pilla, S. *Polym. Degrad. Stab.* **2013**, *98*, 1439.
59. Roman, M.; Winter, W. T. *Biomacromolecules*. **2004**, *5*, 1671.
60. Kilzer, F. J.; Broido, A. *Pyrodynamics*. **1965**, *2*, 151.
61. Maiti, S.; Jayaramudu, J.; Das, K.; Reddy, S. M.; Sadiku, R.; Ray, S. S.; Liu, D. *Carbohydr. Polym.* **2013**, *98*, 562.
62. Martelli-Tosi, M.; Masson, M. M.; Silva, N. C.; Esposto, B. S.; Barros, T. T.; Assis, O. B. G.; Tapia-Blácido, D. R. *Carbohydr. Polym.* **2018**, *198*, 61.
63. Jankowska, I.; Pankiewicz, R.; Pogorzelec-Glaser, K.; Ławniczak, P.; Łapiński, A.; Tritt-Goc, J. *Carbohydr. Polym.* **2018**, *200*, 536.
64. Mandal, A.; Chakrabarty, D. *J. Ind. Eng. Chem.* **2014**, *20*, 462.
65. Mondragon, G.; Peña-Rodriguez, C.; González, A.; Eceiza, A.; Arbelaiz, A. *Eur. Polym. J.* **2015**, *62*, 1.
66. Cheikh, S.; Ben; Cheikh, R.; Ben; Cunha, E.; Lopes, P. E.; Paiva, M. C. *Plast. Rubber Compos.* **2018**, *47*, 297.
67. Nagalakshmaiah, M.; el Kissi, N.; Mortha, G.; Dufresne, A. *Carbohydr. Polym.* **2016**, *136*, 945.
68. Neto, W. P. F.; Silvério, H. A.; Dantas, N. O.; Pasquini, D. *Ind. Crops Prod.* **2013**, *42*, 480.
69. Rowe, A. A.; Tajvidi, M.; Gardner, D. J. *J. Therm. Anal. Calorim.* **2016**, *126*, 1371.
70. Yin, Y.; Tian, X.; Jiang, X.; Wang, H.; Gao, W. *Carbohydr. Polym.* **2016**, *142*, 206.
71. Sessini, V.; Navarro-Baena, I.; Arrieta, M. P.; Dominici, F.; López, D.; Torre, L.; Kenny, J. M.; Dubois, P.; Raquez, J. M.; Peponi, L. *Polym. Degrad. Stab.* **2018**, *152*, 126.
72. Razali, N.; Hossain, M. S.; Taiwo, O. A.; Ibrahim, M.; Nadzri, N. W. M.; Razak, N.; Rawi, N. F. M.; Mahadar, M. M.; Kassim, M. H. M. *BioResources*. **2017**, *12*, 6773.
73. Fortunati, E.; Luzi, F.; Puglia, D.; Petrucci, R.; Kenny, J. M.; Torre, L. *Ind. Crops Prod.* **2015**, *67*, 439.
74. Abdul Rashid, E. S.; Muhd Julkapli, N. B.; Abdul Hadi Yehya, W. *J. Appl. Polym. Sci.* **2018**, *135*, 1.
75. Ni, C.; Wang, H.; Zhao, Q.; Liu, B.; Sun, Z.; Zhang, M.; Hu, W.; Liang, L. *Solid State Ion.* **2018**, *323*, 5.
76. Flauzino Neto, W. P.; Mariano, M.; da Silva, I. S. V.; Silvério, H. A.; Putaux, J. L.; Otaguro, H.; Pasquini, D.; Dufresne, A. *Carbohydr. Polym.* **2016**, *153*, 143.
77. El Miri, N.; Abdelouahdi, K.; Zahouily, M.; Fihri, A.; Barakat, A.; Solhy, A.; El Achaby, M. *J. Appl. Polym. Sci.* **2015**, *132*, 1.
78. Filipova, I.; Fridrihsone, V.; Cabulis, U.; Berzins, A. *Nanomaterials*. **2018**, *8*, 640.
79. Aydemir, D. *Drv. Ind.* **2015**, *66*, 35.
80. Tomé, L. C.; Fernandes, S. C. M.; Perez, D. S.; Sadocco, P.; Silvestre, A. J. D.; Neto, C. P.; Marrucho, I. M.; Freire, C. S. R. *Cellul.* **2013**, *20*, 1807.
81. Shih, Y. F.; Chou, M. Y.; Lian, H. Y.; Hsu, L. R.; Chen-Wei, S. M. *Express Polym. Lett.* **2018**, *12*, 844.
82. Nair, S. S.; Chen, H.; Peng, Y.; Huang, Y.; Yan, N. *ACS Sustain. Chem. Eng.* **2018**, *6*, 10058.
83. Raquez, J.-M.; Habibi, Y.; Murariu, M.; Dubois, P. *Prog. Polym. Sci.* **2013**, *38*, 1504.
84. Krishnan, K. A.; Jose, C.; Rohith, K. R.; George, K. E. *Ind. Crops Prod.* **2015**, *71*, 173.
85. Frone, A. N.; Berlioz, S.; Chailan, J. F.; Panaitescu, D. M. *Carbohydr. Polym.* **2013**, *91*, 377.
86. Mariano, M.; Mukurumbira, A.; Amonsou, E. O.; Dufresne, A.; Mellem, J. J. *Int. J. Biol. Macromol.* **2017**, *102*, 241.
87. Jun, D.; Guomin, Z.; Mingzhu, P.; Leilei, Z.; Dagang, L.; Rui, Z. *Carbohydr. Polym.* **2017**, *168*, 255.
88. Jiang, L.; Xu, X. *Handb. Nanocellulose Cellulose Nanocompos.* **2017**, *168*, 553.
89. El-Wakil, N. A.; Hassan, E. A.; Abou-Zeid, R. E.; Dufresne, A. *Carbohydr. Polym.* **2015**, *124*, 337.
90. Niazi, M. B. K.; Jahan, Z.; Berg, S. S.; Gregersen, Ø. W. *Carbohydr. Polym.* **2017**, *177*, 258.
91. Ilyas, R. A.; Sapuan, S. M.; Ishak, M. R.; Zainudin, E. S. *Carbohydr. Polym.* **2018**, *202*, 186.
92. Li, M.; Tian, X.; Jin, R.; Li, D. *Ind. Crops Prod.* **2018**, *123*, 654.
93. Cataldi, A.; Dorigato, A.; Deflorian, F.; Pegoretti, A. *J. Mater. Sci.* **2014**, *49*, 2035.
94. Mandal, A.; Chakrabarty, D. *Carbohydr. Polym.* **2015**, *134*, 240.
95. Haafiz, M. K. M.; Hassan, A.; Khalil, H. P. S. A.; Fazita, M. R. N.; Islam, M. S.; Inuwa, I. M.; Marliana, M. M.; Hussin, M. H. *Int. J. Biol. Macromol.* **2016**, *85*, 370.
96. Cao, L.; Huang, J.; Chen, Y. *ACS Sustain. Chem. Eng.* **2018**, *6*, 14802.
97. Fortunati, E.; Luzi, F.; Puglia, D.; Dominici, F.; Santulli, C.; Kenny, J. M.; Torre, L. *Eur. Polym. J.* **2014**, *56*, 77.
98. Fortunati, E.; Puglia, D.; Luzi, F.; Santulli, C.; Kenny, J. M.; Torre, L. *Carbohydr. Polym.* **2013**, *97*, 825.
99. Jahan, Z.; Niazi, M. B. K.; Gregersen, Ø. W. *J. Ind. Eng. Chem.* **2018**, *57*, 113.
100. Virtanen, S.; Vartianen, J.; Setälä, H.; Tammelin, T.; Vuoti, S. *RSC Adv.* **2014**, *4*, 11343.
101. Abdulkhani, A.; Hosseinzadeh, J.; Ashori, A.; Dadashi, S.; Takzare, Z. *Polym. Test.* **2014**, *35*, 73.
102. Lee, J. H.; Park, S. H.; Kim, S. H. *Macromol. Res.* **2013**, *21*, 1218.
103. Fujisawa, S.; Zhang, J.; Saito, T.; Iwata, T.; Isogai, A. Polymer (Guildf). **2014**, *55*, 2937.

104. Boujemaoui, A.; Cobo Sanchez, C.; Engström, J.; Bruce, C.; Fogelström, L.; Carlmark, A.; Malmström, E. *ACS Appl. Mater. Interfaces*. **2017**, *9*, 35305.
105. Siqueira, G.; Bras, J.; Follain, N.; Belbekhouche, S.; Marais, S.; Dufresne, A. *Carbohydr. Polym.* **2013**, *91*, 711.
106. Xu, X. X.; Liu, F.; Jiang, L.; Zhu, J. Y. Y.; Haagenson, D.; Wiesenborn, D. P.; Wiesenborn, P. D. *ACS Appl. Mater. Interfaces*. **2013**, *5*, 2999.
107. Boufi, S.; Kaddami, H.; Dufresne, A. *Macromol. Mater. Eng.* **2014**, *299*, 560.
108. Salehpour, S.; Rafieian, F.; Jonoobi, M.; Oksman, K. *Ind. Crops Prod.* **2018**, *121*, 1.
109. Saba, N.; Safwan, A.; Sanyang, M. L.; Mohammad, F.; Pervaiz, M.; Jawaid, M.; Alothman, O. Y.; Sain, M. *Int. J. Biol. Macromol.* **2017**, *102*, 822.
110. Bettaieb, F.; Khiari, R.; Dufresne, A.; Mhenni, M. F.; Belgacem, M. N. *Carbohydr. Polym.* **2015**, *123*, 99.
111. Jose, C.; Mathew, L.; Hassan, P. A.; Mozetic, M.; Thomas, S. *Int. J. Biol. Macromol.* **2014**, *69*, 274.
112. Geng, S.; Haque, M. M. U.; Oksman, K. *Compos. Sci. Technol.* **2016**, *126*, 35.
113. Kargarzadeh, H.; Sheltami, R. M.; Ahmad, I.; Abdullah, I.; Dufresne, A. *Polymer*. **2015**, *71*, 51.
114. Bastiurea, M. S.; Bastiurea, M.; Andrei, G.; Murarescu, M.; Dumitru, D. In 15th International Conference on Nanotechnology, Rome, 2015; pp 327.
115. Cataldi, A.; Berglund, L.; Deflorian, F.; Pegoretti, A. *Nanocomposites*. **2015**, *1*, 195.
116. Uetani, K.; Okada, T.; Oyama, H. T. *Biomacromolecules*. **2015**, *16*, 2220.
117. Zhao, J.; Li, Q.; Zhang, X.; Xiao, M.; Zhang, W.; Lu, C. *Carbohydr. Polym.* **2017**, *157*, 1419.
118. Park, Y.; You, M.; Shin, J.; Ha, S.; Kim, D.; Heo, M. H.; Nah, J.; Kim, Y. A.; Seol, J. H. *Sci. Rep.* **2019**, *9*, 1.
119. Diaz, J. A.; Ye, Z.; Wu, X.; Moore, A. L.; Moon, R. J.; Martini, A.; Boday, D. J.; Youngblood, J. P. *Biomacromolecules*. **2014**, *15*, 4096.