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Abstract

Fiber-reinforced polymer composites have gained popularity through their advantages over conventional metallic materials. Most polymer composites are traditionally made with reinforcing fibers such as carbon or glass. However, there has

Book Chapter in, “Technological advancement in polymer nano- composites of cellulose nano-particle: processing, performance and applications”

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been recent interest in sourcing these reinforcing fibers from renewable, natural resources. Nanocellulose-based reinforcements constitute a new class of these naturally sourced reinforcements. Some unique behavior of nanocellulose creates both opportunities and challenges. This chapter reviews the progress and some of the remaining issues related to the materials, processing, and performance of nanocellulose reinforced thermosetting composites.

Keywords

Nanocellulose • Thermosets • Mechanical properties • Nonmechanical properties • Applications

1 Introduction

Fiber-reinforced polymer composites have gained popularity through their advantages over conventional metallic materials. The composites can be tailored to achieve desirable characteristics including low weight, high mechanical properties, and low temperature processing [1]. Most polymer composites are traditionally made with reinforcing fibers such as carbon or glass. However, there has been recent interest in sourcing these reinforcing fibers from renewable, natural resources. For example, composite manufacturers are seeking to take advantage of the favorable balance of properties (e.g., low density, good mechanical properties) by using bast fibers from plants in composite applications in automotive, packaging, sporting goods, and furniture applications [2–6].

Nanocellulose-based reinforcements constitute a new class of these naturally sourced reinforcements. Trees, plants, some marine creatures such as tunicates, and certain bacteria and algae form microfibrils from cellulose molecules [7]. These microfibrils have a complex structural hierarchy and often act as the main reinforcing element in their respective organisms. These fibrils are about 5–50 nm in diameter and several microns in length [7]. In part, it is the high reinforcing potential of native crystalline cellulose within these microfibrils that has recently led researchers to extract nanocellulose from them for use in composites. Table 15.1 compares the

Table 15.1 Comparison of crystalline cellulose with other selected reinforcements

Material	Density (g cm ⁻³)	Strength (GPa)	Elastic modulus (GPa)	Strain to failure (%)	References
Crystalline cellulose	1.6	7.5–7.7	110–220	–	[7]
E-glass fiber	2.6	3.5–3.8	69–72	4.5–4.9	[142]
S-2 glass fiber	2.5	4.6–4.8	86–90	5.4–5.8	[142]
K-49 aramid fiber	1.4	–	124–131	2.5–2.9	[142]
AS4 carbon fiber	1.8	–	221–234	1.5–1.6	[142]

Fig. 15.1 Luminescence of an organic light-emitting diode deposited onto a flexible, low coefficient of thermal expansion (CTE) and optically (Reprinted from Okahisa et al. [17], with permission from Elsevier)



mechanical properties of crystalline cellulose with other reinforcements. The listed properties for crystalline cellulose represent a range of values from a survey of mechanical performance by different researchers and techniques and do not reflect the actual inherent variability of the properties. While not as high performance as some reinforcements such as carbon nanotubes, crystalline cellulose is derived from natural resources, and its reinforcing potential is sufficiently high that there is considerable interest in finding ways to economically extract it and efficiently use it in composite materials. However, reinforcement is not the only reason for adding nanocellulose to polymers. Others are trying to make transparent, dimensionally stable cellulose nanocomposites for electrical applications [8–17] or exploit other features of nanocellulose such as its good barrier properties [18–21]. Figure 15.1 shows an organic light-emitting diode on a flexible nanocellulose-based composite. Different types of nanocellulose materials have been investigated for use in polymer composites. These are briefly described below, but more detailed information can be found elsewhere in this book or in recent reviews [7, 22–28].

Cellulose nanocrystals (CNCs), also called *cellulose whiskers*, *nanowhiskers*, or *nanorods*, are produced by transverse cleavage of cellulose by acid hydrolysis. This results in high modulus, rodlike structures with aspect ratios of around 10–100 but which depend on the source of the cellulose and the exact preparation conditions [7]. Plant-based sources yield crystallites with diameters of about 5 nm and lengths of about 100–400 nm. Tunicate and algae yield crystallites with diameters of 10–20 nm and length up to several micrometers [29]. A transmission electron micrograph of CNCs is shown in Fig. 15.2.

Other forms of nanocellulose are also being investigated as polymer reinforcements. For example, severe, mechanical refining of highly purified pulps results in a fibrillated form of cellulose with fibril widths on the same order of magnitude as the cellulose microfibrils in the original pulp. This *microfibrillated cellulose* (MFC) has more of a network structure than CNCs (see Fig. 15.3) and often forms gels in water even at low concentrations (e.g., less than 1 % by weight). Certain preprocessing steps (e.g., enzymatic or chemical pretreatments) can be used to weaken hydrogen bonding and facilitate processing. *Nanofibrillated cellulose*, *cellulose nanofibrils*, and *cellulose*

Fig. 15.2 TEM of CNCs from wood [7]

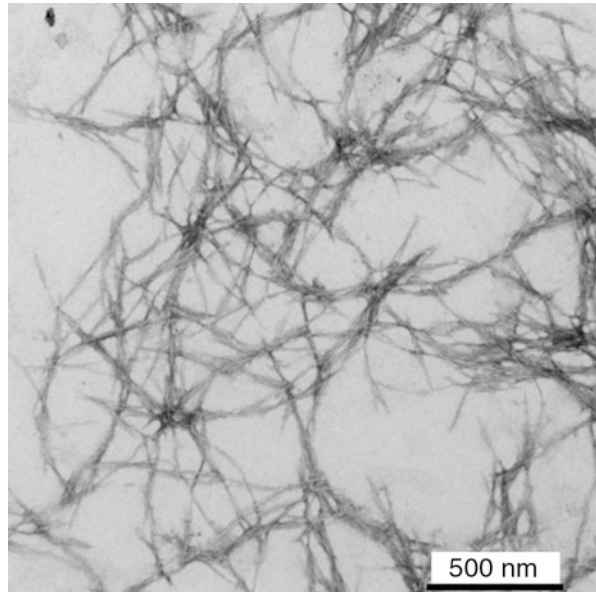
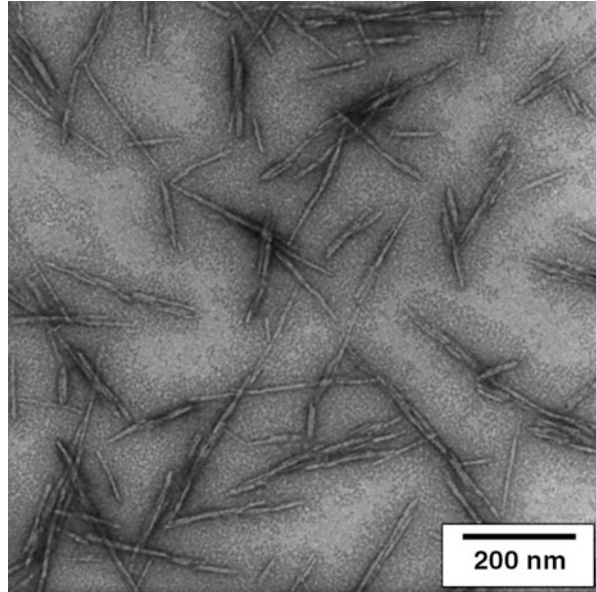


Fig. 15.3 TEM of NFC

nanofibers are terms that are sometimes used to describe fibrillated cellulose with a finer structure or to reflect that the fibril diameters are of nano-scale dimension. However, the use of the terms is inconsistent, and the variability between samples of fibrillated cellulose due to differences in preparation methods, starting materials, etc. or

even variability within samples makes clear distinction between fibril diameters difficult. In this chapter, we use the term nanofibrillated cellulose (NFC) for this type of nanocellulose. Besides from pulps, nano-scale, cellulose reinforcements have also been produced from cellulose secreted by certain bacteria (e.g., *Gluconacetobacter xylinus*) under special culturing conditions [7]. They are usually specifically referred to as *bacterial cellulose microfibrils* or *bacterial cellulose nanofibers* to distinguish them from their pulp-derived counterparts.

Some unique behavior of nanocellulose creates both opportunities and challenges. For example, preparation of nanocellulose results in aqueous gels or suspensions that may need to be dried into a fiber and film or otherwise converted into a form more useful for reinforcing thermosets. Nanocellulose's strong tendency to hydrogen bond can lead to challenges in redispersing them if they are dried but can also result in fairly strong and stiff films that can be used in laminated composites [30]. Nanocellulose is very hydrophilic, which can create difficulties in dispersing them and bonding them to some thermosets and can lead to swelling during composite manufacture.

The use of nanocellulose as a reinforcement in polymer composites is in its infancy. While much recent progress has been made, there are many challenges remaining to efficiently and economically use nanocellulose as a reinforcement. This chapter reviews the progress and some of the remaining issues related to the materials, processing, and performance of nanocellulose reinforced thermosetting composites.

2 Materials

Various forms of nanocellulose have been incorporated into numerous thermoset resins using a wide range of forms and techniques. An overview of the types of nanocellulose used, the various forms of reinforcement, and the types of resins used to make composites will be provided in this section.

These different types of nanocellulose can be used as is or converted into various forms of reinforcement, including distributed reinforcements, planar reinforcements, or continuous networked structures. Each type of nanocellulose has certain advantages and limitations for these various reinforcement structures. One recurring challenge for creating these reinforcements is to remove the water from the hydrophilic nanocellulose while retaining properties favorable for incorporation into resins, which are typically hydrophobic. Some of the approaches for creating these reinforcements, along with their physical and mechanical properties, are discussed below.

2.1 Dispersed Fibrous or Particulate Reinforcements

Nanocellulose materials have been mixed or dispersed in various resins using a variety of processing techniques. While these techniques vary in complexity, they typically involve physically mixing and dispersing the nanocellulose and resin in a solvent system. In many cases, solvent exchange techniques are used, often

along with surface modification of nanocellulose to make it compatible with organic solvents and/or the resin system. Here, an overview of various techniques to blend, modify, or prepare nanocellulose for distribution in resins is provided.

Nanocellulose is typically produced in aqueous suspensions, so removal of the water is critical for producing composite materials, and since most resins are hydrophobic, the water is typically removed prior to mixing nanocellulose with resins. Methods of delivering dried nanocellulose for incorporation into composites are highly desirable and thus the subject of numerous research and development efforts [31–37]. These methods typically involve freeze-drying or spray-drying of modified or unmodified nanocellulose. Because nanocellulose tends to agglomerate during drying, the redispersibility and morphology of the dried material are often different than the original material, although recent work has shown that the negative impact of these drying techniques can be minimized by optimizing processing conditions and/or surface modification [32–34]. For example, CNC dispersions neutralized with sodium hydroxide were found to be much more readily dispersible after drying than CNCs without sodium counter ions [33]. The drying rate, duration, temperature, and method are all factors that affect the dispersibility and morphology of nanocellulose, and practical methods for delivering dried nanocellulose are emerging.

Numerous research studies have reported the modification of nanocellulose for compatibility in nonpolar solvents and hydrophobic polymers [38–45]. Although many of these modifications were made with the aim of incorporating nanocellulose into thermoplastics, the hydrophobization of these CNCs and NFCs is equally applicable for distribution in thermoset resins. For example, Ljungberg et al. found that CNCs with an adsorbed surfactant (phosphoric ester of polyoxyethylene (9) nonylphenyl ether) dispersed in toluene [40]. Various methods of chemically reacting compounds with nanocellulose surfaces have also been used to facilitate compatibility and dispersion of nanocellulose in hydrophobic polymers [41, 42]. Goussé et al. modified CNCs with chlorosilanes resulting in stable suspensions in organic solvents [41]. The chlorosilanes were found to be reactive with the CNCs provided that water was removed from the solvent. However, if the reactions were carried out too far, the integrity of the CNCs was destroyed. Therefore, the CNCs were not able to be dispersed in solvents, such as toluene, with polarity lower than that of tetrahydrofuran (THF). Tunicin CNCs were acylated using aqueous alkenyl succinic anhydride (ASA) emulsions by mixing the two materials, freeze-drying, and heating to 105 °C [38]. The length of heating was crucial to the degree of substitution achieved. After approximately 1 hour at 105 °C, the modified CNCs were dispersible in low-polarity solvents including 1,4-dioxane [38]. NFCs have also been chemically modified to change the surface properties and to facilitate their dispersion in nonpolar media [42, 46–48]. For instance, polycaprolactone (PCL) was grafted to NFCs via ring-opening polymerization [46]. The resulting grafted material was stable in nonpolar solvents and had excellent thermal stability. Siqueira et al. found that modification of nanocellulose with *n*-octadecyl isocyanate improved their dispersion in organic solvents [42]. Silane chemistry also has enormous potential as a surface modifier for NFCs, and such modifications

have been explored [47]. Another approach being explored is the in situ modification of nanocellulose during spray-drying [49]. However, clear and practical strategies for modifying NFCs for incorporation into polymers have not been established.

2.2 Planar Reinforcements

Planar nanocellulose reinforcements or films are typically made from NFCs either by casting or by using a papermaking-like process. These films have been coined “nanopaper” and have been touted as the “strongest cellulose-based material made by man” [50, 51]. Films or sheets from CNCs are rarely used as a reinforcing phase because of their brittleness and difficulty in handling. Some of the methods of producing these NFC films and their properties are discussed here.

Dewatering NFC solutions presents a practical challenge because of their affinity for water. Casting is a slow process and not readily scalable, so NFC films (Fig. 15.4) are often formed by filtering NFC solutions with membranes or fine filters and drying the wet mats under pressure. Press conditions vary throughout the literature, but wet films are commonly pressed for days at temperatures of 55–70 °C and low pressures [52, 53]. For example, Nakagaito and Yano produced films by vacuum filtering a solution of NFC, separating the wet mats from filter papers, and drying the sheets between metal plates at 70 °C for 48 h followed by vacuum drying for another 5 h at 70 °C [53]. Films are also often simply cast by slowly evaporating the water from the NFC suspension [54]. Sehaqui et al. developed an accelerated



Fig. 15.4 Nanofibrillated cellulose film

procedure similar to papermaking, which resulted in the production of NFC sheets about 60 μm thick in 1–2 h [55]. This process for making NFC films is similar to the process for making paper, and efforts to develop pilot-scale processes for producing continuous NFC films are underway [56].

The mechanical properties of NFC films are dictated by a variety of factors, and the effects of these variables are difficult to discern based on results in the literature. The tensile strengths of NFC films range from about 70 MPa to over 300 MPa, and tensile moduli range from about 3 GPa to nearly 20 GPa [23]. Stelte and Sanadi showed that softwood pulp resulted in cellulose nanofiber sheets with higher tensile strength than those from hardwood pulp, whereas the effect of species was reversed for tensile modulus [57]. However, they also demonstrated that the softwood pulps required extremely reduced levels of refining and homogenizing to yield NFC. On the other hand, some of the highest tensile strengths of cellulose nanofiber sheets reported in the literature are those made from hardwood fibers. For example, cellulose nanofiber sheets prepared from TEMPO-oxidized hardwood fibers resulted in sheets having tensile strength of over 300 MPa [58], which is the highest reported value found for unoriented NFC films.

Orientation of nanocellulose has been shown to significantly enhance the mechanical properties of films along the direction of orientation [30, 59]. For example, Sehaqui et al. produced NFC films with as high as 89 % degree of orientation parallel to the plane of the film by cold drawing wet NFC films [30]. The wet films, or “hydrogel cakes” containing 70–90 % water, were oriented by stretching them in a tensile testing machine at constant elongation, resulting in enhanced tensile stiffness and strength compared to randomly oriented films. The modulus of the films increased from about 10 GPa with no drawing to about 33 GPa with a draw ratio of 1.6. The strength of random films was about 185 MPa, which is typical of other reports in the literature, while the strength of oriented films reached over 400 MPa in one case. The optimum achievable mechanical properties for aligned nanocellulose structures and composites are not known, but oriented NFC reinforcements clearly have potential.

2.3 Continuous Fibrous Forms

Most fibrous reinforcements (e.g., carbon, glass) for advanced composites are continuous fibers or yarns, fabrics, and preforms made from them, which allow broad flexibility in design and manufacturing approaches. Recently, there has been increasing interest in using plant-based materials, which use cellulose as their main structural component, as a source for continuous polymer reinforcements. A potentially promising area of investigation is the use of nanocellulose (e.g., CNC, NFC) as continuous fiber reinforcement in polymers. However, it is useful to first review other approaches for producing plant-based continuous reinforcements for comparison.

One obvious approach to producing continuous, plant-based reinforcements is to simply extract fibers from the plants directly and spin them into yarns.

Table 15.2 Comparison of the properties of selected natural fibers and continuous glass fibers

Material	Density (g cm ⁻³)	Strength (GPa)	Elastic modulus (GPa)	Strain to failure (%)	References
E-glass fiber	2.6	3.5–3.8	69–72	4.5–4.9	[142]
S-2 glass fiber	2.5	4.6–4.8	86–90	5.4–5.8	[142]
Flax ^a	1.4–1.5	0.5–0.9	50–70	1.5–4.0	[143]
Hemp ^{a,b}	1.5	0.3–0.8	30–60	2–4	[143]
Jute ^a	1.3–1.5	0.2–0.5	20–55	2–3	[143]
Softwood	1.4	0.1–0.2	10–50	–	[143]

^aFiber bundles

^bIndustrial hemp is listed as a controlled substance in the United States and cannot be used in commercial production of composites

The composition and mechanical properties of several natural fibers from plants are shown in Table 15.2 along with more common continuous reinforcing fibers. Flax and hemp bast fibers have the highest mechanical performance of the fibers listed partly due to their high cellulose content. Not surprisingly, they are some of the most investigated natural fibers for polymer reinforcement [4, 6]. Natural fibers such as flax, hemp, and jute have sufficiently long fibers that they can readily be made into continuous reinforcing yarns or rovings using textile technologies. Modifications to existing textile technologies (e.g., to produce low-twist rovings) are often made to better target composite applications [6]. While the mechanical performance of these yarns or rovings fall short of the more commonly used continuous synthetic fibers, they are of interest because of their specific properties (i.e., property divided by density) and their damping abilities, for example. These roving or yarns can be sold as reinforcement directly or fabricated into mats, fabrics, and prepregs for use in composites for automotive, sporting goods, or boating applications [6, 60]. However, the potential of these reinforcements in advanced composites is somewhat limited by their inherent variability in structure and composition.

Regenerated cellulose fibers have been made for over a 100 years [61], and although they have been traditionally been used in textiles, there has been growing interest in their use as polymer reinforcements as well [62, 63]. These fibers are attractive partly due to their lower variability than natural fibers such as flax [62]. Regenerated fibers are made by several technologies that first dissolve cellulose and then recrystallize it during fiber production. Their mechanical performance is typically less than glass fiber (Table 15.3). However, new regenerated cellulose fibers with high orientation and crystallinity have been recently developed and show significant improvements. For example, Bocell fiber, an experimental regenerated cellulose fiber, has a tensile modulus and strength of 46.6 ± 6.5 GPa and $1,170 \pm 165$ MPa, respectively (Table 15.3). Since its density is only about 1.5 g cm⁻³, its specific modulus is comparable to some glass fibers. However, the crystalline structure of regenerated cellulose (referred to as Cellulose II) is different from that of cellulose in its native state (i.e., Cellulose I). While reported values for

Table 15.3 Average tensile properties of continuous, regenerated cellulose fibers

Fiber	Strength (GPa)	Elastic modulus (GPa)	Strain to failure (%)	References
Viscose	0.34 ± 0.07	10.8 ± 2.5	15.4 ± 2.2	[62]
Modal	0.44 ± 0.07	13.2 ± 2.2	10.4 ± 1.8	[62]
Lyocell	0.56 ± 0.08	23.4 ± 3.9	8.7 ± 1.6	[62]
Rayon tirecord	0.78 ± 0.06	22.2 ± 1.0	10.7 ± 1.4	[62]
Bocell	1.17 ± 0.17	46.6 ± 6.5	6.1 ± 0.8	[144]

the mechanical performance of these two types of crystal structures vary considerably and depend on the measurement technique, the values for Cellulose I are clearly considerably higher [7]. This is one of the reasons that researchers have recently begun investigating spinning continuous fibers from nanocellulose, which maintains its Cellulose I crystal structure when it is produced [64, 65].

To date, approaches for reinforcing thermosets with nanocellulose have largely focused on (1) dispersing CNCs or NFC into thermosets and then casting composites [66–68] or (2) preparing films from nanocellulose and then laminating or impregnating them [8, 9, 14, 69–73]. However, until very recently, there has been no work in the literature on producing continuous fibers from nanocellulose [64, 65] despite the considerable efforts of doing so with other nano-scale reinforcements such as carbon nanotubes [74].

Ideally, these fibers would have high crystallinity, high orientation, and a fine, homogeneous structure with no defects. From a spinning standpoint, nanocellulose lies between natural fibers and regenerated cellulose in that the starting point for spinning is neither comprised of macro-scale fibers (as with spinning natural fibers into yarns or tows) nor molecular-scale solutions (as with spinning of regenerated cellulose). Instead they are usually aqueous gels or dispersions of nanocellulose particles with very different characteristics depending on their method of preparation, both in terms of structure and chemistry. For example, NFCs tend to form more of a network structure compared to the rigid rodlike structure of CNCs. This allows their gels to stretch somewhat without breaking in order to induce some alignment but also limits the ultimate alignment that can be achieved. NFCs form thick aqueous gels at lower concentrations than CNCs, and their higher viscosities and water content need to be considered. Different surface chemistries result from different methods of nanocellulose preparation, which have a significant effect on approaches to spinning. For example, CNC production most often results in sulfated surfaces, while NFCs often have carboxylated surfaces, for instance, due to chemical pretreatment.

Continuous fibers have been readily spun from NFC and coagulated using acetone or ethanol followed by drying [64, 65]. Unfortunately, the tensile properties of the fibers resulting from this approach are below those of commercial regenerated celluloses, even if some alignment is induced [64]. However, this research area is very much in its infancy, and improved spinning methods (e.g., that result in better alignment) and new approaches are likely. Optimizing methods for extracting nanocellulose that result in characteristics more favorable for spinning fibers

(e.g., higher crystallinity) may also improve the situation. Also, other characteristics besides mechanical performance (e.g., transparency, biodegradability) may prove useful in a composite system, or other functionalities may be achieved through chemical modification (e.g., electrical conduction, magnetism) [65]. As with other types of continuous reinforcements, surface treatments will likely be necessary for optimal performance for a given resin type, processing method, and application.

Because of the limitations imposed by the structure and chemistry of nanocellulose gels and dispersions, other materials may very well need to be added to produce a dope that is easily spun and has high performance. For example, adding a different polymer may improve gel elasticity and result in better alignment or allow different approaches to coagulation. Small amounts of nanocellulose have been added to wet spun [75, 76] or electrospun [77–79] polymer fibers. While somewhat beyond the scope of this chapter, these investigations may offer some insight into the production of continuous nanocellulose fibers. Because of high surface area and low percolation thresholds of nanocellulose, some of the issues related to spinning at high nanocellulose content (e.g., control of hydrogen bonding) are present even when little nanocellulose is used.

2.4 Thermoset Resins

Polymers are generally divided into thermoplastic and thermosetting varieties. The advantage of using thermosets stems from distinct advantages in mechanical properties and processing. Thermosetting composites can be cured with low or no heat applied, which can be advantageous since nanocellulose has limited thermal stability. Thermosetting plastics are polymer materials that irreversibly cure. The curing may be initiated through heat, through radiation, or through a chemical reaction (e.g., a two-part epoxy). Uncured thermosetting materials have low viscosities, which is a critical feature in the construction of composites that allows for infiltration and wetting of the fibers. However, once the curing is complete, the thermoset cannot be melted into a liquid form as can be done with a thermoplastic material.

A variety of thermosets, including epoxies and various formaldehydes, have been investigated for use in nanocellulose composites. Epoxy-based nanocellulose composites, for example, have the potential for wide application partly due to the relatively high mechanical properties. Epoxy is a thermosetting copolymer, also known as polyepoxide, formed from reaction of an epoxide “resin” with polyamine “hardener.” Bio-based resins have been explored for the manufacturing of macroscopic, cellulose-based composites and are of interest in nanocellulose composites. These resins have the benefit of reducing the amount of petrochemical-based materials used. Resins from soybean-based oil and methacrylic anhydride-modified soybean oil (MMSO) were used as matrices and were combined with various flax fibers. Lactic acid-based thermosets have also been proposed for use in cellulose-based composites for creating prepreg-type reinforcement for use in sheet molding compound applications [80]. Fiber volume fractions of near 70 % have been reported in the literature [81]. Similar resins are of interest for use in nanocellulose composites.

Adekunle et al. [82] used a soybean oil-based thermosetting matrix in their composites. Despite the bio-content and processing improvements, these thermosets still have the detrimental property of not being as readily recyclable as thermoplastics.

Chemical compatibility between the filler and the matrix plays a critical role in the filler dispersion within the matrix and in the adhesion between both phases. Part of the issue arises from the hydrophobic nature of many matrices and the hydrophilic nature of the cellulose materials. The use of cellulose in nanocomposites with hydrophobic matrices often results in weak filler–matrix interactions, low moisture resistance, and interfiber aggregation. Another limitation to the application of NFCs related to the hydrophilic nature is the high water absorption capacity, which is undesirable in many potential applications [83]. Abdelmouleh et al. [84] used silane-treated cellulose fibers in unsaturated polyester and epoxy resin matrices, but the immersion into water induced a large loss of mechanical properties of the materials indicating that the silane treatment was insufficient for preventing cellulose from water absorption. Lu et al. [85] reported successful surface treatments of NFC with three different coupling agents: 3-aminopropyltriethoxysilane(APS), 3-glycidoxypropyltrimethoxysilane, and a titanate coupling agent. These were incorporated into an epoxy resin using an acetone solvent. Better and stronger adhesion between the NFC and the epoxy polymer matrix was observed resulting in a modulus increase for APS-treated material from 10 MPa to over 65 MPa at 130 °C [85]. The results of the surface treatments show no consensus on the best treatment and remain an open area of investigation.

3 Processing of Nanocellulose Composites

Challenges remain in the ability to integrate the nanocellulose reinforcements into composite structures using composite processing techniques. As mentioned earlier in this chapter, nanofibrillated cellulose has incredible potential as a reinforcement material. However, such materials have seen limited use to date as a polymer reinforcements and methods for producing scalable cellulose nanofiber reinforcements are lacking. Moreover, there are a number of challenges in using nanofibrillated cellulose for reinforcement in traditional liquid composite molding (LCM) processes, including the dense structure of the fiber networks in these films as well as the swelling of such networks due to liquid absorption during their wetting by resins during processing. Here, some of the approaches for incorporating nanocellulose into thermoset resins are described.

3.1 Dispersed Fibrous or Particulate Reinforcements

The incorporation of distributed nanocellulose reinforcements into resins presents many challenges, and a number of approaches have been proposed to overcome them. These typically involve casting the composite from some type of solvent. Much of the

research in thermosetting nanocellulose composites has focused on methods of dispersing the various nanocellulose forms in the matrix. In the simplest cases, unmodified nanocellulose is simply blended with water-soluble resins or resin-in-water emulsions. In some cases, the aqueous dispersions of nanocellulose are solvent exchanged to a solvent compatible with the resin, and the resin and nanocellulose are blended together in the solvent. In other cases, freeze-dried nanocellulose, often modified, has been mixed directly into solvents and blended with the resin. Capadona et al. describe a sol-gel process by which nanocellulose can be dispersed in hydrophobic polymers [86]. The process involved converting an aqueous dispersion of CNCs into a “three-dimensional template of well-individualized nanofibers, which is filled with any polymer of choice.” The water in which the CNCs are dispersed is replaced by a miscible but weaker hydrogen-bonding solvent forming a gel with dispersed but networked CNCs. This gel is then placed in a polymer solution, allowing the polymer to diffuse into the gel, and the gel can be dried and cast.

Casting methods have been employed with a variety of thermoset systems. For example, Lu et al. [85] reported using epoxy (EPON™ Resin 863) with a polyether amine (D-230) curing agent for making NFC composites. This resin system has a low viscosity (300 cP at 25 °C) and a gel time of 6 h at 33 °C. In their procedure, the epoxy was added to an acetone suspension, sonicated, and then stirred. The curing agent was then added followed by further mixing [85]. The suspension was poured into dishes, and the solvent was evaporated with mild heating, which facilitated simultaneous curing of the resin. The results from differential scanning calorimetry showed that the nanocellulose has a catalytic effect on the epoxy-amine cure and increased the glass transition temperature and the heat of reaction at a low level of NFC reinforcement [67]. Epoxy resin was also used by Ruiz et al. [87] but in the form of an aqueous suspension.

3.2 Planar Reinforcements

Composites from planar NFC reinforcements have been made using a variety of methods, often using a wet lay-up type of approach. Films or “nanopaper” of NFCs have also shown superior mechanical properties and have been used as a reinforcement phase in composites. Masoodi et al. [88] used a bio-based epoxy (Super Sap 100/1000) made by Entropy Bio-Resins Co [89]. The bio-based epoxy is an epoxy resin that is made from up to 37 % bio-content obtained as coproducts of other green industries including wood pulp and biofuel production. The resin has a total calculated biomass of 50 %. NFC films were used as reinforcements and were integrated into the composites using a hand lay-up technique. The resin was degassed using a degassing chamber prior to application for a period of 5 min to allow for the volatiles and voids introduced during the mixing of the hardener and resin to dissipate. However, as discussed later in this chapter, the use of such films is not ideal for composite processing and can result in less-than-desirable stress transfer between the layers. Thus, the ability to use nanocellulose reinforcements in more traditional liquid molding processes is desirable.

3.3 Liquid Molding Processes: Resin Transfer Molding and Its Derivatives

Liquid composite molding (LCM) processes, which include technologies such as resin transfer molding (RTM), vacuum-assisted RTM (VARTM), and vacuum-assisted resin infusion, are used to produce net-shaped composites parts (see Fig. 15.5). For LCM processes, a preform is first created from reinforcing fibers, typically in the form of random, woven, or stitched fiber mats made from carbon, glass, or other materials. Next, the preform is inserted in a mold that matches the dimensions of the desired part, and the mold is closed (in case of the rigid mold processes such as RTM) or covered with a flexible sheet (in case of the soft mold processes such as VARTM). Then, a low viscosity thermosetting resin such as epoxy, polyester, phenolic, or vinyl ester resin is mixed with a hardener and injected under pressure (in the case of the RTM-like processes) or imbibed under vacuum (in the case of the VARTM-like processes) into a closed mold containing the preform. The resulting part is cured at room temperature or under a strictly controlled mold-temperature cycle till the end of the curing reaction. Finally, the cured hardened part is extracted and ready for use after minimal machining.

Of the different LCM processes, RTM is characterized by small cycle times and is appropriate for mass-producing medium-sized parts with good dimensional control. VARTM, on the other hand, is a method of choice for producing large composites parts such as boat hulls; however, it is hampered by large cycle times. The resin and fibrous reinforcements for LCM processes are usually obtained from artificial, man-made sources.

Swelling of fibers, used as reinforcing materials, affects the porosity and permeability of fiber mats; thus, swelling plays an important role in the mold-filling simulations. Swelling reduces pore size and porosity, which results in a reduction in permeability. The thickness growth or swelling measurement can enable mold designers to estimate the porosity and permeability change during the mold-filling processes such as LCM. In the swelling tests on nanocellulose films [72], the thickness of NFC films increased up to averages of 242 % and 159 % for water and the bio-derived epoxy after 2 min. The rate of the increase is significant at the initiation of the soaking procedure then stabilizes within a minute of the initiation of the swelling tests (Fig. 15.6). The variability in the thickness within the sheet, which results in different starting points for each specimen can be attributed to some of the variability observed. The main reason for higher swelling rate of NFC films in water is hydrogen bonding of water molecules to the free OH groups present in cellulose molecules.

Recently NFCs in the form of aerogel-like or scaffolds with elaborate structures at different scales have been produced [90–94]. Such structures with high porosities and large surface area for NFCs suggest a way forward for the use of NFCs as composite reinforcement in the form of LCM preforms. If successful, such an approach will lead to a new way of producing scalable nanocomposites through the LCM technology.

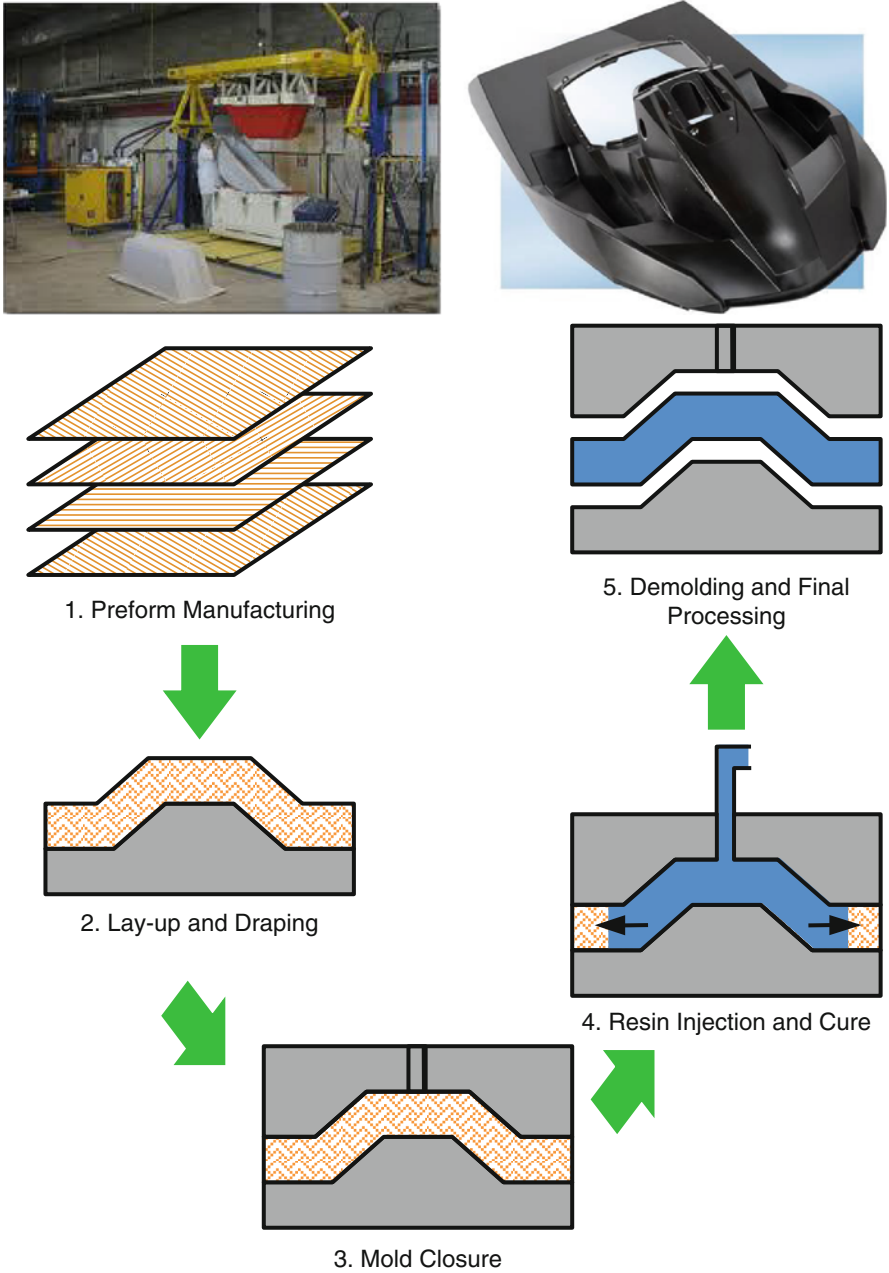
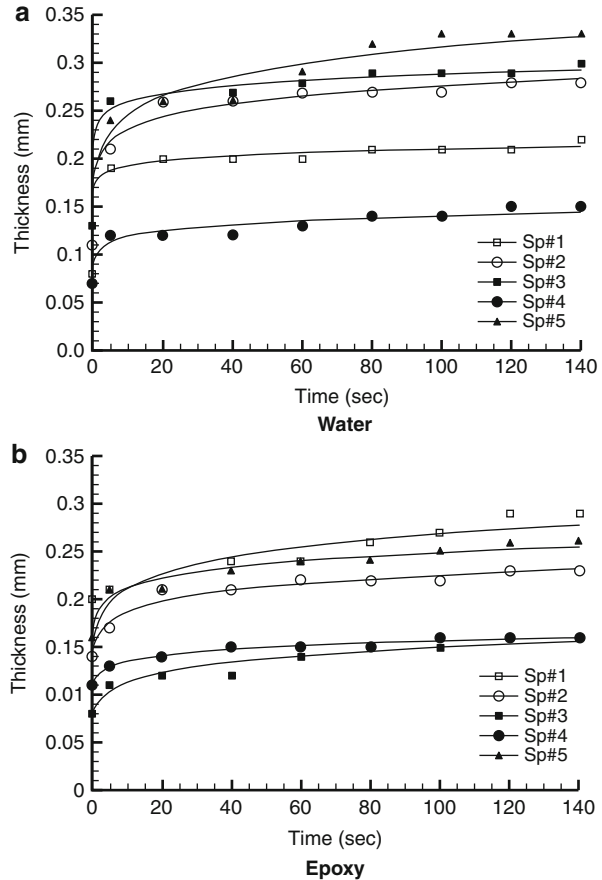


Fig. 15.5 (Top left) An example of RTM setup. (Top right) A Jet-Ski part made using RTM. (Bottom) The main process steps while making the RTM part

Fig. 15.6 Swelling of cellulose nanopaper in water and epoxy (Reprinted from Masoodi et al. [88], with permission from Elsevier)



Some preliminary studies were conducted by the authors to test the effectiveness of using a NFC aerogel-like structure as a reinforcement in LCM processes. First, we investigated whether the pore space inside the spongelike NFC reinforcement was interconnected and hence amenable to complete wetting through a forced resin flow inside an RTM/VARTM mold. An effort was made to study the morphology of pores through a micro-CT scan of the aerogel samples where significant interconnection of pores was observed. The use of liquid hexane with its low surface energy enabled it to be spontaneously imbibed (“wicked”) into the reinforcement (Fig. 15.7, left). A fairly high degree of saturation with the liquid behind a sharp liquid front indicated the presence of a large fraction of interconnected micro-sized pores and pointed to its suitability as an LCM preform. Later, a small RTM mold was prepared, and slices of NFC aerogels created through the freeze-drying process were placed inside the mold and closed. Later an epoxy resin was injected in order to completely impregnate the NFC preform and was allowed to cure. The dog-bone specimen extracted

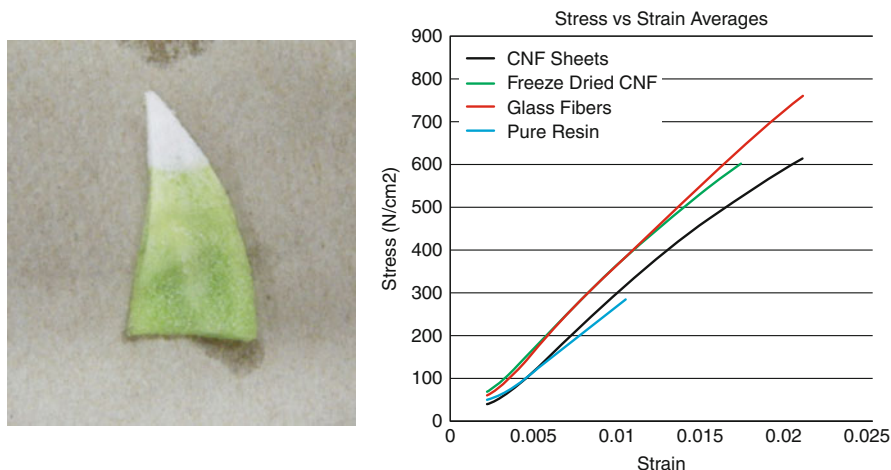


Fig. 15.7 (Left) A wicking test done with a freeze-dried NFC preform created at Forest Products Lab, Madison, shows the clear movement of a green-dyed hexadecane through the porous specimen, thereby demonstrating the interconnection of pores and the possibility of creating polymer composites by impregnating the specimen with resin using the RTM technology. (Right) A comparison of the uniaxial tension test results indicates that the freeze-dried NFC is performing as well as glass fiber in reinforcing the epoxy-based composite

from the mold was subjected to a uniaxial tension tests according to ASTM standards. Figure 15.7 (right) compares the stress–strain curves for the freeze-dried NFC sample vis-à-vis the glass and pure resin samples for different volume fractions. These results may indicate that freeze-dried NFC structures or aerogels are capable of creating large NFC nanocomposites parts using the LCM technology.

3.4 Outlook on Process Modeling LCM for Making NFC Composites

In any LCM process, complete filling of the mold with adequate wetting of fibers is the mold designer's primary objective [95]. Incomplete filling in the mold leads to the production of defective parts with dry spots. It is also important for the mold designer to minimize fill time and fluid pressure buildup during the filling process (especially in RTM) to make the technology cost-effective in a manufacturing environment. Many factors affect the filling of a mold, including the permeability of the fiber mats, the presence of gaps in the mold, the positions of inlet and outlet gates, and the rates of resin injection from different inlet ports. Often, it is not possible for the mold designer to visualize and design an adequate system for resin infusion by intuition alone; as a result, mold-filling simulations are used to optimize mold performance [96–107]. Numerical simulations allow designers to optimize mold design in virtual space quickly and economically.

The trend of using LCM for making natural-fiber composites is beginning to grow [108–111] due to the short cycle time and automation friendliness of the process that lends itself particularly well to use in the high-volume automotive sector; however, unlike synthetic fibers, natural fibers absorb liquid and swell, thereby exhibiting a very different response during LCM mold filling. Until recently, the conventional approaches to model mold filling in natural-fiber mats involve changing the permeability of fiber mats in an ad hoc manner [109]. However, Masoodi and Pillai [112] were the first to propose a completely new set of flow governing equations for isothermal conditions (under low curing rate and test conditions) that were derived using the rigorous and reputed volume-averaging method for natural-fiber mats. Pillai et al. were also the first to incorporate these equations into their finite element/control volume-based LCM mold-filling simulation [96]. The new mold-filling physics developed for swelling LCM preforms, when rigorously tested against experiments, was found to be superior to the conventional flow physics used for non-swelling preforms [112, 113].

Until very recently, NFCs have been produced in very small quantities, thereby rendering them exorbitantly expensive for mass production-type engineering applications; hence, there had been little attempt to use them as reinforcement in LCM processes until now. However, due to the establishment of several pilot plants around the world (including one at Forest Products Lab, Madison) for the production of NFC, the cost of NFC is likely to come down drastically and its availability is being ramped up. As a result, it may become economically feasible to use NFC reinforcements in LCM for making industrial-scale green composites. Consequently there have been some attempts to study the swelling and liquid-absorbing properties of NFC reinforcements [114] as well as develop mathematics for modeling resin flow in liquid-absorbing, swelling porous media created by NFC inside an LCM mold [115]. The future will witness a rapid development of the processing science for producing NFC-based thermoset composites using NFC reinforcements with LCM processes.

4 Mechanical Characterization

Thermoplastic materials have been previously used with nanocellulose materials and offer important advantages of recyclability and high fracture toughness [116–118], and a review of the mechanical properties of these composites can be found elsewhere, for example, in Siró et al. [23]. In this section, we discuss some of the mechanical characterization results of nanocellulose thermosetting composites. Continuous nanocellulose reinforcements have not progressed sufficiently that they have been used in composites yet and are not discussed. A summary of the properties reported for thermosetting materials is shown in Table 15.4.

4.1 Stiffness and Strength Properties

The stiffness and strength properties are highly dependent on the form of nanocellulose reported. The mechanical testing in the literature is mainly for thermoplastic resins;

Table 15.4 Survey of mechanical properties of several thermosetting NFC composites

Resin	Nanocellulose form	Process	Strength (MPa)	Initial elastic modulus (GPa)	Strain to failure (%)	References
Phenol formaldehyde	NFC film (5–20 %wt fibers)	Press	201–216	4.16–4.84	12.6–14.7	[145]
Phenol formaldehyde	NFC (14.4–27.9 %wt resin)	Press	300–375 (bending)	16–20 (bending)	–	[146]
Melamine formaldehyde	NFC film (13 % wt fiber)	Press	142	16.6	0.81	[147]
Epoxy	NFC film (0–5 % fiber vol.)	Press	–	1.5–2.9	–	[88]

however, limited work has been reported. Of these studies reported, using a hot press process is generally the most preferred. Distributed or particulate composites based on nanocellulose benefit from the interactions with the resin and relatively high aspect ratios of the cellulose particles or fibers. In work by Ruiz et al. [87] on composites from NFC and aqueous suspensions of epoxy, NFC displayed large aspect ratios and an ability to associate by means of H-bonds. Using an aqueous suspension of epoxy avoided the problem of high viscosity that would result if a conventional, reactive epoxy was simply mixed with the CNCs. The reinforcement benefits were linked to strong interactions between the CNCs and epoxy network and the percolating network linked by H-bonds between the NFC. The effect of fiber content on the mechanical and thermal expansion properties of biocomposites based on NFC has also been reported [119]. A linear increase in Young's modulus was observed at fiber contents up to 40 wt%, using a phenolic resin. The results also showed a correlation between the coefficients of thermal expansion (CTE) relative to fiber content, indicating the effective reinforcement attained by the NFC.

The incorporation of NFC into epoxy has been found to greatly increase the glassy storage modulus. At 30 °C, this modulus increases from 2.6 GPa for neat epoxy to 3.1 GPa for 5 wt% NFC–epoxy film [85]. Higher increases are reported for temperatures above the glass transition temperature temperatures. The rubbery storage modulus at 130 °C increases from 9.7 MPa for neat epoxy to 37.3 MPa for 5 wt% NFC–epoxy film. In another example, Ruiz et al. found that adding NFC up to about 2 % in an epoxy resin increased the mechanical properties, but further addition of NFC led to agglomeration and reduced thermal and mechanical properties [87]. The pressing method has been found to be the most common in the literature for processing of thermosetting composites with NFC reinforcements. Nakagaito and Yano [120] used a compression molding technique of NFC sheets impregnated with phenol formaldehyde to achieve a Young's modulus and bending strength of up to 19 GPa and 370 MPa, respectively. Compared to a starch matrix with 70 wt% NFC which showed a modulus of 6.2 GPa and a tensile strength of 160 MPa [121]. The differences between regular cellulose and NFC and their relationship to pressing

pressure have been previously examined [53]. Processing the same pulp to NFC, the researchers found increased modulus and strength from the NFC-based composites when combined with a phenol formaldehyde matrix. The Young's modulus of NFC-based and pulp-based composites using phenolic resin as binder was very similar, around 18–19 GPa; however, the bending strength peaked at 370 and 260 MPa for NFC and pulp-based composites, respectively [88, 120]. The planar NFC reinforcements also result in significant amounts of porosity ($\sim 10\%$) that can affect the stiffness values [52]. Improving the processing of these composites can yield some improvements in the matrix-dominated properties.

4.2 Fracture Properties

Although the tensile properties are commonly tested, the amount of research on fracture properties of nanocellulose composites is limited. Researchers have proposed hierarchical systems of reinforcement incorporating NFC to take advantage of the fracture toughness benefits provided at different length scales. While not in a thermosetting resin material, Okubo et al. [122] dispersed NFC reinforcement around bamboo fibers in a polylactic acid (PLA) matrix and showed that the additional NFC improved the fracture properties by preventing sudden crack growth. Adding 1 wt% of NFC resulted in an increase of the fracture energy by 200%. Although this approach has not been investigated in thermosets, hybrid systems incorporating NFC have also been proposed for carbon fibers reinforced with an epoxy matrix [123]. Adding 2 wt% of NFC resulted in improved fracture toughness and higher glass transition temperatures but with limited increases in the tensile strength and modulus. Fracture testing on NFC sheet-reinforced composites panels has also been reported [88]. Figure 15.8 shows the lack of fiber bridging observed in the propagating crack in a layered NFC/epoxy composite [88]. The crack is retarded manually by not having a self-similar growth behavior. The fracture surface does not show significant mechanical interlocking between the two surfaces. Increasing the fracture energy required to separate the surfaces across

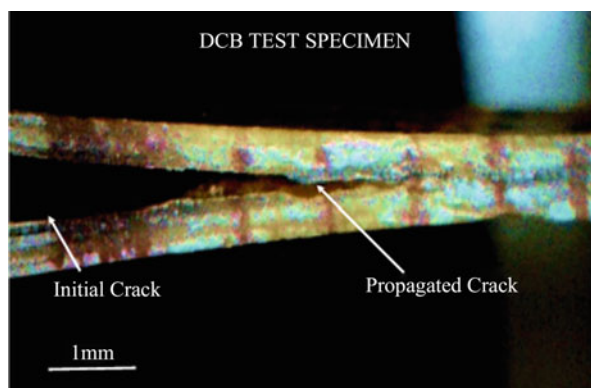


Fig. 15.8 Crack propagation in a nanpaper composite specimen (Reprinted from Masoodi et al. [88], with permission from Elsevier)

the NFC sheets will result in a larger fracture toughness of the NFC composite and overcome the limitations associated with discrete layers of the nanocellulose material. The planar reinforcements clearly have benefits when loaded in the in-plane directions; however, out of plane stresses show the potential for the crack growth in between the planar layers.

5 Nonmechanical Characteristics

The benefits of nanocellulose are not restricted to mechanical property improvements of composites. Researchers have envisioned that, with proper processing, they can lead to environmentally safe, lightweight composites with unique properties (e.g., transparency and barrier properties) for application in automotive manufacturing, packaging, medicine, energy storage devices, sensors, and electronics [16, 23, 124]. Nanocellulose films could be used as barrier materials, or conversely, high-porosity aerogels could be used to allow flow of gases while absorbing moisture due to their hydrophilic nature [125]. Nystrom et al. [126] coated wood-based nanocellulose with polypyrrole using in situ chemical polymerization to obtain an electrically conducting composite. Many of these applications are in their infancy as work continues to better characterize the behavior of these materials. Some of the attributes that highlight the potential of nanocellulose for these various applications are discussed here.

Nanocellulose composites can offer transparency for a variety of potential applications ranging from flexible display devices to armor applications. The small cross section of the fibers does not result in light scattering even at high reinforcement ratios; thus, strong, transparent composites are possible using NFC. Excellent transparency of 80 % or more has been reported for neat NFC films [12, 127] and NFC composites [8, 17]. Polishing or coating NFC films with resins has been used as a method to increase the transparency by eliminating the surface scattering [12, 17]. For example, Okahisa et al. [17] studied the use of optically transparent wood–cellulose nanocomposite as a base substrate for flexible organic light-emitting diode displays. Acrylic resins were used to achieve the desirable combination of high flexibility and low coefficient of thermal expansion.

Low coefficient of thermal expansion (CTE) in composites is desirable in electronic applications as expansion can lead to device failure [16, 17]. Okahisa et al. suggest CTE values should be below about 20 ppm K⁻¹ for printed OLED displays, whereas many foldable plastics have CTE values more than an order of magnitude higher than this target [17], and polyethylene terephthalate (PET) has a CTE of about 50 ppm K⁻¹. Okahisa et al. achieved a coefficient of thermal expansion of 12.1 ppm K⁻¹ by removing excess surface resin layers from the NFC composite. CTE values of less than 10 ppm K⁻¹ for NFC composites have also been reported [12]. Such low CTE values, along with high transparency, suggest that NFC composites may be useful for a wide variety of applications including substrates for flexible electronics or display devices.

Nanocellulose films have been shown to exhibit excellent barrier properties, especially at low levels of humidity [18–21, 128]. The water vapor barrier of

polymer films has been observed to be improved by cellulose nanoreinforcements [129]. The mechanism is related to creating a more complex path leading to a slower diffusion and lower permeability. Azeredo et al. [130] studied the barrier properties of a nanocomposite film with 15 % NFC and plasticized with 18 % glycerol and compared to synthetic polymer films. The strength and stiffness were found to be comparable to the synthetic polymer. The water vapor barrier properties were enhanced but not to the level of the synthetic materials. The surface rather than the core dominated the diffusion process. CNC film was found to be much more permeable to gases than NFC [131]. Related to this is application of nanocellulose in the area of active packaging. In this application, cellulose nanocomposites have been proposed where nanoparticles can be used for scavenging purposes in removing oxygen and odor chemicals or to release preservatives or color where and when required [132]. Biodegradable cellulose nanocomposites are a potential material for replacing synthetic materials in the food packaging industry. They can be used to improve the mechanical and barrier properties of bio-polymers and also provide antimicrobial activity, enzyme immobilization, and biosensing [133].

Cellulose nanocrystals, like many polysaccharides, are self-ordering and thus produce a number of interesting optical properties. The birefringence of cellulose nanocrystals has long been known, and ordered chiral nematic phases were seen to be preserved in films of cellulose and cellulose derivatives more than two decades ago [134, 135]. Gray and colleagues observed that when solidified by evaporation, cellulose nanocrystal films produced “helical structures resembling those in various biological skeletal structures” [136]. Revol et al. describe cellulose nanocrystal films that have helical arrangement of nanocrystals and that reflect polarized light [137, 138]. The wavelength of light reflected by these films was reported to be controllable across the visible, infrared, and ultraviolet spectrum. The colors were reported to change with viewing angle, thus making them suited for security papers and other applications.

6 Future Trends

With changing consumer perceptions, increased ecological considerations, and technological advances, recent trends in sourcing materials from rapidly renewable, natural resources are likely to continue. From a composites perspective, this includes not only the polymer matrices and additives but the reinforcements as well. Reinforcements from nanocellulose offer one interesting possibility. Nanocellulose reinforcements offer potential advantages in specific properties related to their lower density and other advantages such as low CTE, transparency, barrier properties, etc.

However, the use of nanocellulose as a reinforcement is in its infancy, and the full reinforcing potential of these materials has yet to be realized partly because of issues related to scaling manufacturing processes. To date, the availability of significant quantities of nanocellulose has prevented more rapid wide-scale research and development efforts related to their use. However, recent

announcements of commercial and government pilot- and plant-scale production facilities will likely improve the situation [139]. NFCs have begun receiving additional attention as a reinforcement material because of reductions in the energy requirements for breaking down cellulose fibers to NFC [140]. While much recent progress has been made, there are many challenges remaining to efficiently and economically use it as reinforcement. More efficient and effective strategies need to be found for producing nanocellulose with optimal characteristics. Widespread application of these materials will require additional research to address the issues related to their hydrophilic nature in many applications. Techniques and appropriate chemistry are needed to adequately disperse nanocellulose reinforcements or convert them into a useful form for incorporation into a variety of matrices and strongly bond them to it. More efficient control of structure on multiple scales is needed to tailor performance. For example, better control of the porosity and fiber volume is likely to result in improvements in strength, stiffness, and fracture behavior. Development of new analytical methods is necessary for simulation of processing and also prediction of the mechanical properties of nanocellulose-based structures. The process modeling effort will be required to link the modeling of NFC distributions to optimize properties. Appropriate applications need to be identified, investigated, and demonstrated. Health and safety issues related to nano-scale size need to be understood and addressed as well.

It is unlikely that these developments will occur in isolation and will need to be incorporated in to larger infrastructures. For example, paper mills could be repurposed for the production of biofuels and materials that could potentially mitigate climate change through the reduction of greenhouse gas emissions [141]. If high-value applications can be found, it may be possible to integrate nanocellulose production into the material flow of these biorefineries, where it could potentially help improve economics [141].

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