



Towards industrial-scale production of cellulose nanocomposites using melt processing: A critical review on structure-processing-property relationships

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ARTICLE INFO

Keywords:

Mechanical properties
Interface/interphase
Surface treatments
Thermoplastic resin

ABSTRACT

Cellulose nanomaterials (CNMs) naturally exist in plant biomass. The success of extraction of CNMs opened up a new era of using plant biomass for innovative industrial applications. Because CNMs are abundant, renewable, biodegradable, transparent, light weight and low in cost, they are ideal materials for large volume applications such as packaging, automotive, building and infrastructure. In many potential application areas, CNM-enabled products appear in a composite form, mostly polymer composites. The industrial-scale manufacturing of CNM/thermoplastic composites remains as a set of unsolved problems for academia and industry. A prime challenge in applications is the nanoscale dispersion of CNMs in thermoplastic matrices during melt processing. Both bench-scale and pilot-scale studies have been conducted to solve the dispersion issue of CNMs. In this article, research related to the dispersion of CNMs in thermoplastic matrices during melt processing were critically reviewed. All research papers were classified into three groups: chemically-aided dispersion, physically-aided dispersion and mechanically-aided dispersion. Numerous factors affect the CNM dispersion and the mechanical performance of its nanocomposites. There are material-related factors, including CNM types and forms, polymer matrices, surface modification, coupling agents, etc. Extrusion processing parameters also play a significant role, covering screw rotation speed, extrusion barrel temperature settings and screw design. In addition, the material-related factors interact with the processing-related factors. Understanding all factors and their interactions are important for moving CNM nanocomposites research a step further towards industrial-relevant production, which is the final ambitious goal of this manuscript.

1. Introduction

Polymeric materials are widely used in many industrial sectors for a variety of applications. Most petroleum-based materials are not biodegradable. Today, the increasing use of fossil-based non-biodegradable products is becoming a serious concern for the future of the earth because of their impact on increased greenhouse gas emissions, air and

ocean pollution, habitat destruction and global climate change. So, it is becoming crucial to retreat from depleting fossil fuel-based materials and utilize environmentally benign renewable bio-based feedstocks. The most common and extensively used sustainable materials nowadays are cellulosic materials. Cellulose is the most abundant natural polymer on earth [1]. When cellulose is mechanically fibrillated or chemically hydrolyzed under controlled conditions, nanoscale cellulose materials are

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<https://doi.org/10.1016/j.compositesb.2020.108297>

Received 5 March 2020; Received in revised form 17 July 2020; Accepted 23 July 2020

Available online 26 August 2020

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generated [2–4]. Cellulose nanomaterials (CNMs) are a unique category of nanomaterials that have been intensively investigated by the scientific community over the last two decades with a number of review articles published [3,5–7]. Like other nanomaterials, CNMs are strong and stiff [8]. The unique attributes of CNMs that set them apart from other nanomaterials include biodegradability, light weight, transparency and relatively low cost [1,3]. CNMs can be generated from many sources such as wood, plants, tunicates, algae and bacteria [3]. There are many types of CNMs including cellulose nanofibrils (CNFs), cellulose nanocrystals (CNCs), (2,2,6,6-tetramethylpiperidin-1-yl)oxodanyl (TEMPO)-CNFs, tunicate cellulose nanocrystals, algae cellulose and bacterial cellulose (BCs) [3]. The morphology of different types of CNMs is shown in Fig. 1. CNCs and CNFs are the most popularly researched among all CNM types because of their general availability. CNCs and CNFs possess distinct features. CNCs are of rice-like appearance, with a diameter of tens of nanometers and a length of 50–500 nm, 100% cellulose and high crystallinity (54–88%) [3]. CNFs are of spaghetti-like shape, with 10–100 nm wide and up to several micrometers long. CNFs contain both cellulose and hemicellulose, with a medium crystallinity (51–69%) [3]. The axial tensile strength and modulus of CNFs are estimated to be ~3 GPa and ~136 GPa [9]. CNCs are projected to possess similar values (~7 GPa in strength and ~110 GPa in modulus) [10,11]. Another special form of CNMs is microfibrillated cellulose (MFCs) which also appeared in many studies [12–15]. There still remains some debates about CNM terminology [5]. Based on our own observations from cited research, MFCs have a lower degree of fibrillation and larger portion of microscale fibers as compared to CNFs. The excellent mechanical properties of CNMs are comparable to conventional materials like glass fibers, carbon fibers and Kevlar fibers, which make them a potential green replacement for synthetic fibers used in the polymer composites industry [3,5].

Among consumed plastics, 90% are thermoplastics and the rest are thermosets [20]. Thermoplastics are recyclable and near zero emission during processing, which makes them favored by consumers compared to thermosets. However, thermoplastics are not as mechanically robust as thermosets. Because of this, fillers (e.g. fibers) are used to reinforce thermoplastics to create stronger composites. With the development of nanotechnology, nanofibers have been widely explored in reinforcing thermoplastics [21]. Along with other nanofibers, CNMs are heavily investigated as a filler for polymers, especially by researchers in the wood and paper industry and academia [3,5–8]. The high research activity is stimulated by the enormous potential applications of cellulose/polymer nanocomposites as a new class of materials for use in fields including packaging, automobile, electronics, textile, infrastructure, construction, medical devices, membranes, batteries and many more [3,6]. In terms of processing cellulose nanocomposites, almost half of the published research reports used the solvent casting method, which is not easily industrially scalable [8]. In a conventional industrial setting,

fibers and thermoplastics are melt mixed to generate compounds, followed by profile extrusion, compression molding or injection molding processes to yield composite products at high production rates. There are several processing challenges involved in applying CNMs into conventional thermoplastic processing systems.

- 1) CNMs are typically produced as aqueous suspensions with low solids content. CNMs are required to be in a dry form, for direct incorporation into thermoplastics under current production systems. However, CNMs agglomerate during drying, attributable to water evaporation and extensive intermolecular hydrogen bonding (H bonding) [22].
- 2) Using CNM suspensions in melt compounding is not ideal because thermoplastic pellets also have to be dried before compounding to avoid moisture impacts on the final compounds.
- 3) Another issue regarding the mixing of CNMs with thermoplastics is the limited dispersion of nanofibers in the polymer matrix. Thermoplastics are usually hydrophobic and low in surface energy, while CNMs are often hydrophilic with high surface energy. During melt mixing, thermoplastics cannot adequately interact (wetting) with the surface of CNMs and disperse them effectively throughout the polymer matrix. Therefore, many efforts have been spent on surface modification of CNMs via chemical or physical approaches [5, 23–31]. Currently, no single surface modification approach can address the large-scale manufacturing of CNM/thermoplastic composites without production/environmental concerns.

Many dry forms of CNMs can be generated: films from air/oven drying, micron-size powder from spray drying, porous and micron-size powder from freeze-spray drying and aerogels from freeze drying and supercritical drying [32]. So far, the direct products of freeze and spray drying have been found suitable for melt compounding with current technology. Besides obtaining dry CNMs for melt mixing, other innovative incorporation methods are also being investigated. Those studies include in-situ polymerization, polymer wrapping, wet compounding and in-situ fibrillation from pulp, etc. [12,33–36].

2. Objectives

Most review articles on cellulose nanocomposites have a rather broad coverage of content including CNM production, CNM modification, CNM/thermoplastic composites, CNM/thermoset composites, etc. [1,3,5,6,8,37,38]. There has been a sizeable research (~100 articles) over the years, attempting to address issues related to the dispersion of CNMs in thermoplastic polymers during melt processing. A comprehensive summary and deep analysis on these research is highly desirable. This review will solely focus on efforts to improve the dispersion of

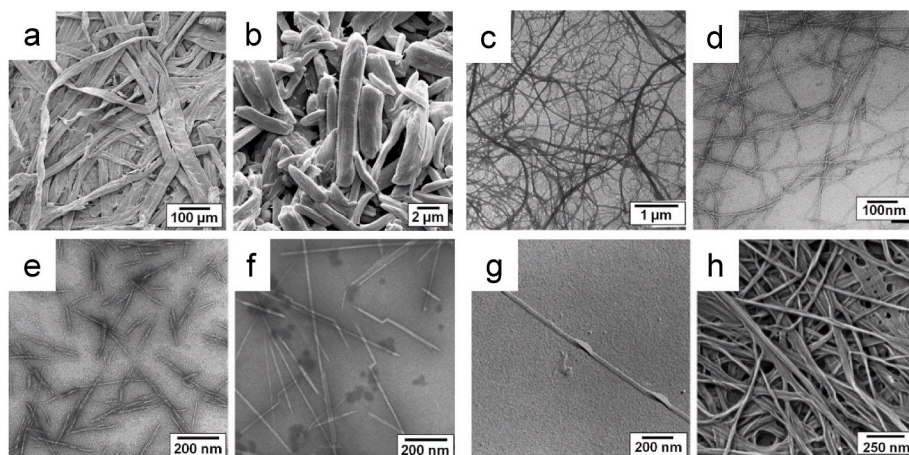


Fig. 1. Cellulose material types: (a) Scanning electron microscopy (SEM) image of wood fiber, (b) SEM image of microcrystalline cellulose, (c) Transmission electron microscopy (TEM) image of MFC, (d) TEM image of TEMPO-CNFs, (e) TEM image of CNCs from wood, (f) TEM image of CNCs from tunicate, (g) TEM of algae cellulose particles and (h) SEM image of BCs. Fig. 1 (a), (b), (e) and (f) were reprinted from Refs. [3] with permission from the Royal Society of Chemistry. Fig. 1 (c) was reprinted from Ref. [16] by permission of John Wiley & Sons, Inc. Fig. 1 (d) was reprinted with permission from Refs. [17], copyright (2007) American Chemical Society. Fig. 1 (g) was reprinted from Ref. [18]. Fig. 1 (h) was reprinted with permission from Ref. [19], copyright (2007) American Chemical Society.

CNMs in thermoplastics using the melt mixing approach because of its high industrial relevance. Information obtained from the myriad research activities was critically extracted, summarized and evaluated. The dispersion characteristics and mechanical properties are summarized in Tables 1–3, corresponding to the chemical, physical and mechanical treatments used in the CNM-thermoplastic mixing processes. Variables affecting the dispersion and mechanical performance of cellulose/thermoplastic composites are summarized in Table 4. A comparison of all the treatments cited in this manuscript is summarized in Table 5. It is expected that this review will help gains insight, guidance, and inspiration towards the pilot/industrial-scale production of cellulose/thermoplastic nanocomposites.

3. Chemically-aided dispersion

Hydroxyl groups contained on the cellulose backbone in CNMs are the primary cause of extensive agglomeration and insufficient dispersion of CNMs in various polymer matrices. One straightforward solution is to convert hydroxyl groups to other functional groups (typically hydrophobic in nature) that do not induce H bonding. The hydroxyl groups on the surface of CNMs offer facile routes for surface modification, including polymer grafting, silanization, acetylation, esterification, etc.

3.1. Polymer grafting

Polymer grafting modification of CNMs refers to a chemical process where functional polymers are added onto the surface of CNMs [45]. Polymer grafting offers desirable properties to cellulose such as hydrophobicity, wrinkle resistance, wear resistance, etc. [46] Polymer grafting occurs in two major approaches: “grafting to” and “grafting from” as shown in Fig. 2 [46]. The “grafting to” method depicts an occasion where the reactive end functional group of long chain polymers are directly added onto backbone polymer [47]. “Grafting to” approach tends to provide low graft density because the bulky chain of the

polymer hinders its attachment to a targeted surface [48]. The most common method is “grafting from” where monomers are first added onto the CNMs surface, followed by polymerization [47]. Grafting using this method results in high grafting density because the living end of polymer during polymerization is easy to access. “Grafting from” can be achieved in several ways: free radical polymerization, ionic & ring opening polymerization and living radical polymerization [45]. As seen in Table 1, both “grafting to” and “grafting from” methods were applied to modify CNM surface with long chain polymers for their subsequent melt compounding with thermoplastics [24,33,39,40]. Success was achieved on improving the dispersion of CNMs in a thermoplastic matrix via the “grafting from” method [33,39]. For example, ϵ -caprolactone (ϵ -CL) was grafted and polymerized from CNC surfaces by ring opening polymerization [39]. Modified CNCs were recovered by precipitation, filtering and vacuum drying, followed by nanocomposite preparation via melt compounding and injection molding. AFM topology, as shown in Fig. 3, exhibits well-dispersed CNCs in the PCL matrix, estimating an average fiber diameter of 40 nm. The “grafting from” modification doubled the E' of CNC (8 wt%)/PCL at 20 °C [39]. However, no static mechanical properties were reported in this study. In another study, small amounts of maleic anhydride polypropylene (MAPP) pellets (~2 wt%) were added during melt compounding of spray-dried (SD) CNF and polypropylene (PP) by the “grafting to” method [40]. There was no visual evidence for better dispersion of SDCNF in PP after being modified by MAPP. One of the reasons for the lack of dispersion of CNMs in PP may be the low ratio of chemicals/glucose as shown in Table 4 [24,40]. Low ratio means most hydroxyl groups were not modified. Therefore, H bonding-induced agglomeration was most likely not prevented. To be more convincing, the degree of substitution (DS) should be reported in future studies to prove the grafting efficiency. Regardless of insufficient dispersion, the tensile properties of SDCNF/MAPP/PP composites were better than the untreated SDCNF/PP or MAPP/PP composites, indicating the benefit of using coupling agents for mechanical-property enhancement [40].

Table 1
Chemical modifications performed on CNMs for melt processing.

Methods	Chemicals ^a	CNM type loading	Polymer ^b	Dispersion ^c	Tensile Properties ^d			
					Modulus (GPa)	Strength (MPa)	Elongation at break (%)	Ref.
Grafting from	PBG	CNC/10%	PBAT	Yes	0.12→0.12 ^e (0%) ^f	6.5→6.5 (0%)	-	[33]
	PCL	CNC/(2,4,8)%	PCL	Yes	-	-	-	[39]
Grafting to	MPEG-NH ₂	CNC/(2-20)%	PS	Unsure	-	-	-	[24]
	MAPP	CNF/30%	PP	No	4.0→3.8 (-5%)	24.5→33.0 (35%)	4.4→4.0 (-10%)	[40]
Silanization	APS	CNF/0.5%	PLA	N.A.	1.39→1.87 (35%)	42→43 (2%)	9→14 (56%)	[41]
	MPS	CNF/30%	PP	No	2.67→3.09 (16%)	24.4→26.0 (7%)	-	[14]
Acetylation	AA	CNF/5%	PLA	No	3.6→3.5 (-3%)	71→69 (-3%)	2.7→2.9 (7%)	[42]
	AA	BC/6%	PLA	Unsure	4.6→5.0 (9%)	74→84 (14%)	0.6→0.8 (33%)	[43]
	AA	MFC/(1,3,5)%	PA(4,10)	No	-	-	-	[15]
	AA	MFC/10%	HDPE	No	2.08→2.25 (8%)	34.2→39.6 (16%)	-	[23]
Esterification	ASA	MFC/10%	HDPE	Yes	2.08→3.38 (63%)	34→54 (59%)	7.5→3.5 (-53%)	[29]
	MAH	CNC/(1,3)%	LDPE	No	-	-	-	[26]
	Acid, HA, DA	BC/5%	PLA	N.A.	1.89→1.98 (5%)	60.9→68.5 (12%)	2.41→2.69 (12%)	[44]
	DDC	CNC/0.5%	PLA	Unsure	2.81→1.93 (-31%)	42→43 (2%)	9→13 (44%)	[41]
	BA	CNC/1%	PLA	Yes, slightly	3.29→4.74 (44%)	52.76→59.91 (14%)	2.82→3.64 (29%)	[25]
	VA	CNC/1%	PLA	Yes	3.29→5.28 (60%)	52.7→65.0 (23%)	2.82→4.79 (70%)	[27]
	Acid, AC	MFC/~10%	HDPE	Yes	2.08→3.32 (60%)	34.2→51.2 (50%)	-	[23]

^a PBG: poly(butylene glutarate), MPEG-NH₂: Methoxypoly(ethylene glycol) amine, PCL: poly(ϵ -caprolactone), MAPP: maleic anhydride polypropylene, PHBV: poly(3-hydroxybutyrate-co-3-hydroxyvalerate), APS: 3-aminopropyl triethoxysilane, MPS: [3-(methacryloyloxy)propyl] trimethoxysilane, AA: acetic anhydride, ASA: alkenyl succinic anhydride, MAH: maleic anhydride, Acid: acetic acid, HA: hexanoic acid, DA: dodecanoic acid, DDC: dodecanoyl chloride, BA: benzoic acid, VA: valeric acid, AC: acid chlorides.

^b PBAT: poly(butylene-adipate-co-terephthalate), PS: polystyrene, PP: polypropylene, PLA: polylactic acid, PA(4,10): polyamide(4,10), HDPE: high-density polyethylene, LDPE: low-density polyethylene.

^c The dispersion degree was judged by authors based the electroscopic (EM) graphs in references, instead of what reference authors claimed. Yes means nanoscale dispersion was achieved, No means nanoscale dispersion was not achieved. Unsure means we cannot confirm the dispersion from related EM graphs. N.A. means related EM graphs cannot be found.

^d Some of the mechanical property data were directly estimated from graphs containing such information if no table format was provided in original papers.

^e numbers before “→” are for control samples and numbers after “→” are for treated samples.

^f numbers in the parenthesis are change percentages of tensile properties

Table 2
Physical modification of CNMs for dispersion and melt processing.

Methods	Chemicals ^a	CNM type loading	Polymer ^b	Dispersion ^c	Tensile Properties ^d			Ref.
					Modulus (GPa)	Strength (MPa)	Elongation at break (%)	
Carrier	PHB	CNF/(1-10)%	PLA	No	-	-	-	[65]
	PVOH	CNF/(1-10)%	HDPE	No	-	-	-	[66]
	TPS	CNF/(10,15)%	PP	Unsure	-	-	-	[62]
	EVOH	BC/2%	PLA	Yes	1.89→2.05 ^e (8%) ^f	42.67→46.29 (8%)	2.67→2.54 (-5%)	[67]
Coating	PA6	CNC/1%	PA6	Yes	1.87→1.44 (-23%)	50→52 (4%)	33→73 (121%)	[68]
	PEO	CNC/(3,9)%	LDPE	Unsure	-	-	-	[69]
	PEO	*CNC/(2-20)%	PS	No	-	-	-	[24]
	PVOH	CNC/5%	PLA	Yes	2.69→3.64 (35%)	55.5→67.7 (22%)	9.7→2.4 (-75%)	[34]
	PEG	CNC/(2,5)%	PHBV	No	-	-	-	[70]
Electrospin	PLA	BC/2%	PLA	Yes	1.89→2.16 (14%)	42.67→61.36 (44%)	2.7→3.3 (22%)	[67]
Surfactants	Cationic	CNC/5%	PLA	Yes	2.7→3.1 (15%)	55.5→52.4 (-6%)	9.7→3.1 (-68%)	[30]
	Cationic	CNC/3%	PP	No	0.32→0.23 (-28%)	10.3→11.0 (7%)	15.4→109 (607%)	[28]
	Nonionic	CNC/10%	PP	N.A.	1.3→1.1 (-15%)	24→24 (0%)	5.4→97 (17 times)	[71]
	Nonionic	CNC/10%	HDPE	Yes	0.63→1.54 (144%)	19→35 (84%)	>15→4.8 (-)	[72]
Wet compounding	DMAc/LiCl	CNC/5%	PLA	Yes, partly	? →3.9	? →77.9	? →2.7	[35]
	-	CNC/1%	Plasticized PLA	Yes	? →1.1	? →24.2	? →309	[73]
	Acetone	CNC/1%	Plasticized PLA	Yes	? →0.8	? →28.8	? →31.1	[74]
	-	CNC/5%	PLA /PVOH	Yes	3.64→3.71 (2%)	67.7→66.5 (-2%)	2.4→2.3 (-42%)	[34]
	-	CNC/4%	PP	No	1.2→1.3 (8%)	21.9→21.0 (-4%)	6→5 (-17%)	[75]
	-	MFC/30%	PP	Unsure	? →3.9	? →56.3	? →5.3	[13]
	-	MFC/30%	PP	Unsure	? →4.6	? →71.8	? →3.8	[12]
Solvent masterbatch	Acetone, chloroform	CNC/3%	PLA	Yes, partly	? →3.4	? →65.1	? →2.7	[76]
	Chloroform	CNC/15%	PLA	No	-	-	-	[25]
	Chloroform	CNC/15%	PLA	No	-	-	-	[27]

^a PHB: polyhydroxybutyrate, PVOH: polyvinyl alcohol, TPS: thermoplastic starch, EVOH: ethylene vinyl alcohol, PA6: polyamide6, PEO: polyethylene oxide, PEG: polyethylene glycol, PLA: polylactic acid, MPEG: methoxypolyethylene glycol,

^b HDPE: high-density polyethylene, PP: polypropylene, LDPE: low-density polyethylene, PS: polystyrene, PHBV: Poly(3-hydroxybutyrate-co-3-hydroxyvalerate). PS: polystyrene.

^c The dispersion degree was judged by authors based the electron scopic (EM) graphs in references, instead of what reference authors claimed. Yes means nanoscale dispersion was achieved, No means nanoscale dispersion was not achieved. Unsure means we cannot confirm the nanoscale dispersion from EM graphs. N.A. means related EM graphs cannot be found.

^d Some of the mechanical property data were directly estimated from graphs containing such information if no table format was provided in original papers.

^e numbers before "→" are for control samples and numbers after "→" are for treated samples.

^f numbers in the parenthesis are change percentages of tensile properties.

^g ? means the mechanical properties of control samples of CNM/polymer without any treatment were not reported in the references.

* carboxylated CNC.

3.2. Silanization

Silanes are common coupling agents that are used for polymer composites containing inorganic fillers to improve interfacial compatibility between the fibers and polymer matrix [49]. Among the benefits of using silanes is the reaction medium can be a water/alcohol system, instead of harmful organic solvents. Structurally, water-immiscible silanes contain bi-functional groups. One end of the silane, i.e. alkoxy, should first be converted to silanols before reacting with the hydroxyl groups on cellulose [50]. The other end of a silane is of various functional groups and should be carefully selected based on the physicochemical properties of the targeting polymer matrix. For nonpolar polymers, silanes bearing vinyl groups can be used for potential free radical grafting to the polymer matrix [51]. In this case, initiators should be used to commence the chemical reaction [52–56]. For polar polymers, aminosilanes are better options for improving the interaction with the polymer matrix by acid-based interactions, dipole-dipole interaction or ring-opening grafting [57,58]. The chemistry of silanes can be rather complicated, depending on many factors like the solvent, temperature, pH, concentration, etc. [59] In general, the hydrolysis of silanes into silanols often takes place in acidic (pH = 4) alcohol/water solution with excess alcohol (>80%). The acidic reaction condition promotes the formation of alkoxy silanol mono-, di- and tri-ols, while suppressing the self-condensation of silanols from forming –Si-O-Si- bonds [60].

Reaction time for the hydrolysis of silanes and the following adsorption of silanols onto the cellulose surface should be carefully regulated to reduce the degree of self-condensation [60]. After adsorption and dewatering processes, a heat treatment (>80 °C) for 2 h is required to form the final chemical link (–C-O-Si-) between cellulose and silanols [50]. In reported studies, silanization did not improve the dispersion of CNMs in thermoplastics as displayed in Fig. 4 [14,41]. Reasons for the failures are manifold. First, the chemical/glucose ratios were very low (Table 4), indicating an insufficient surface modification by silanization [14,41]. Second, silanized CNMs may not be properly handled for melt compounding. For example, (3-aminopropyl)triethoxysilane (APS)-treated CNFs were oven dried, and (3-methacryloyloxy)propyltrimethoxysilane (MPS)-treated CNFs were vacuum-oven dried, without mentioning the pulverization process to break dry CNFs into pieces for compounding [14,41]. It is well known that oven drying can create severely agglomerated CNM films. Silanes improved the mechanical properties of CNM/thermoplastic composites by enhancing the interfacial compatibility, just like MAPP. For instance, the tensile modulus and elongation at break of APS-modified CNF (0.5 wt%)/PLA composites were 35% and 56% higher than the unmodified CNF/PLA composites [41]. Increments of 16% and 7% in tensile modulus and strength were observed for CNF (30 wt%)/PP composites after the CNF being treated with MPS [14].

Table 3
Mechanical treatment of CNMs for their dispersion during melt processing.

Method	Factors	CNM ^a	Matrix ^b	Dispersion ^c	Tensile properties ^d			Ref.
					Modulus (GPa)	Strength (MPa)	Elongation at break (%)	
Melt extrusion	screw speed	MFC, FD ^a (1,3,5)%	PA (4,10)	No	-	-	-	[15]
	Compounding routes	CNC, FD 1%	PLA	No	-	-	-	[88]
	screw speed, temp., time	MFC, 4%	Starch	Yes, partly	0.075→0.095 ^e (27%) ^f	2.7→4.0 (48%)	18→17.5 (-3%)	[36]
Extensional flow mixing	C-D plate geometry	MFC 4%	HDPE	No	0.75→0.83 (11%)	15.5→15.9 (3%)	13.3→13.8 (4%)	[89]
Ball mill	ball size, speed, time	BC, 0.5%	PLA	Yes, partly	? ^g →2.31	?→45.4	?→3.4	[90]
Jet mill	pressure, speed	CNF, FD (0.1,0.5)%	PA11	No	?→0.7	?→42	?→167	[91]
Chilled extrusion	screw speed	CNC, FD 10%	LDPE	Yes	0.18→0.27 (50%)	7→13 (86%)	20→460 (22 times)	[92]
	screw speed	CNC, FD 0%	PP	Yes	1.48→1.83 (24%)	34→38 (12%)	7→12 (71%)	[92]
Dry kneading	speed, temp.	LCNF, FD 5%	PP	Yes, partly	1.31→1.45 (11%)	32→35 (9%)	7→566 (80 times)	[93]
Wet kneading	speed, temp.	CNF, wet 10%	HDPE	No	?→2.08	?→34	?→7.5	[23]
	speed, temp.	Pulp, wet 10%	HDPE	No	?→2.15	?→38	?→6.8	[29]
	speed, temp.	CNF, wet 0.05%	PE	N.A.	-	?→15	?→300	[94]

^a FD: freeze drying. LCNF: lignocellulose nanofibrils.

^b PA(4,10): polyamide(4,10), PLA: polylactic acid, PA11: polyamide11, LDPE: low-density polyethylene, PP: polypropylene, HDPE: high-density polyethylene, PE: polyethylene.

^c The dispersion degree was judged by authors based the electroscopic graphs (EM) in references, instead of what reference authors claimed. Yes means nanoscale dispersion was achieved, No means nanoscale dispersion was not achieved. N.A. means related EM graphs cannot be found.

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^g ? means the mechanical properties of control samples of CNM/polymer without any treatment were not reported in the references.

3.3. Acetylation/esterification

Acetylation is a process that creates acetyl groups, $-\text{CH}_3\text{C}(=\text{O})-$, on the CNM surface [31]. Acetylation is a well-known process which has been commercially used for producing cellulose derivatives for many decades [31]. Acetylation typically occurs in organic solvents containing acetic anhydride with catalysts [15,42,43]. CNMs were either dried or solvent-exchanged to organic solvents before acetic anhydride being incorporated. The acetylation reaction lasts for several hours at elevated temperature (30–100 °C). CNMs are subsequently washed to remove remaining chemicals, followed by oven drying before compounding. There appears to be no direct evidence of acetylation improving the dispersion of CNMs in a thermoplastic matrix using acetic anhydride (Fig. 5). One exception was recently reported by Igarashi et al. [29], where alkenyl succinic anhydride (ASA)-acetylation was coupled with kneading to provide satisfactory dispersion (Fig. 19). This will be discussed in greater detail in the section of “mechanically-aided dispersion.” Leszczyńska et al. [15] did not provide information on the chemical/glucose ratios or DS, making it hard to ascertain the reasons for the limited dispersion. Even with a medium DS (~0.4) of CNMs after acetylation, acetylated CNMs were not well dispersed in polymer matrices [23]. One of the reasons the authors pointed out was the alkyl chain length of acetic anhydride was too short to extensively block intermolecular interactions [23]. Another possible reason is that the studied materials were long nanofibers, either BCs or CNFs. Long fibers are harder to disperse than short fibers. Within the long fibers, BCs are morphologically different from CNFs. The dispersion of BCs was better than CNFs based on the SEM graphs provided in their studies [43]. In the BC/PLA composites, it is difficult to discern BC from PLA [43]. While in CNF/polymer composites, CNF agglomerates are prominent even after acetylation treatment [15,42]. More detail will be provided in the section of “Discussion”. Even so, acetylation increased the tensile properties of CNM/thermoplastic composites slightly. The tensile modulus, tensile

strength and elongation at break of BC (6 wt%)/PLA composites were improved by 9%, 14% and 33%, respectively [43]. The tensile modulus and tensile strength of acetylated CNF(10 wt%)/HDPE composite were 8% and 16% higher than the CNF/HDPE composite [23].

Esterification forms ester ($\text{O}-\text{C}=\text{O}$) links on the surface of cellulose through the condensation reaction between the hydroxyl groups of cellulose and the carboxylic acid/chloride groups on acids [31]. Various kinds of acids were investigated to esterify CNMs, including acetic acid (AAcid), hexanoic acid (HA), dodecanoic acid (DA), benzoic acid (BA), benzylacetic acid (BAacid), phenylacetic acid (PA), myristoyl chloride (MC), stearoyl chloride (SC), pivaloyl chloride (PC), cyclohexanecarbonyl chloride (CC), t-butylcyclohexanecarbonyl chloride (tBC) and dodecanoyl chloride (DDC) [23,25,27,41,44]. The starting materials can be dry fibers, CNM suspensions or solvent exchanged colloids. Solvents like toluene and pyridine are typically used for the reaction which occurs at various temperatures (25–130 °C) for several hours. Purification and drying were also required at the conclusion of the process to obtain clean modified fibers for compounding. Because acids are corrosive, the degree of reaction should be controlled to ensure esterification only occurs on the surface of the cellulose. If cellulose fibers are “over esterified”, their mechanical properties (stiffness and strength) will be degraded [31]. “Green” esterification methods were proposed in a couple of studies where CNMs were directly esterified in the acid medium without drying the CNMs or the use of organic solvents [25,61]. The temperature of such reactions was kept above the melting temperature of the acids and the boiling point of water (130 °C) to evaporate the large amount of water existing in CNM suspension during esterify CNMs. Using long-chain acids, successful esterification occurred with a medium DS (0.3–0.5), showing improved dispersion of CNMs in polymers [23,27]. The mechanical properties of modified CNM/thermoplastic composites were higher, even though there was limited interaction between the chemicals’ end functional groups and the polymer matrices [23,25,27]. For example, the tensile modulus, tensile

Table 4
Factors affecting the dispersion of CNMs during melt processing.

Polymer ^a		Modification	Coupling agent ^d	CNMs		Processing				Ref.
Type	MW/MFI ^b	(Chemical/glucose) Ratio ^c /DS		Type	Form ^e	Temp. Setting (°C) ^f	Screw speed (rpm)	L/D ratio ^g	Residence time (min)	
PLA	-/20	-/1.07	No	CNC	Solvent mixture	165-200	120	-	-	[42]
	110/-	-/0.02	No	BC	OD	190	100	-	10	[43]
	150/-	N.A.	No	BC	TIPS and FD	180	10-40	-	30	[44]
	-/-	0.7(mol.)/-	No	CNF	OD	145	80	24	15	[41]
	-/-	0.004(mol.)/-	APS(-)	CNF	OD	145	80	24	15	[41]
	98/-	12.5(mol.)/-	No	CNC	Solvent masterbatch	157-162	170	-	-	[25]
	98/-	0.77(mol.)/0.35	No	CNC	Solvent masterbatch	155-160	170	-	-	[27]
	-(15-30)	0.1-1(wt.)/-	No	CNF	Wet mixed with PHB	170	60	-	-	[65]
	-/-	1-4(wt.)/-	No	CNC	FD	175	100	8	-	[30]
	130/-	5.6(wt.)/-	No	BC	Composite mat	160	60	-	3	[67]
	130/-	5.6(wt.)/-	No	BC	FD	170	100	-	3	[67]
	220/-	5.6(wt.)/-	No	CNC	Wet mixture	170-200	150	44	-	[34]
	-/20	2 (mol.)/-	-	CNF	Solvent masterbatch	165-200	120	-	-	[76]
	-/8	-	-	CNC	Suspension	70-200	300	-	-	[73]
	-/-	-	No	CNF	Solvent	170-200	300	-	-	[74]
	205/2-5	4(mol.)/-	MAPLA(10%) ^h	CNC	Solvent	170-200	150	-	-	[35]
PCL	50/-	10(mol.)/-	No	CNC	VD	120	75	-	10	[39]
PBAT	-/-	10(mol.)/-	No	CNC	OD, solvent	-	-	-	-	[33]
PHBV	-/-	0.6(wt.)/-	No	CNC	FD mix.	145-160	150	40	-	[70]
Starch	-/-	1.5(wt.)/-	No	CNC	Hybrid aerogel	160	60	-	-	[106]
PS	280/-	0.01(mol.)/-	No	CNC	FD	200	150	-	10	[24]
	280/-	1.9(wt.)/-	No	CNC	FD mix.	200	150	-	10	[24]
	280/-	0.2(wt.) /-	MPEG(~20%)	CNC	FD mix.	200	150	-	10	[24]
PA(4,10)	-/24	3.3(mol.)/-	No	MFC	FD	-	50, 100, 150	-	3	[15]
PA6	-/-	2(wt.) /-	No	CNC	OD, precipitate	180-230	600	40	-	[68]
PA11	-/-	-	-	CNF	Milled particles	180-215	200	40	5	[91]
LDPE	-/-	-/0.38	No	CNC	FD	130-150	300	-	-	[26]
HDPE	-/-	1.25(wt.)/-	No	CNC	FD mix.	160	-	-	-	[69]
	-/5	1-9(wt.)/-	No	CNF	Wet mix.	(180)180	(60)60	-	-	[66]
	-/-	-(0.38-0.46)	No	MFC	Solvent mix.	110-140	200	45	-	[23]
	-/-	-/0.44	MAPP(4%)	MFC	Kneaded mix.	140	200	45	-	[29]
PP	-/-	1 (wt.)/-	No	CNF	VD mix.	120-140	200	-	-	[72]
	-/19	0.02(wt.)/-	MAPP(2%)	CNF	SD	200	250	-	-	[40]
	32/30	0.03(mol.)/-	MPS (-)	CNF	OD	100-180	300	40	-	[14]
	-/35	1.5(wt.)/-	No	CNF	OD	190	60	-	10	[62]
	337/-	0.1(wt.)/-	No	CNC	FD	190	150	-	8	[28]
	-/9	4(wt.)/-	MAPP(10%)	CNC	FD	-	-	-	-	[71]
	-/35	-	-	CNF	Suspension	190	60	-	40	[75]
	200/-	-	MAPP(2-6%)	MFC	Wet mix.	(0)180	(400)200	45	15	[13]
	200/-	-	MAPP/CPPA(4%/3%)	MFC	Wet mix.	(0)180	(400)200	45	-	[12]

^a PLA: polylactic acid, PCL: polycaprolactone, PBAT: polybutylene adipate terephthalate, PHBV: poly(3-hydroxybutyrate-co-3-hydroxyvalerate), PS: polystyrene, PA(4,10): polyamide(4,10), PA6: polyamide6, PA11: polyamide11, LDPE: low-density polyethylene, HDPE: high-density polyethylene, PP: polypropylene.

^b MW: molecular weight (kg/mol); MFI: melt flow index (g/10 min).

^c This ratio is either molar ratio (mol.) or weight ratio (wt.), calculated from information provided in manuscripts if not given directly.

^d APS: (3-Aminopropyl)triethoxysilane, MAPP: maleic anhydride polypropylene, MPEG: methoxypolyethylene glycol, MPS: 3-(methacryloyloxy) propyl trimethoxysilane, CPPA: cationic polymer possessing a primary amino group, MAPLA: maleic anhydride PLA,

^e OD: oven drying, TIPS: thermally induced phase separation, FD: freeze drying, VD: vacuum drying, SD: spray drying, mix.: mixture.

^f Values inside () were the parameters used for the mechanical pretreatment before melt compounding.

^g L/D: length/diameter.

^h values in the parenthesis are based on the total weight of composites.

Table 5

A comparison of all the treatments cited in this study.

Methods	Subcategories	Advantages	Disadvantages
Chemically-aided dispersion	Polymer grafting	1. Good dispersion ("grafting from" method). 2. Improvement in mechanical performance.	1. Use of solvents. 2. Interference with monomer polymerization from the moisture in CNM suspension.
	Silanization	1. High efficiency in improving mechanical performance of composites. 2. Water/alcohol reaction medium with less environmental impact.	1. Expensive chemicals. 2. No improvement in CNM dispersion if used at low dosage.
	Acetylation/Esterification	1. Industrially compatible. 2. Improvement in CNM dispersion and mechanical performance of CNM composites. 3. Potential solvent-free reaction medium 4. High grafting efficiency	1. No improvement in CNM dispersion. 2. Mostly organic solvents reaction medium.
	Other techniques (ultrasound, plasma, electric and magnetic fields)	1. Environmental friendly. 2. Improved nanofiber dispersion in polymers.	1. Special machine configuration. 2. Surface modification is needed in some cases to obtain charge and magnetism. 3. Some are not
Physically-aided dispersion	Polymer wrapping	1. Improvement in CNM dispersion. 2. Water-soluble polymers readily available. 3. Easy to perform.	1. Limited wrapping polymers which have compatibility with both CNMs and thermoplastic matrices. 2. Limited mechanical performance improvement in most cases.
	Surfactants	1. Improvement in CNM dispersion. 2. Water-soluble surfactants readily available.	1. Limited/no mechanical performance improvement in most cases. 2. Organic solvents are required when using polymeric surfactants.
	Wet compounding	1. Improvement in CNM dispersion. 2. No need to dry before compounding. 3. CNM suspension is safer to operators.	1. Potential processing difficulties with water evaporation. 2. Potential polymer degradation if moisture existed in melt.
	Solvent-aided masterbatch	1. Improvement in fiber dispersion and material mechanical performance.	1. Noncontinuous process. 2. Environmental impact from using organic solvents. 3. Limited improvements in CNM dispersion if missing surface modifications.

Table 5 (continued)

Methods	Subcategories	Advantages	Disadvantages
Mechanically-aided dispersion	Milling	1. Equipment readiness.	applicable to melt processing. 1. CNM damage if milled at dry form. 2. No improvement in CNM dispersion. 3. No improvement in mechanical properties.
	Melt extrusion	1. Simple to operate. 2. Equipment readiness.	1. No improvement in CNM dispersion. 2. No improvement in mechanical properties.
	Extensional flow mixing	1. Equipment readiness 2. Easy to operate.	1. No improvement in CNM dispersion. 2. No improvement in mechanical properties.
	Chilled extrusion	1. Improvement in CNM dispersion. 2. Improvement in mechanical performance.	1. Nonconventional process. 2. Investment in equipment. 3. Potentially energy intensive. 4. Limited mechanical performance enhancement. 5. Potential fiber damage if processed with dry CNMs.
Dispersion related to novel drying approaches	Kneading (<i>Kyoto Process</i>)	1. Improvement in CNM dispersion. 2. Large improvement in mechanical performance when coupled with proper surface treatments. 3. Equipment readiness. 4. Pulp as starting materials.	1. Organic solvents used during surface modification.
	Spherical aerogels	1. Improvement in CNM dispersion. 2. Improvement in mechanical performance.	1. High drying cost. 2. Restricted reinforcing ability of CNMs if presented as spherical instead of fibril.

strength and elongation at break of valeric acid (VA) esterified CNC/PLA composites were 60%, 23% and 70% higher than pristine CNC/PLA composites with only 1 wt% CNMs [27]. The tensile modulus and tensile strength of CNF/HDPE composites containing 10 wt% CNF were improved by 60% and 50% after esterifying CNF with phenylacetic acid [23]. However, the efficacy of using esterification alone on the dispersion of CNMs in polymers is uncertain because extra material-handling steps were also performed in those "successful" studies before compounding. For example, a masterbatch film, containing 15 wt% CNMs and 85 wt% PLA originally dissolved in chloroform, was first solvent cast [27]. The films were then chopped and compounded with fresh PLA pellets to obtain the final composites. The CNM dispersion of this study is presented in Fig. 6. In another study, never-dried and esterified MFCs were placed in isopropyl alcohol (~3 wt% solid content), mixed with HDPE powders (MFC/HDPE = 0.3 (w/w)) using a food mixer, followed by filtering and pressing [23]. The wet mixture was kneaded and dried in a mixer at 70 °C and then diluted with fresh HDPE powders for extrusion to achieve final solids concentrations. The later method (wet mixture) provides a faster production speed than the former solvent-aid masterbatch film method. The role of solvent-masterbatch and

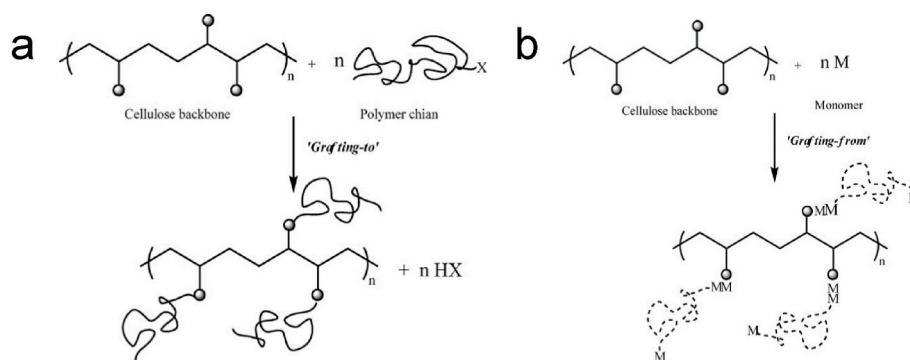


Fig. 2. Schematic drawing of (a) grafting to and (b) grafting from. Adopted from Ref. [45].

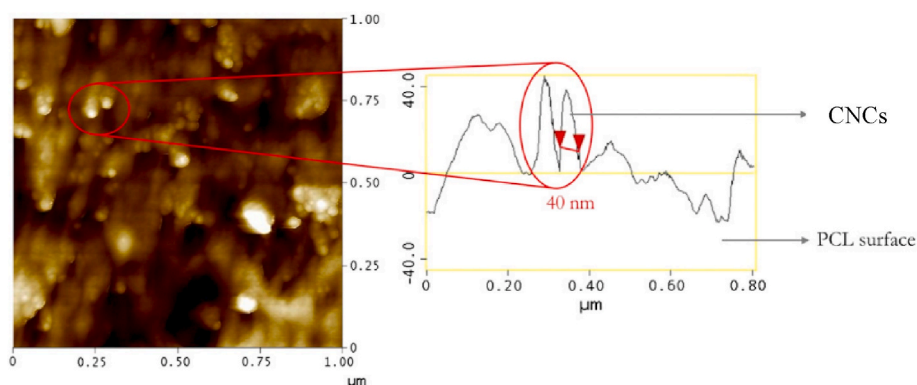


Fig. 3. Atomic Force Microscope (AFM) topography of CNC-g-polycaprolactone (PCL) (CNC/PCL = 0.08) and section across the sample. Reprinted and modified from Refs. [39] with permission.

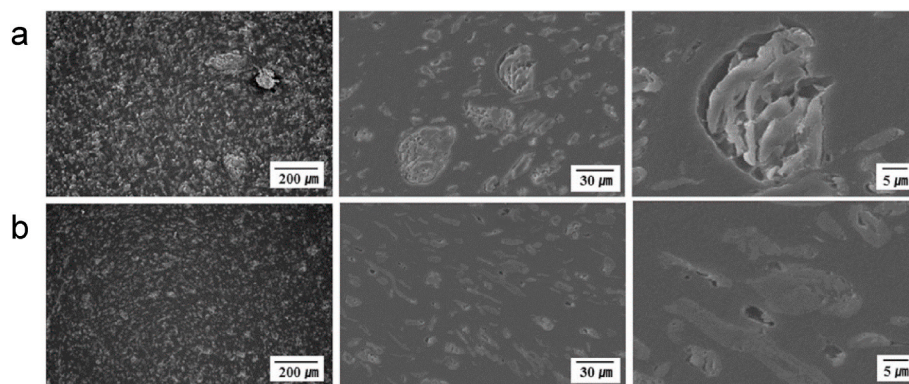


Fig. 4. Morphology of MFC (30 wt%)/PP composites (a) untreated MFC and (b) silylated MFC. Reprinted from Ref. [14] with permission.

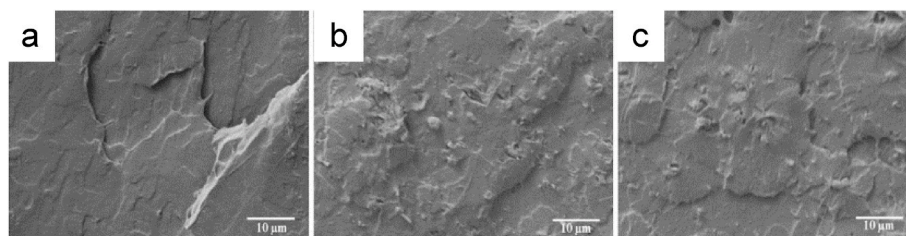


Fig. 5. Fractured surface of pure PLA (a) and CNF (5 wt%)/PLA composites with no acetylated (b) and acetylated nanofibers (c). Reprinted from Refs. [42] with permission.

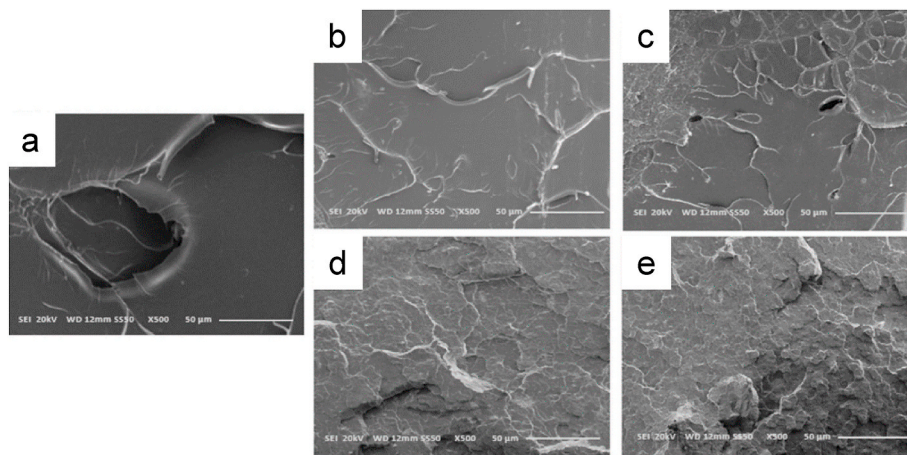


Fig. 6. SEM micrographs of: (a) pure PLA, (b) CNC(1 wt%)/PLA composite, (c) CNC(3 wt%)/PLA composite, (d) esterified-CNC(1 wt%)/PLA composite, (e) esterified-CNC(3 wt%)/PLA composite. Chemical: valeric acid. Reprinted from Ref. [27] with permission.

kneading-aided dispersion used in those studies will be discussed in the physically-aided and mechanically-aided dispersion sections.

4. Physically-aided dispersion

Besides forming covalent bonding via chemical modification, the hydroxyl groups on CNMs can also be physically attached through H bonding and dipole-(induced) dipole interactions with other molecules. One example is the use of amphiphilic polymers as wraps for CNMs for better dispersion in hydrophobic polymers as shown in Fig. 7 [62]. Some CNMs contain anionic groups on their surface. For example, CNCs obtain sulfate ester groups ($-\text{HSO}_3^-$) during their production in sulfuric acid [63]. TEMPO-CNFs contain negative charges ($-\text{COO}^-$) as a result of their oxidation pretreatment [64]. Those anionic groups provide locations for physical adsorption of surfactants and polyelectrolytes [3]. Other physical methods were also investigated including wet compounding, solvent-aided masterbatch, etc. and are also discussed here.

4.1. Polymer wrapping (carrier system/coating/electrospinning)

Polymers used to wrap CNMs in thermoplastic matrices are amphiphilic in nature. A large amount of wrapping polymers should be used to cover the surface of CNMs and aid their dispersion. The hydrophilic portion of wrapping polymers can interact with CNMs to provide a polymer shield against self-agglomeration. The hydrophobic part acts like a compatibilizer during compounding with polymer matrices. The

concept of using a carrier/coating system for dispersing CNMs in thermoplastics is interesting, but challenging in several respects. First, the dispersion of CNMs in wrapping polymers is difficult. There are a limited number of water-soluble polymers (PVOH, PEO, starch, etc.) that can be used to directly wrap CNMs in aqueous suspension. Otherwise, solvents or co-solvents are needed [68]. CNMs also require proper surface modification to assist their dispersion in those solvents. Even if CNMs can be dispersed well in their wrapping polymers, the interfacial compatibility/bonding between those wrapping polymers and targeted thermoplastics are poor, thus creating incompatibility issues in composites [34,62,67]. Several studies used polymer wrapping methods, achieving fair CNM dispersion and mechanical property enhancement (Fig. 8) [34,67]. Other wrapping polymers did not significantly improve the dispersion of CNMs or the mechanical properties of the CNM/thermoplastic composites (Table 2). Different material-handling procedures after polymer wrapping were observed which may cause a difference in CNM dispersion. If samples were freeze-dried before compounding at relatively low CNC loading level (<20 wt%), the fiber dispersion and performance enhancement were improved [34,67]. If the fiber mass exceeded the wrapping polymers [24,70], or the samples were wet compounded as shown in Table 4 [65,66], then the results were not satisfactory. CNMs can severely agglomerate if surface wrapping is insufficient or the drying method is inappropriate.

Another effective wrapping method is to electrospin CNMs with target polymers from their solvents (Fig. 9) [67]. The electrospun BC/PLA composite mats were chopped and melt compounded with fresh

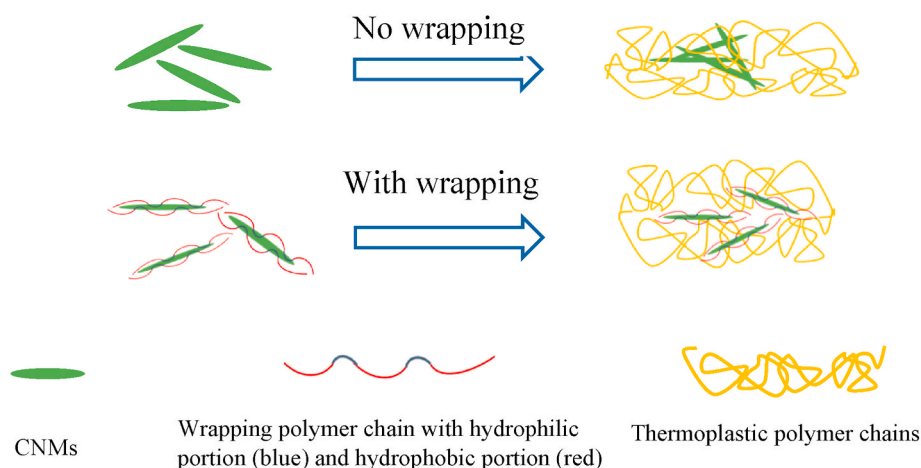


Fig. 7. A scheme of the dispersion of CNMs in thermoplastic polymers with or without wrapping.

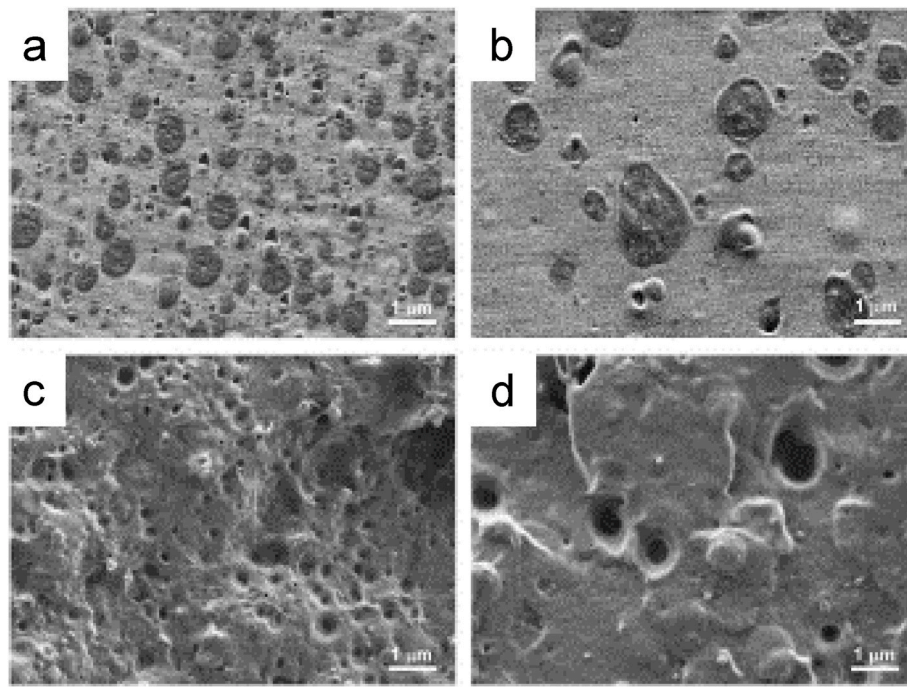


Fig. 8. Microtomed surface of (a) PLA-PVOH/CNC (5 wt%) composites from dry compounding and (b) PLA-PVOH/CNC (5 wt%) from wet compounding, and fractured surface of (c) PLA-PVOH/CNC (5 wt%) composites from dry compounding and (d) PLA-PVOH/CNC (5 wt%) composites from wet compounding. Reprinted from Refs. [34] with permission. Copyright Elsevier 2007.

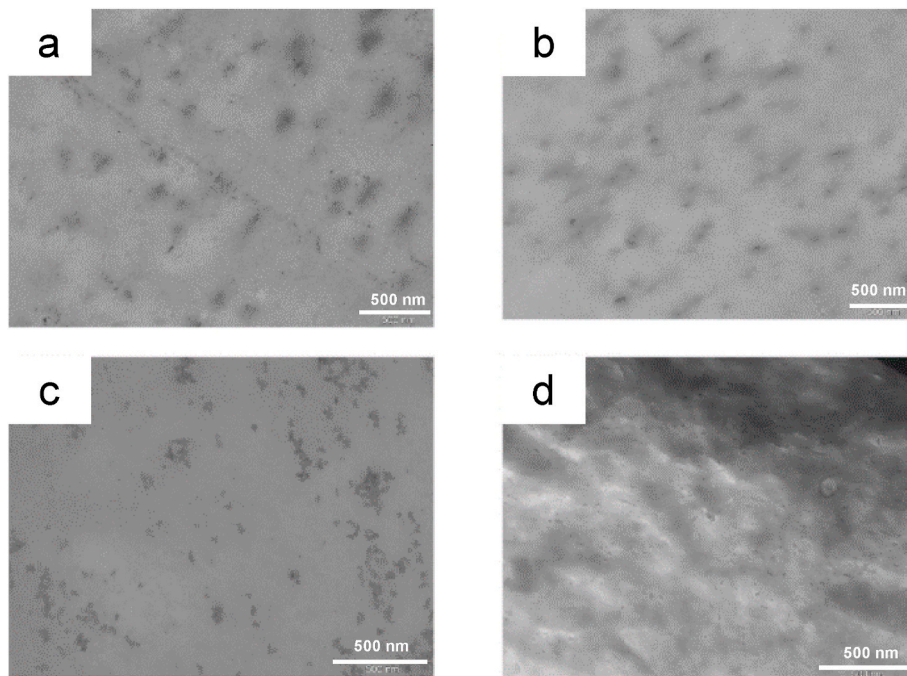


Fig. 9. TEM micrographs of PLA films containing (a) 2 wt% BC from electrospinning; (b) 3 wt% BC from electrospinning; (c) 1 wt% BC from freeze drying; and (d) 2 wt% BC from EVOH coating. Reprinted from Ref. [67] with permission.

PLA to generate materials for compression molding. Using this method, both the dispersion of BCs and the mechanical properties of the BC/PLA composites were improved. The tensile modulus, tensile strength and elongation at break of BC (2 wt%)/PLA composites prepared with the assistance of electrospinning were increased by 14%, 44% and 22% [67]. Nano-scale BC fibers in the PLA matrix were observed from SEM and TEM graphs (Fig. 9). An issue with the electrospinning method is the

use of solvent and related surface modification on CNMs to form stable colloids in the polymer solvent, if the polymer matrices are not water-soluble.

4.2. Surfactants

Surfactant treatment has been used to promote the dispersion of the

nanomaterials in polymer matrices [72,77,78]. Because some CNMs bear functional groups of negative charge, the most reasonable class would be cationic surfactants that can be readily attracted to the CNM surface [28,30]. Nonionic surfactants should also be appropriate because of their amphiphilic structure where the hydrophilic part can interact with CNMs, with the hydrophobic part interacting with polymer matrices [79]. Low-molecular-weight (LMW) surfactants were first investigated by directly adding them into aqueous CNM suspensions at calculated mass ratios [28,71]. The CNM suspension mixture then went through various steps (freeze-drying, melt compounding, etc.) for producing nanocomposites. LMW surfactants can effectively improve the dispersion of CNMs in thermoplastic matrices if added in a large amount (Fig. 10) [30]. However, LMW surfactants, like acid phosphate ester of ethoxylated nonylphenol, can degrade the mechanical properties of the polymer because they form a weak interphase between the CNMs and polymers [28,30,71]. The addition of coupling agent (MAPP) to LMW surfactant-modified CNF/polymer composites was reported to be an effective way to compensate for the mechanical property loss. For instance, CNF/Polyoxyethylene (10) nonylphenyl ether (surfactant)/MAPP/PP composites are 10% (tensile modulus), 21% (tensile strength) and 8% (strain at break) better than the composite without MAPP [71]. In some cases, LMW surfactants also significantly improved the tensile toughness of CNM/thermoplastic composites [28,71]. Because a LWM

surfactant can weaken the intermolecular interaction among CNMs or polymer chains by acting as a plasticizer, it causes the molecular chains to move with less hindrance [28]. To overcome the weakness of LMW surfactants, a polymeric surfactant was studied [72]. One problem with polymeric surfactants was their immiscibility with water. A mixture of water/organic solvent (N-Methyl-2-pyrrolidone) was prepared to improve dispersion of the surfactant, poly(lauryl methacrylate)-block-poly(2-hydroxyethyl methacrylate) (PLMA-b-PHEMA), before adding into a CNM suspension [72]. Afterwards, the mixture of CNMs, surfactants and their solvents were dehydrated under vacuum, dispersed in ethanol, mixed with polymer powders and vacuum dried for melt extrusion and injection molding. With a polymeric surfactant, the dispersion and mechanical properties of CNF/HDPE composites were both improved (Table 2). The “Method 2” in this study added additional PLMA-b-PHEMA to the CNF/PLMA-b-PHEMA/HDPE (10/10/80) wet mixture before drying and compounding, yielding sufficient fiber dispersion and higher mechanical-property enhancement (Table 2). Such a result indicates that removing excessive surfactants before drying and compounding may not be necessary if the surfactant addition level is moderate ($m_{\text{surfactant}}/m_{\text{cellulose}} \leq 1$). Non-adsorbed surfactants can still provide steric hindrance to prevent H-bond-induced agglomeration during drying.

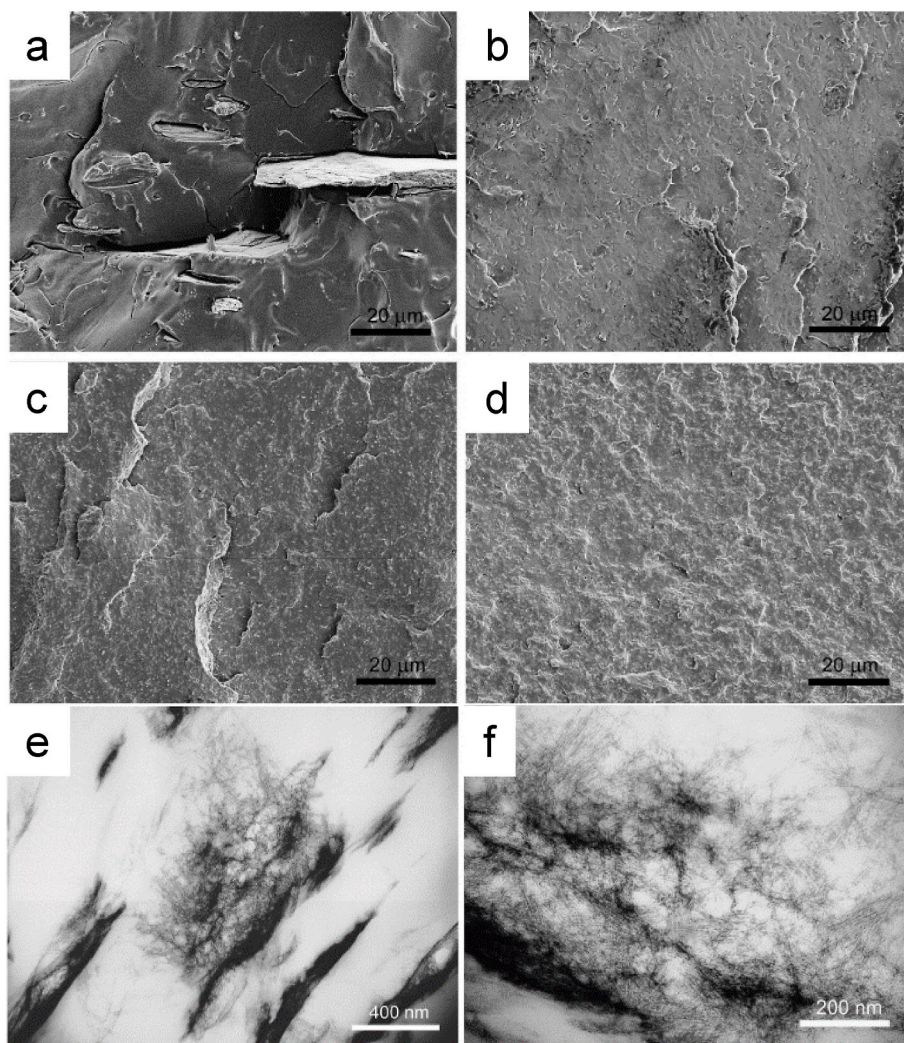


Fig. 10. SEM graphs of fractured surfaces of (a) PLA/CNC (5 wt%), (b) PLA/surfactant (5 wt%)/CNC (5 wt%), (c) PLA/surfactant(10 wt%)/CNC (5 wt%) and (d) PLA/surfactant (20 wt%)/CNC (5 wt%). TEM graphs of (e & f) PLA/surfactant (20 wt%)/CNC (5 wt%). Chemical: acid phosphate ester of ethoxylated nonylphenol. Reprinted from Ref. [30] with permission.

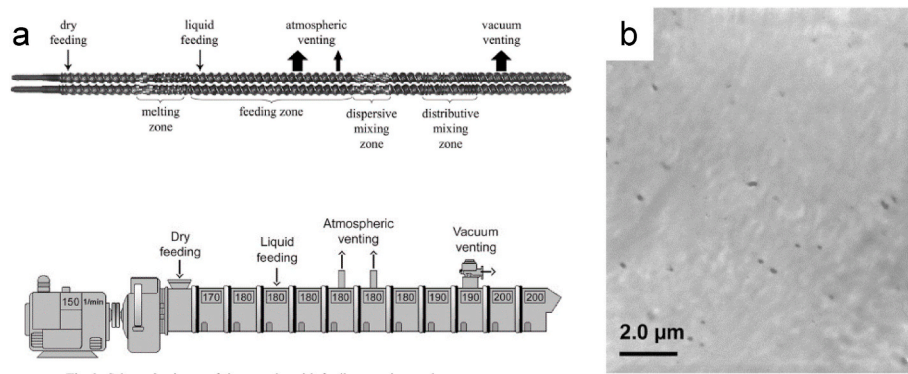


Fig. 11. Schematic layout of (a) the wet compounding process and (b) TEM graph of CNC (5 wt%)/maleic anhydride PLA (10 wt%)/PLA composites. Reprinted from Ref. [34,35] with permission. Copyright Elsevier 2006 & 2007.

4.3. Wet compounding

Drying CNM suspensions causes CNMs to agglomerate, thus losing their nano scale. Some studies investigated the wet compounding method performed by Oksman's research group in Europe, aimed at improving the fiber dispersion [34,35,73,74]. In general, CNM suspensions were added into a zone of a heated barrel during extrusion

manually or by a peristaltic pump as shown in Fig. 11a [34]. Suspensions can be heated prior to compounding to assist water evaporation. The heated barrel must be equipped with vent openings to allow water vapor to escape during extrusion. As CNMs lose their surrounding water, they adhere to the polymer melt upon contact, reducing the chance for self-agglomeration. Wet compounding did show improvement on the dispersion of CNMs in PLA with a starting aqueous suspension of low

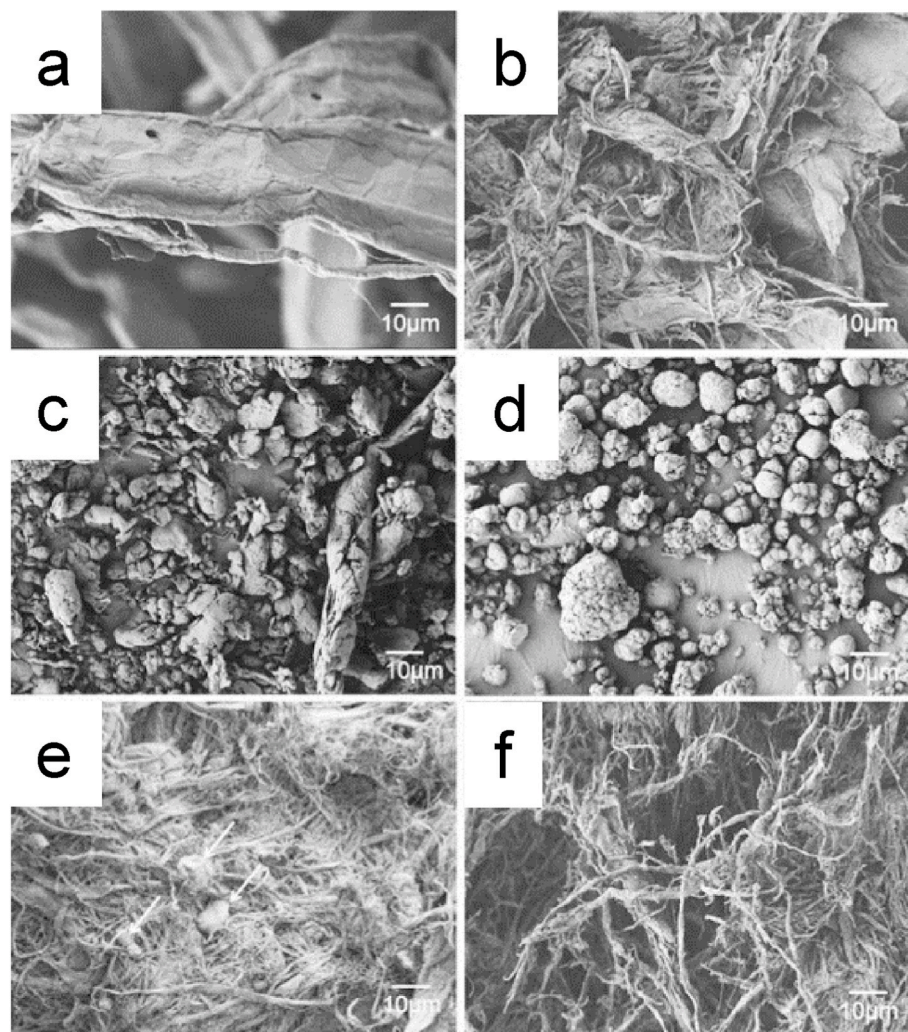


Fig. 12. SEM graphs of materials: (a) needle-leaf unbleached Kraft pulp (NUKP), (b) refiner-treated NUKP, (c) PP, (d) MAPP, (e) mixture of refiner-treated NUKP, powdered PP, and MAPP after wet kneading (arrows indicate powdered PP), (f) after matrix removal by xylene washing. Scale bar: 10 μm. Reprinted from Ref. [13] with permission.

CNC concentration (<5%) (Fig. 11b) [74]. If the fiber content is high or the CNMs employed were CNFs instead of CNCs, CNM agglomeration occurs [65,75]. However, the mechanical-property improvement by wet compounding is difficult to evaluate because of the lack of a control group processed using a dry form of CNMs [35,73,74]. For those studies where control groups were provided, the mechanical properties of CNM/PLA composites produced via wet compounding were not significantly higher than those produced via dry compounding [34,75]. Moisture is a known factor which lowers the molecular weight of PLA during compounding, therefore, may degrade the mechanical properties of PLA [80]. The side effect of moisture may adversely impact the goal of this method. One may observe a high tensile strength of PLA/CNC composites from the work of Oksman et al. [35]. The key was the use of maleate PLA in the formulation (Table 4). This underlines the importance of incorporating coupling agents in the composite formulation.

Another category of wet compounding is the process developed by Yano's research group in Japan [12,13]. There are some degrees of differences between the Yano's method and the Oksman's method. In Yano's method, refiner-treated wet pulp, polymer powder and coupling agents are kneaded together in a twin-screw extruder set at low temperature (0 °C) and high screw rotation speed (~400 rpm). The wet kneading process produces fibrillated cellulose in the wet stage, and possibly presses and fixes cellulose fiber deep into polymer pellets by compression forces (Fig. 12). The wet mixture is then fed into an extruder for wet-state melt compounding. There can be some alteration in the kneading process. For example, when CNFs were also used as a starting material, the intensity of wet kneading can be reduced [23,29]. A wet mixture of CNF and HDPE was dried and kneaded simultaneously at 70 °C in a mixer to obtain a solid form for additional compounding with fresh HDPE [23,29].

It is likely that the success of wet compounding relies on whether the CNMs are fixed to the polymer before extensive self-agglomeration can occur. A low solids content and agitation force during kneading are essential. Yano's method is a unique process for its capability for high-fiber loading (up to 50 wt%), large mechanical performance enhancement and continuous, industrially scalable production. Fibers existing in the final composites are not all in nanoscale. Instead, microscale fibers are also present. This raises the question as to whether nanoscale cellulose is an absolute requirement to obtain composites with significantly enhanced mechanical properties?

4.4. Solvent-aided masterbatch

Instead of using melt processing completely, a masterbatch of CNM/thermoplastic composites can also be made through solvent casting, followed by melt extrusion [25,27,76]. In general, mixing CNMs with thermoplastics in organic solvents did not improve the fiber dispersion as exhibited in Fig. 13. One possible reason is the fiber content in the solvent masterbatch was high (15–40 wt%), creating a high likelihood of aggregation. Another important factor is the missing of external dispersion forces. Ultrasonication or high shear mixing are needed to disrupt the H bonding among CNMs and assist their dispersion in an organic solvent [27]. However, CNMs tend to re-aggregate after the external force is removed. Since solvent casting often takes many hours

to complete, CNMs may have already aggregated. The dispersion effect of using such an approach is compromised. Therefore, solvent-aided masterbatch is often coupled with surface modification to improve the stability of the colloids and the dispersion of the fiber [25,27,71,81]. The influence of solvent-involved processes remains a significant issue as organic solvents are expensive, flammable and pose health concerns.

4.5. Other techniques

There are also other physical techniques which have been explored for improving the dispersion of nanofibers in polymers other than CNMs. Because CNMs are not the focus of such processes, only a brief introduction is made aiming at providing additional sources for future research. Isayev et al. studied the dispersion of carbon nanotubes during melt extrusion by attaching an ultrasound device to the end of an extruder [82]. Planellus et al. added an ultrasound component to a micro-injection molder to assist the dispersion of nanoclays in biodegradable polymers [83]. The ultrasound treatment can improve the fiber dispersion and the mechanical properties of resulting composites if treating parameters were properly controlled. Plasma was utilized in several studies to treat various nanofibers (carbon nanotube, nanoclays, etc.) at solid form to ameliorate their compatibility and dispersion in polymer matrices (polyamide and polyimide) [84,85]. Plasma treatment induces oxidation and improves polarity of the nanofiber, enabling a more compatible interface and stronger composites [84]. Dispersion of nanofibers was also improved by modifying the surface of nanofibers and applying electric or magnetic fields to the compounds of nanofibers and polymers [86,87]. Such approaches of using magnetic/electric fields only seem to benefit thermoset-based composite systems so far.

5. Mechanically-aided dispersion

Mechanical methods have been applied to deagglomerate CNMs after their agglomeration during drying. It is anticipated that bundled dry CNM film/foam can be separated by large mechanical shear forces. Investigated mechanical methods include melt-state extrusion, chilled extrusion, wet kneading, dry kneading, ball milling and jet milling and extensional flow.

5.1. Melt extrusion

The melt extrusion process itself provides shear forces that can be used to break up bundles of agglomerated nanomaterials [77]. Such an approach has been successfully applied to the nanoclay/polymer system [95]. It was reported that the degree of dispersion of nanoclay was positively correlated with the screw rotational speed. The effect of screw rotational speed on fiber dispersion was also investigated for MFC/PA (4,10) composites [15]. As screw speed increased from 50 to 150 rpm, the degree of distribution of MFCs in PA was improved. However, nanoscale dispersion of MFCs was not observed as shown in Fig. 14. Extrusion alone is not sufficient to adequately disperse agglomerated MFCs into their nanoscale fibers [40]. The estimated shear stress during melt extrusion was 0.2 MPa [96]. Likewise, in an effort to disperse FD CNCs in PLA using a melt blending approach, no improvement in CNC

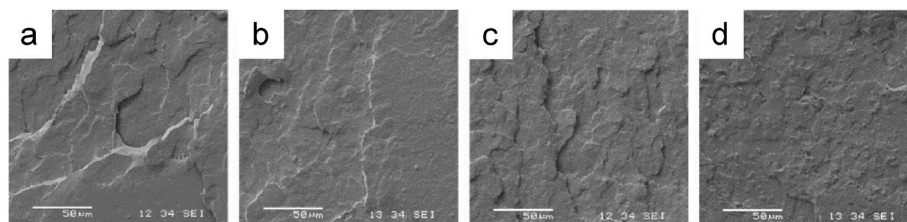


Fig. 13. SEM graphs of fractured surfaces of (a) neat PLA, (b) CNF(1 wt%)/PLA, (c) CNF(3 wt%)/PLA and (d) CNF(5 wt%)/PLA composites. Reprinted from Refs. [76] with permission. Copyright Elsevier 2010.

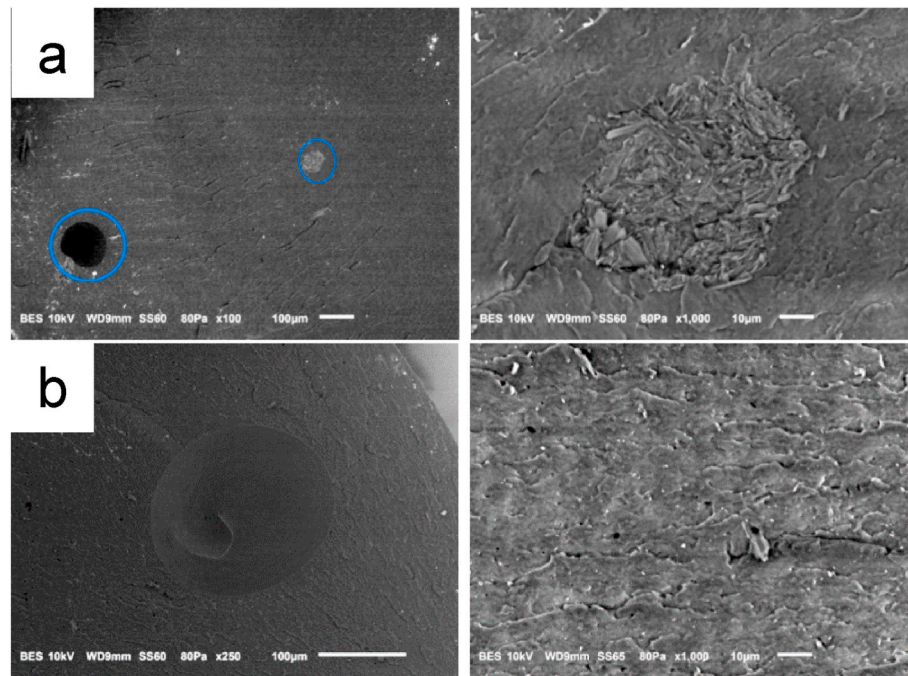


Fig. 14. SEM graphs of acetylated MFC(3 wt%)/PA composites processed at 2 different screw speeds: (a) 50 rpm, (b) 150 rpm. Reprinted from Refs. [15].

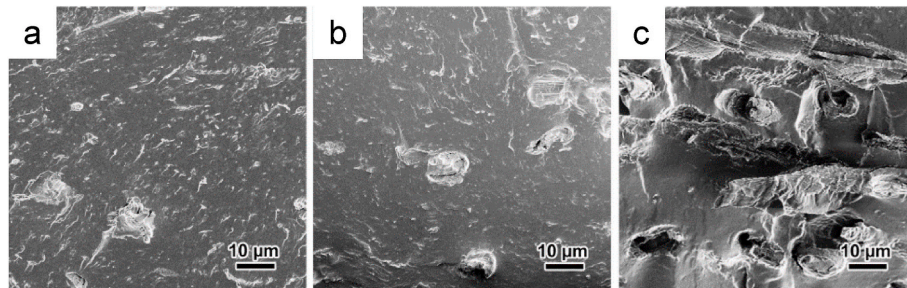


Fig. 15. SEM images of surfaces of cryo-fractured composites: (a) thermoplastic starch (TPS)/CNF (10 wt%), (b) TPS/CNF (in-situ fibrillated) (10 wt%), (c) TPS/pulp fibers (10 wt%) without pretreatment. Reprinted from Refs. [36]. Copyright Elsevier 2020.

dispersion was achieved [88]. Starch, plasticizer and wet oxidized pulp fibers were compounded using a one-step extrusion at 110 °C and 200 rpm for 15 min [36]. Bundles, as well as fibrillated fibers were observed for the treated pulp fibers (Fig. 15). As compared to composites made from CNFs, the tensile modulus and tensile strength of one-step extruded cellulose (4 wt%)/starch composites gained increments of 27% and 48%

respectively.

5.2. Extensional flow mixing (EFM)

Shear mixing occurred during melt extrusion is considered as energetically inefficient [97]. Extensional flow mixing (EFM) provides

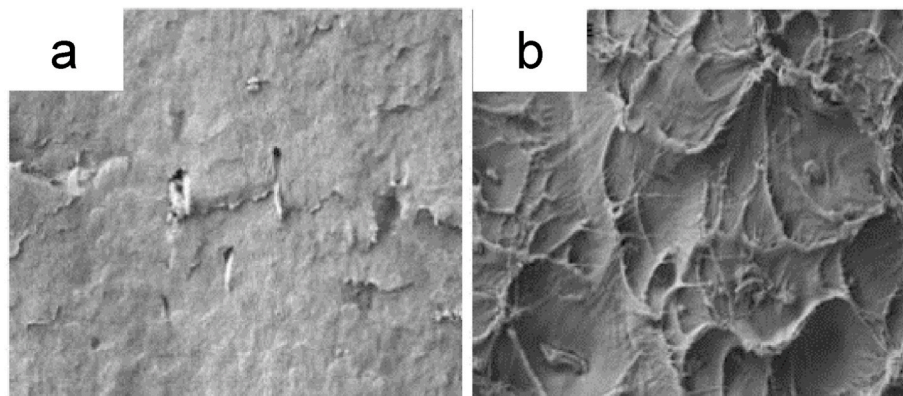


Fig. 16. SEM graphs of HDPE/MAPE/MFC (a) without EFM and (b) with EFM treatment. Reprinted from Ref. [89].

several benefits over shear mixing, including more energy-efficient, better dispersive and distributive mixing, small temperature rise during mixing and no secondary agglomeration of particles after dispersion [97,98]. The composite melt experiences convergent (C) and divergent (D) flow inside the mixer with extensional stress being controlled by varying C-D plate geometry [97]. EFM has been proven to be efficient in dispersing organoclays in thermoplastic polymers [97]. When applied to CNMs, EFM did not show a satisfactory dispersion as nanoclays, possibly attributed to the strong intermolecular forces among CNMs (Fig. 16) [89].

5.3. Milling

Milling is another method used in nanocomposite manufacturing to assist nanomaterial dispersion [99]. During ball milling, materials are reduced to smaller size in a concealed container by the collision and cascading effect of rigid balls [78]. Dried BC mats were first ground, then ball-milled with PLA powder in a centrifugal ball mill [90]. Five steel balls of 10 mm in diameter were included in a steel jar (50 cm³) to mill the materials at 650 rpm for 1 h. Nanoscale particles were observed in the TEM graph as well as microscale fibers. The authors concluded the method was not sufficient to achieve proper BC dispersion (Fig. 17a). In another study, freeze-dried CNFs were milled with PA11 powder in a jet mill operated at a pressure of 2 bars and a speed of 5 g/min [91]. The compressed gas used in a jet mill moves like a vortex, resulting in collision and pulverization of materials. The jet milling and melt extrusion process appeared to improve the dispersion of CNFs in PA11 (Fig. 17b). However, no mechanical property improvement was found. Ball milling carbon nanotubes was reported to disrupt their nanostructure if milling parameters were not well selected [100]. CNMs become less flexible once dried. Therefore, more damage can be caused when CNMs are milled at dry stage than wet stage, lowering their mechanical properties. The aspect ratio of CNMs after milling was also reduced.

5.4. Chilled extrusion

Original papers used solid state shear pulverization (SSSP) as the name for the chilled extrusion process [92,101]. We discovered reports of several forms of SSSP later. Therefore, it is referred to as chilled extrusion here for differentiation [102]. Chilled extrusion uses special equipment to process material under cooling, instead of heating. The extrusion temperature is held below the glass transition temperature of amorphous polymers and below the melting temperature for crystalline polymers [92]. Larger shear forces and compression forces compared to melt extrusion are placed upon the material during chilled extrusion. Advantages of chilled extrusion include being solvent free, near-ambient-temperature, good dispersion and no chemical modification. Freeze-dried CNCs and polyolefin pellets were fed into a pulverizer using a powder feeder and pellet feeder simultaneously. CNCs and

polyolefins were pulverized at a screw speed of 200 rpm. The extrusion barrel was kept cool by the recirculation of an ethylene glycol/water mix at -7°C . The extrusion screw needs a special design to exert high specific energy to materials. Nanoscale dispersion of CNCs in polyolefin were observed in SEM graphs (Fig. 18). Tensile properties of CNC (10 wt %)/polyolefin composites were largely improved after being processed by chilled extrusion [92]. Composites of CNC (10 wt%)/LDPE prepared by chilled extrusion are 50% (tensile modulus), 86% (tensile strength) and 22 times higher (elongation at break) than their melt extruded counterparts. After being chilled extruded, the CNC (10 wt%)/PP composites received 24%, 12% and 71% increase in tensile modulus, tensile strength and elongation at break. Cardboard and microcrystalline cellulose were also investigated using chilled extrusion [101]. However, those two materials did not achieve nanoscale fibrillation using the same parameters applied for CNCs.

5.5. Kneading

Freeze-dried lignocellulose nanofibrils (LCNF) were kneaded with PP and MAPP in a batch-type kneader at 120°C and 60 rpm for various times (10–60 min) [93]. After kneading, the mixture was melt compounded in a twin-screw extruder operated at 170°C and 30 rpm into pellets for injection molding. The LCNF can be well-dispersed at the nanoscale after the kneading treatment. Potential fiber degradation may occur because the treatment was performed in the dry state. Tensile modulus, tensile strength and elongation at break of LCNF/MAPP/PP composites were improved by 10%, 9% and 80 times compared to the composites without a kneading treatment. Considering the relatively low crystallinity and reinforcing ability of LCNF, this improvement was satisfactory compared to a relevant study [103]. In another study, wet pulp/CNF, together with MAPP, HDPE and CaCO_3 powders, were suspended in isopropanol solution and filtered to generate a 50 wt% solid [29]. The wet mixtures were kneaded, and simultaneously dried at $20\text{--}70^{\circ}\text{C}$ in a mixer before melt compounding. Temperature was maintained low to possibly maintain higher shear and compression forces. The kneading did not improve the CNF dispersion in the HDPE without proper surface treatment (Fig. 19), indicating that wet kneading of CNM suspension cannot directly prevent the severe agglomeration induced by solution evaporation. One exception is where the fiber content in the mixture is extremely low (0.05 wt%) [94]. After treating the surface with alkenyl succinic anhydride (ASA) ($\text{DS} = 0.43$), the mechanical performance of kneaded CNF/HDPE composites were drastically improved, attributed to improved dispersion [29]. The tensile modulus and tensile strength of kneaded ASA-pulp (10 wt%)/HDPE composites gained improvements of 61% and 47% respectively, with a reduction in strain at break. Kneading, coupled with chemical surface treatment and coupling agent, remains the best processing method explored in terms of producing sufficient CNM dispersion, high CNM loading level (up to 50 wt%), large mechanical performance improvement and high industrial relevancy. Such a process was named “Kyoto

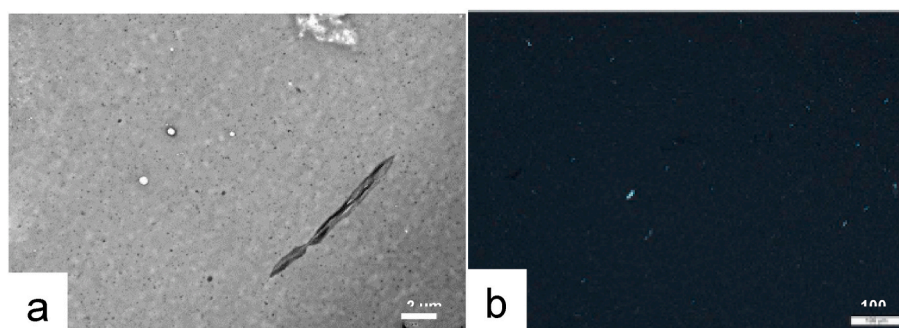


Fig. 17. TEM graph of (a) BC(1 wt%)/PLA composites after ball milling. Reprinted from Ref. [90] by permission of John Wiley & Sons, Inc.. Polarized optical microscopy images of (b) CNF(0.5 wt%)/PLA composites film. Reprinted from Ref. [91] with permission.

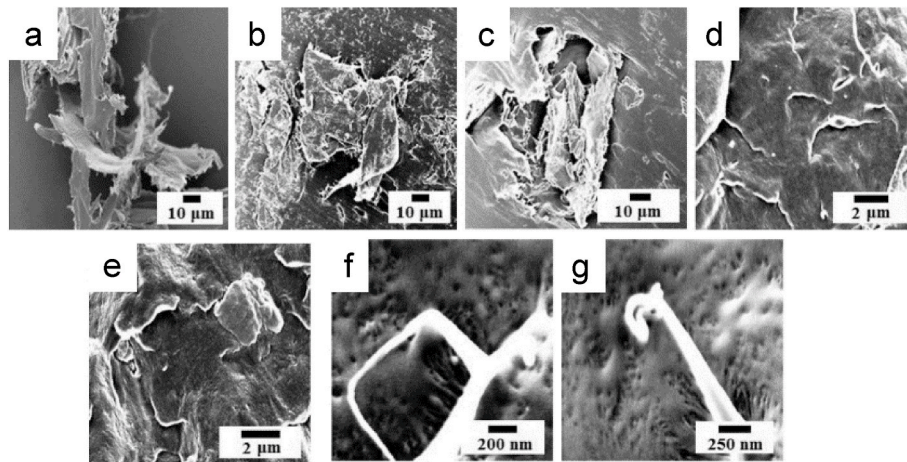


Fig. 18. FE-SEM images of (a) as-received CNC, (b) LDPE/CNC (10 wt%) treated with melt mixing, (c) PP/CNC (10 wt%) treated with melt mixing, (d) LDPE/CNC (10 wt%) treated with chilled extrusion, (e) PP/CNC (10 wt%) treated with chilled extrusion, (f) high magnification image of (d) and (g) high-magnification image of (e). Reprinted from Refs. [92]. Copyright Elsevier 2015.

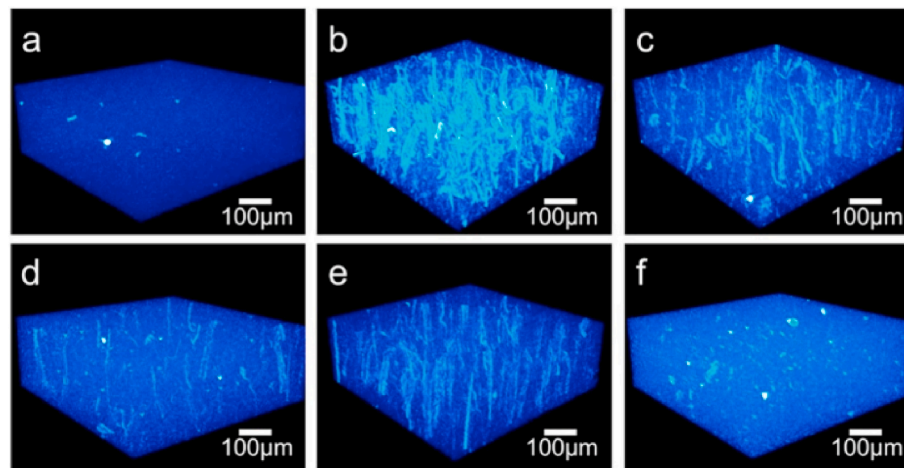


Fig. 19. X-ray CT images: (a) neat HDPE, (b) Pulp DS = 0, (c) Pulp DS = 0.22, (d) Pulp DS = 0.43, (e) Pulp DS = 0.57, (f) Bead mill fibrillated CNFs DS = 0.44. Chemical: alkenyl succinic anhydride (ASA). Reprinted from Ref. [29]. Copyright Elsevier 2018.

Process" by its inventors [29].

6. Dispersion related to novel drying approaches

Researchers explored the use of porous powders of nanoparticles, followed by polymer infiltration to make clay nanocomposites [105]. A similar approach was also applied to forming CNM/thermoplastic

composites [106]. The experiment was started by preparing a suspension containing CNMs and alginate [106]. The suspension was added to a crosslinking solution (CaCl_2) drop-by-drop to form hydrogels. The hydrogels were filtered and freeze-dried to form aerogels for melt compounding with a starch-based polymer. Unfortunately, the cross-linking among CNM/CNM or CNM/alginate was too strong to be separated into individual fibers during compounding, failing to improve the

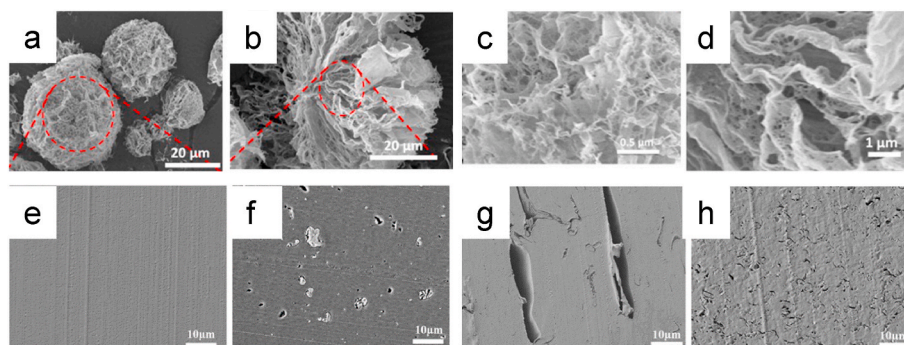


Fig. 20. SEM graphs of CNCs and its interior structure at different magnifications (a, b, c, d). SEM graphs of (e) pure PP, (f) SD-CNC(5 wt%)/PP, (g) FD-CNC(5 wt%)/PP, and (h) SFD-CNC(5 wt%)/PP composites. Reprinted from Refs. [104]. Copyright Elsevier 2014.

dispersion of CNM or reinforce the polymer. Another study also used aerogel powder CNMs for melt compounding with PP, but with a different processing technique [107]. The CNM aerogel was formed by first spray droplets of CNC suspension into a liquid nitrogen tank, followed by a freeze drying. This process is called spray-freeze drying (SFD). The CNC aerogels achieved a spherical and porous structure which can be infiltrated by polymer melt (Fig. 20). The SFD procedure increased the tensile modulus and tensile strength of CNC (5 wt%)/PP composites by 45% and 27% compared to the SDCNC/PP composites [104]. When comparing the SEM from the above two studies, SFD study showed PP molecules penetrating into the CNC aerogel extensively [107]. The dispersion information was not provided in the alginate study [106]. As such, it is unclear if the extent of polymer infiltration was responsible for the difference in the aerogel performance. Because spherical aerogels lack the ability to entangle with each other, their reinforcing ability may not be as good as in fibril form.

Another area of ongoing research activity is to obtain dried powders from nanomaterial suspensions, while still maintaining their nanoscale structures [108,109]. Various drying methods were investigated for dehydrating CNM suspensions [32]. Oven drying induces cellulose film production instead of powder. Freeze drying and supercritical drying can preserve the nanoscale of CNMs, however, the final product is in aerogel form. Spray drying can produce powdered CNMs, which is the preferential form for melt compounding. However, most of the powders generated from conventional spray drying are at the microscale, not nanoscale [22]. There are techniques that can provide smaller powders than conventional SD, even down to the nanoscale [110]. More investigation should be conducted with these techniques.

7. Discussion

Dried nanomaterials are bundled together by intermolecular forces. An integration of shear force and extensional force are exerted on the agglomerates during melt mixing. When shear stresses overcome the intermolecular forces of the agglomerate, nanomaterials can be deagglomerated [111]. The deagglomeration occurs in three steps.

1. The surface of nanomaterial agglomerates is wetted by molten polymers.
2. Molecular chains of the polymer melts infiltrate into nanomaterial agglomerates.
3. Nanomaterial agglomerates are dispersed into polymer matrices under shear force.

Depending on the degree of deagglomeration, dispersion has two categories. One is called “erosion” where nanomaterials are slowly eroded from the surface of their agglomerates. Consequently, large agglomerates are broken into small agglomerates. The other one is called “rupture”, where large agglomerates are rapidly reduced to small ones. Rupture requires a much higher shear stress than erosion. Shear forces experienced during melt mixing depend on screw design, extrusion parameters, polymer melt viscosity and their interactions.

7.1. Polymer matrices

As a first step, caution should be placed on the choice of polymer matrices. Besides the polymer type, which leads to a difference in interfacial compatibility, melt viscosity of a single polymer also can affect the dispersion of CNMs. Moreover, the polymer melt viscosity appears to play different roles when nanofibers change their forms. During melt mixing nanoclay with polymers, the use of high melt viscosity polymers resulted in higher shear stresses and better fiber dispersion [112–114]. While for some carbon nanotube (CNT) composites, high shear stresses and fair fiber dispersion are not monotonically related to the increase in polymer viscosity. For instance, one study reported an optimal polymer viscosity which gave a faster CNT

dispersion [115]. Lower polymer viscosity has been shown to be well suited for infiltrating agglomerates, however, is sub-optimal in transferring the mechanical shear force. Therefore, polymer viscosity has opposite effects on agglomerate infiltration and agglomerate dispersion. The polymer melt viscosity relies on processing temperature, polymer molecular weight distribution and shear rate. The rate of infiltration of polymer melt also depends on the pore size of the aggregates which can be altered by nanomaterial isolation process [116].

7.2. CNM types and forms

When it comes to CNMs, their types and final forms before compounding are all important for adequate fiber dispersion. CNCs and CNFs possess completely different morphological structures. Given the same amount of mass, the volume of rice-like CNCs are smaller than the spaghetti-like CNFs because the former has high packing density. It requires less available space to disperse CNCs than CNFs. The long fibril structure of CNFs requires longer time and distance to disentangle. Therefore, the initial dispersion of CNFs is more difficult than CNCs, let alone the higher chance of achieving secondary agglomeration during compounding.

Oven drying (OD), air drying (AD), vacuum drying (VD) and freeze drying (FD) produces bulky solid CNMs, requiring further pulverization steps to be made readily for melt extrusion. OD, AD and VD can significantly lower the surface area of CNMs and reduce the interaction between CNMs and polymer matrices. FD can well preserve the nanostructure of CNMs, but may be expensive to perform. Spray drying (SD) generates powder-like CNMs, ready for melt extrusion. However, CNMs form enclosed solid spheres after SD, which prevents polymer infiltration. Spray-freeze drying (SFD) produces powders with porous structure by combining the advantages of SD and FD. The spherical structure obtained from SFD does not show the same potential in reinforcing matrices as fibril structure does.

7.3. Surface modifications

In chemically modified CNMs, esterified and acetylated samples can, in some instances, achieve fair dispersion and significant improvement in mechanical properties [23,25,27,29]. First, the degree of modification ought to be sufficient. In those “successful” cases, CNMs were well esterified/acetylated based on a high chemical/glucose ratio or medium DS (0.4) (Table 4). Second, the selected chemicals should have proper chain length to form steric hindrance to reduce the H bonding among CNMs. The “grafting from” method, followed by in-situ polymerization, is effective in improving fiber dispersion. However, this method requires a change in the current standard synthesis of polymers. In the groups of physically modified CNMs, selection of chemicals is especially important because the most used chemicals are mechanically weak LMW substances. Such additives can assist the dispersion of CNMs, but cannot improve the mechanical properties of CNM/polymer composites. Polymer wrapping achieved success when there were sufficient interfacial compatibilities between the CNMs and wrapping polymers, and between wrapping polymers and polymer matrices. Often the compatibility among the three components cannot all be satisfactory at the same time. Therefore, additional compatibilizers are needed, adding to the complexity of the system. If no compatibilizers are used, the weak interface among the three materials becomes the failure locations, leading to degraded mechanical performance. Polymeric surfactants, instead of LMW surfactants, can effectively disperse CNMs in polymer matrices and improve their mechanical properties. However, large amount of organic solvents are needed to first disperse polymeric surfactants in CNM suspension. Wet compounding with low-CNM-content suspensions worked for improving fiber dispersion. Yet, its effects on the mechanical properties of polymer matrices are not well documented. Another common issue of wet compounding is the venting of water vapor during melt mixing, which can cause additional processing

difficulties. That may be the reason why recent activities from Kyoto University focused on the dry-pulp direct kneading method. Though the solvent masterbatch method made a huge improvement to the mechanical properties of modified CNC/PLA composites, its production rate is very low. Organic solvents are inevitably used in the process. The use of organic solvents goes against the green nature of cellulosic materials.

7.4. Coupling agents

The effect of adding coupling agents on the improvement of mechanical properties of CNM/thermoplastic composites cannot be over emphasized. For example, MAPP was added into the formulation of modified CNF/polyolefin composites, leading to the best reinforcing effect among its category [29]. Though MAPP is a commercial coupling agent and can be facilely applied as pellets during melt compounding, MAPP works when the polymer matrix is mostly polyolefin. When more “polar” polymers were used like PLA, MAPLA was synthesized in lab for a better coupling effect [35]. In contrast, silanes are more adaptive to different polymer matrices because they offer various end functional groups. A well-selected commercial silane can improve the mechanical performance of the CNF/PLA composites [41]. Water-immiscible silanes can often modify CNMs in their aqueous suspension via hydrolysis, mixing and drying [14]. Coupling agents should be used in CNM/thermoplastic composites to boost the reinforcing effect of CNMs.

7.5. Processing parameters

During melt mixing, processing parameters include length/diameter (L/D), temperature, screw speed and residence time [111]. Although matrix viscosity has a big influence on agglomeration infiltration and dispersion as mentioned above, screw speed sometimes can override the power of matrix viscosity [117]. It was observed that at high speed of mixing (>150–200 rpm), the extent of dispersion of CNTs in polycarbonate (PC) matrix was the same irrespective of the temperature or the melt viscosity. However, at slow speed of melt mixing, good dispersion was attained either at low temperature or at high melt viscosity of PC matrix [117]. Regarding a study involving the effect of changing screw speed on the dispersion of MFC in PA (4,10), increasing the screw speed did not improve the MFC dispersion [15].

The effect of extrusion temperature alone on nanomaterial dispersion may not be significant. For instance, in one study where a high-molecular-weight polymer was used, the extrusion temperature was increased to decrease the melt viscosity of the polymer [118]. However, low viscosity induced by higher temperature did not result in better dispersion. In almost all studies, the temperature settings were not optimized according to the principle of CNM dispersion/deagglomeration.

Usually, the longer the residence time, the better the dispersion, coupled with greater thermal degradation. Longer residence time can be achieved with larger L/D. A comprehensive study on how individual processing parameters and their interactions affect the dispersion of CNMs in thermoplastic matrices is needed. Nevertheless, one thing to note is that even when L/D is large (45), screw speed is high (200 rpm), temperature setting is at normal range (110–140 °C) and wet kneading is applied, unmodified CNF still cannot be dispersed in HDPE [23]. As such, merely regulating processing parameters is not sufficient to achieve the dispersion of CNMs in polymers. Exceptions include chilled extrusion and wet kneading where low temperature (e.g. 0 °C) an high screw speed was used (e.g. 200–400 rpm). In those cases, shear and compression forces are sufficiently high to achieve adequate CNM dispersion.

Neither of the studied milling processes appear promising in achieving better dispersion of CNMs. Chilled extrusion is sufficient in dispersing CNMs, but not good in improving the mechanical performance of the composites as compared to other methods. Wet kneading

performed better than dry kneading in improving the mechanical properties of the final composites. Possibly, water in the wet kneading process acts both as plasticizer for fiber fibrillation and lubricant for preventing severe fiber damage.

8. Conclusions and future work

Many challenges exist in the manufacturing of CNM/thermoplastic composites via melt processing. To illustrate a few, CNMs agglomerate during drying; the interfacial compatibility is insufficient; some thermoplastic matrices have high viscosity in the molten form; CNMs can become degraded if extruded with inappropriate parameters. Achieving optimum dispersion of CNMs into thermoplastic matrices is difficult, and to be successful will likely rely on multiple efforts attributed to the complexity of the processes. The benefits and limitations of each method reviewed in this paper is summarized in Table 5. It appears that only focusing on surface modification, or processing techniques may not be sufficient to address the issue. Meanwhile, understanding each individual step well enough is critical for achieving the overall goal. Following points are suggested when dealing with the dispersion of CNMs in thermoplastic polymers in future work.

1. The polymer matrix should have a proper melt viscosity to facilitate polymer chain infiltration and shear dispersion of CNMs. Studies on how polymer melt viscosity affects CNM dispersion should be conducted.
2. The form of CNMs before compounding plays a critical role on their dispersion and resulting composites' mechanical performance. Developing and investigating new dewatering methods that preserve the nanostructure of CNMs and lower the drying cost will still be an important research area.
3. Both chemical and physical surface treatments have been demonstrated efficient in assisting the dispersion of CNMs in thermoplastic polymers. Proper amount of reagents should be used to sufficiently change the CNM surface to block the hydrogen bonding, without creating a mechanically weak interphase between CNMs and polymers. For the acetylation/esterification approach, future research should focus on green chemistry routes that use reduced solvents or even solvent free systems for surface modifications. More research should be performed on silanes to achieve a similar level of modification with acetylation/esterification as some silanes are already water-compatible and bear interesting end functional groups for targeting polymer matrices. Polymer wrapping ought to be tailored towards their niche composite systems. The research on surfactant method should be furthered to achieve better mechanical performance. Ultrasound and plasma treatments can be applied to CNMs/thermoplastic composites manufacturing to understand their potential.
4. Coupling agents are highly recommended to be incorporated to the CNM/thermoplastic composite systems at proper loading level to further boost the interaction between CNMs and thermoplastic polymers, and improve the composites' mechanical properties.
5. Solid state shear pulverization (SSSP) methods can reduce the size of CNM agglomerates effectively. Fiber damage is severe during SSSP. So, adding lubricants may reduce the fiber damage, which should be further investigated.
6. None of the investigated extruders showed large enough shear force to significantly deagglomerate the bundled CNMs into nanoscale during melt extrusion. A specific screw design that provides higher shear force is highly desired to possibly remove mechanical pretreatment step for a fast industrial-scale production.
7. There is no deep understanding on the relation between extrusion parameters and the dispersion of CNMs. Proper temperature settings across the barrel may provide either low viscosity polymer melt or high viscosity polymer melt required at different phases of CNMs dispersion.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

Authors from Oak Ridge National Laboratory (ORNL) are supported by the U.S. Department of Energy, Office of Energy Efficiency and Renewable Energy, Advanced Manufacturing Office, under contract DE-AC05-00OR22725 with UT-Battelle LLC. ORNL authors also like to thank the staff of Manufacturing Demonstration Facility of the Oak Ridge National Laboratory for their invaluable help. Authors from University of Maine are grateful for the funding support from UT-Battelle LLC with the U.S. Department of Energy under contract DE-AC05-00OR22725 (subcontract # 4000174848). This manuscript has been authored in part by UT-Battelle, LLC, under contract DE-AC05-00OR22725 with the US Department of Energy (DOE). The US government retains and the publisher, by accepting the article for publication, acknowledges that the US government retains a nonexclusive, paid-up, irrevocable, worldwide license to publish or reproduce the published form of this manuscript, or allow others to do so, for US government purposes. DOE will provide public access to these results of federally sponsored research in accordance with the DOE Public Access Plan (<http://energy.gov/downloads/doe-public-access-plan>).

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