Recent Advances and an Industrial Perspective of Cellulose Nanocrystal Functionalization through Polymer Grafting

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ABSTRACT

Cellulose nanocrystals (CNCs) are an emerging nanomaterial for applications ranging from coatings and construction to adhesives and biomedical devices. Owing to their high aspect ratio, stiffness, and reinforcing potential, CNCs have shown great promise to be used in polymer nanocomposites. However, due to their inherent hydrophilicity and compatibility with polar environments, the use of CNCs in hydrophobic polymer matrices or in organic solvent-based formulations has been limited. To overcome this incompatibility, many reports on grafting polymers onto the surface of CNCs have been published over the past ten years. This review describes the recent advances in CNC surface functionalization through polymer grafting, and comprehensively covers the existing work to date. Methods including polymer "grafting *to*" and "grafting *from*" are described in detail, using polymerization techniques such as free radical, ring opening, and controlled radical polymerization. Purification and characterization of polymer-grafted CNCs, the potential for upscaling these functionalization methods, and current perspectives from academic and industrial viewpoints are presented.

Keywords: cellulose nanocrystals; polymer grafting; surface functionalization; grafting to; grafting from; free radical polymerization; ring opening polymerization; controlled radical polymerization; manufacturing considerations; patents

1. Introduction

Since the 12 principles of green chemistry were first proposed by Anastas and Warner in the late 1990s [1], there has been a significant shift towards the use of sustainable materials to replace toxic and petroleum-derived chemicals. Nanoparticles from renewable resources, such as cellulose nanocrystals (CNCs) have the potential to address several of the 12 principles, while additionally imparting new properties and functionality to existing materials. CNCs were first reported by Nickerson and Habrle in 1947 [2], but the widespread interest in their use was spurred by a series of papers published by Derek Gray and coworkers in the 1990s that focused on the physicochemical properties of CNCs [3–5], as well as the first reports on using CNCs in nanocomposites, published in 1995 [6]. CNCs are rigid, rod-shaped nanoparticles derived from natural cellulose sources, most commonly wood pulp and cotton [7]. This unique nanomaterial has piqued the interest of many researchers, and a number of comprehensive review articles describe their structure [8,9], properties [7,10–12], and potential applications [11,13–16].

CNCs differ from other types of cellulose nanomaterials due to their higher degree of crystallinity (leading to higher stiffness and strength) and smaller size, making them a true nanomaterial in all dimensions. The term “cellulose nanomaterials” is often used, along with “nanocellulose”, to define a wide variety of nanoscale cellulosic (or lignocellulosic) materials including cellulose nanofibrils (CNFs), bacterial nanocellulose (BNC), and CNCs [16]. All types of cellulose nanomaterials are fibre, ribbon or rod-like with a range of lengths and widths depending on the isolation method and the starting cellulose source. CNFs are produced primarily through the mechanical disintegration of plant fibers, BNC is produced via a “bottom up” approach by particular genera of bacteria, while CNCs may be produced from many sources (such as plants, BNC, tunicate and algae) via chemical methods [17]. While a number of valuable contributions have been achieved in the case of surface modification of CNFs and BNC via polymer grafting [18–23], this review highlights recent advances focused on polymer grafting with CNCs, including tables that comprehensively summarize all reports on the preparation of polymer-grafted CNCs to date.

CNCs are typically isolated using a sulfuric acid hydrolysis process that preferentially degrades the disordered cellulose regions, yielding nanoparticles with high crystallinity and uniformity [17]. Sulfuric acid hydrolysis results in sulfate half-ester groups grafted to the CNC surface, which impart anionic surface charges. CNCs can also be prepared with hydrochloric acid, which gives uncharged nanoparticles, or through oxidation methods that produce CNCs with surface carboxylic acid moieties [24,25]. The abundance of hydroxyl groups in the cellulose chains means that CNCs are generally considered hydrophilic. However, the packing of cellulose chains within individual CNC particles results in a hydrophobic crystal plane "edge" [26] which leads to amphiphilic properties (that are dependent on the CNC surface charge and isolation method) such that CNCs have been shown to stabilize a variety of emulsions and foams [27].

The colloidal stability of sulfated CNCs (called "unmodified CNCs" herein) in aqueous dispersions has been extensively studied [28], and it is well known that CNCs form stable suspensions in water. These suspensions remain stable over a large range of pH values (if the ionic strength remains below about 50 mM [29]), i.e., from approximately pH 3 to 11. Still, highly acidic conditions are known to destabilize the suspensions due to the protonation of acid groups [30] and further acid-catalyzed hydrolysis of the CNCs [31]. Extreme alkaline conditions are also known to destabilize CNC suspensions as basic conditions can be used to de-sulfate CNCs [32]. Furthermore, CNC colloidal stability has been studied in organic solvents, with dimethyl sulfoxide (DMSO), dimethylformamide (DMF), formic acid and polar organic solvents showing the best ability to disperse CNCs [33–35]. Other organic solvents, such as ethanol, toluene, chloroform etc. are poor dispersing media for CNCs and lead to severe aggregation, meaning that processing or functionalizing CNCs in these solvents will not provide uniform materials. However, if hydrogen bonding between CNCs and solvents are maintained via solvent exchange approaches, CNCs can be introduced into a wider variety of solvents. This process is nevertheless time consuming and typically involves centrifugation steps, which may lead to some degree of CNC aggregation. The limitation of preparing well-dispersed CNC suspensions in organic solvents can be also overcome via polymer grafting, which allows for the modification of CNCs with hydrophobic polymers in order to improve their compatibility with non-polar media and/or induce steric stabilization [8,36,37]

With the goal of using CNCs in commercial and high volume applications, CNC production has been scaled up and the hydrolysis and purification have been optimized using a variety of cellulosic feedstocks. *CelluForce Inc,* located in Windsor, Quebec, Canada currently operates the largest production facility with the capacity to produce ton per day quantities of CNCs via the sulfuric acid hydrolysis of bleached Kraft pulp. *Alberta Innovates Technology Futures* (recently renamed *InnoTech Alberta*), and the *USDA Forest Products Lab* are also producing CNCs at a kg per day capacity and tens of kg per day, respectively, using dissolving wood pulp. These CNCs have properties comparable to those made via lab scale processes [38]. With an expanding variety of producers and cellulose sources, there is a large potential for CNCs to be used in exciting industrially-relevant applications such as packaging, coatings, adhesives, construction materials, biomedical devices [39], and even high volume oil and gas extraction fluids [40].

For many of the envisioned applications, CNCs need to function in hydrophobic polymers, organic solvents, or high salt (e.g., brine) conditions, which require CNC surface modification. A number of reports on CNC surface modifications have been published and patented in recent years [8]. Aside from polymer grafting, which is the focus of this review, other common surface modification routes include non-covalent surface modifications (i.e., adsorption of polymers or surfactants [41–46]) and small molecule covalent surface modifications such as esterification, etherification, silylation, amidation and urethanization [8].

Polymer grafting serves to covalently attach polymer chains to CNCs to give brush or mushroom-like surface morphologies following two methods: "grafting *to*" where pre-formed polymer is attached to the surface of the CNCs, or "grafting *from*" where the polymerization is initiated from the CNC surface (Figure 1). Polymer grafting *to* is beneficial since the polymer can be carefully synthesized and thoroughly characterized before it is grafted to the CNCs and reactions are often carried out in water. However, theoretically steric hindrance limits the density of polymers that can be grafted to a single nanoparticle, and most reports of grafting *to* CNCs do not report a value for polymer graft density. If a graft density is reported, it is typically on the low end compared to the range reported for grafting *from* CNCs via ATRP. Grafting *from* generally allows for a higher grafting density, as many initiating sites are available on the CNC surface, but the method tends to be multi-step and characterizing the polymer chain length and polymerization kinetics can be challenging [47].

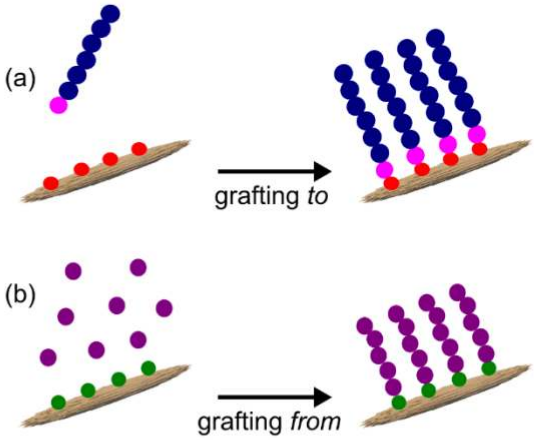


Figure 1. Schematic of (a) grafting *to* CNCs with a given CNC reactive group (red) and a pre-formed polymer (blue) that is end functionalized (pink) and (b) grafting *from* CNCs with inherent (surface hydroxyl groups) or added initiating groups (green). Individual purple circles represent monomers and chains of circles are polymers.

In this review, we aim to provide a comprehensive report of the published work involving polymer grafting *to* and *from* CNCs, while specifically highlighting recent advances and the outlook for scale-up and industrial feasibility. The review is arranged by type of polymer grafting, and should provide the reader with a general understanding of polymer-grafted CNC synthesis and the reported examples to date.

2. Polymer grafting *to* CNCs

The grafting *to* method generally takes advantage of the abundance of reactive hydroxyl groups on the CNC surface and end-functionalized polymers. The main benefit of grafting *to* is the fact that the grafted polymers can be characterized prior to their attachment to CNCs, allowing for a known polymer graft length. However, grafting *to* can be limited due to steric hindrance, as long chain polymers may entangle with one another or hinder the diffusion of subsequent polymer chain ends to reach the CNC surface. In cases such as the work by Araki et al.[48], polymer grafting *to* CNCs was used to impart steric as opposed to electrostatic stabilization. This pioneering work was a seminal contribution to the field of polymer-grafted CNCs. Table 1 summarizes all existing literature using grafting *to* to modify CNCs with polymers, with the most common chemistry being carbodiimide coupling, epoxy ring opening, and isocyanate-mediated grafting, shown in Figure 2.

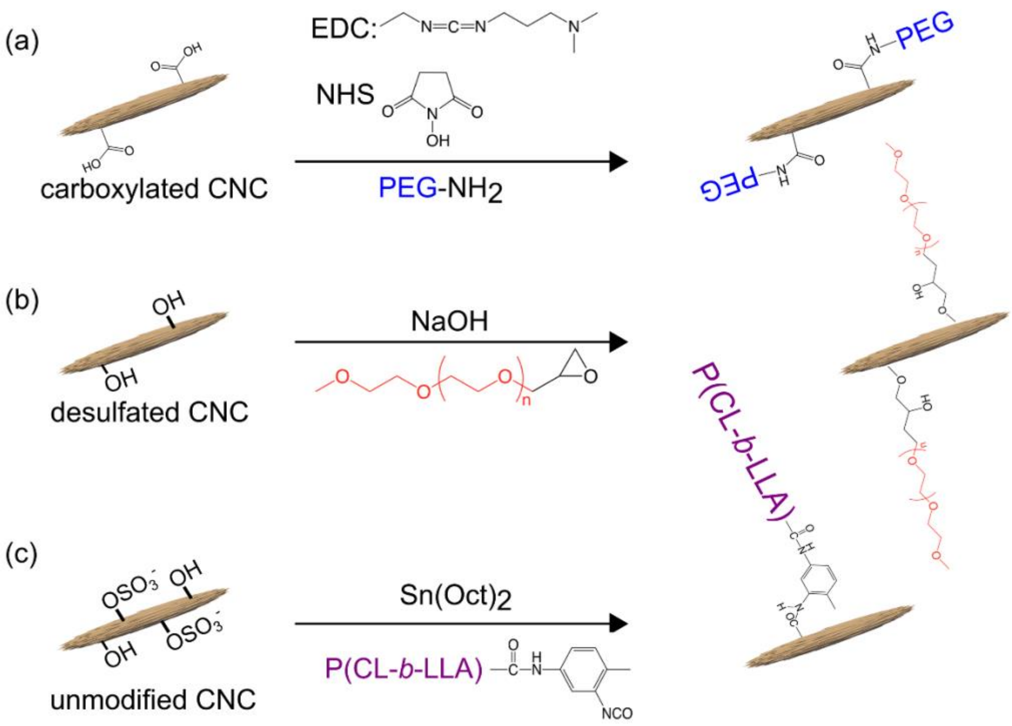


Figure 2. Examples of common grafting *to* reactions to prepare polymer-grafted CNCs: (a) carbodiimide coupling to attach amine terminated poly(ethylene glycol) (PEG-NH_2) to carboxylated CNCs [48], (b) epoxy ring opening in basic conditions to attach epoxy terminated poly(ethylene oxide) to desulfated CNCs [36], and (c) isocyanate mediated grafting *to* to attach poly(caprolactone-*block*-L-lactide) (P(CL-*b*-LLA)) to unmodified CNCs [49].

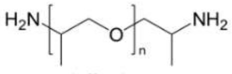
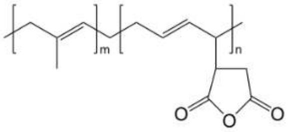
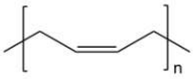
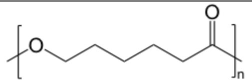
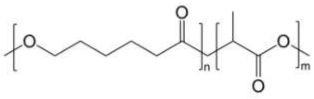
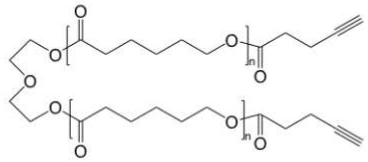
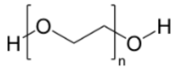
Carbodiimide coupling between polymers and CNCs (Figure 2a) has been performed using amine terminated polymers and carboxylic acid functional groups on the CNC surface. Therefore, unmodified CNCs produced via sulfuric acid hydrolysis containing sulfate half-ester surface groups require additional functionalization (for example, 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO) modification [25]) to impart carboxylic acid surface groups prior to the grafting of polymers. CNCs with carboxylic acid groups can also be produced from HCl hydrolyzed CNCs that are TEMPO oxidized either before [44] or after [25] the hydrolysis. This linker chemistry is favourable as it results in one nitrogen atom per polymer linkage and can therefore be easily characterized to determine graft density via elemental analysis as long as the polymer does not contain nitrogen. Carbodiimide coupling chemistry has proven to be highly effective and can be used to graft polymers to CNCs at relatively high surface coverage. Common solvents used are water (used to graft 400 g/mol [50] and 1000 g/mol [48] poly(ethylene glycol)) and DMF (used to graft hydrophobic 4840 g/mol polystyrene (PS) and 10 530 g/mol poly(tert-butyl acrylate) [51]).

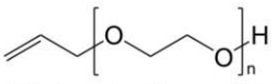
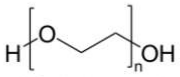
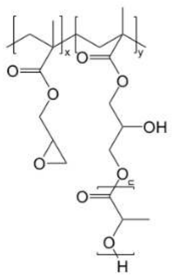
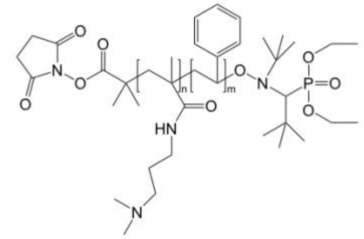
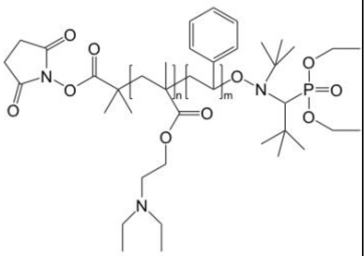
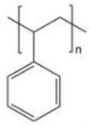
These are ideal solvents for polymer grafting *to* reactions since CNCs are colloidally stable in both water and DMF and more uniform surface functionalization is presumed for systems where CNCs are well dispersed [33].

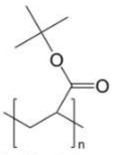
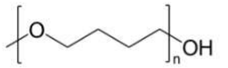
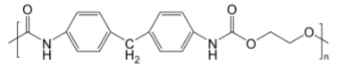
Polymer grafting *to* CNCs via epoxy ring opening (Figure 2b) also requires the polymer to be end functionalized, however with an epoxy ring as opposed to amine terminated for carbodiimide coupling. Epoxy ring opening chemistry relies on the deprotonation of CNC surface hydroxyl groups (therefore no initial CNC modification is required), which occurs at high pH, e.g. pH > 10. This chemistry has been effective in grafting polymers in water [36] and dioxane [52]. Characterization of polymer-grafted CNCs using epoxy ring opening can be challenging since the polymer is attached to the CNC via an ether bond already present in unmodified CNCs, however, characterization methods such as water contact angle [52] and matrix-assisted laser desorption/ionization-time of flight mass spectrometry [36] have been used to confirm successful polymer grafting reactions.

Isocyanate-mediated polymer grafting *to* CNCs (Figure 2c) has been used to prepare hydrophobically modified CNCs with polymers such as poly(caprolactone) homopolymer [53] and copolymers [49], poly(urethane) [54], and poly(tetramethylene glycol) [55], typically in a multi-step procedure in order to ensure the reaction is strictly between polymer end groups and CNCs. Isocyanate-mediated linker chemistry results in the formation of a carbamate with the CNC hydroxyl groups, but since TDI is most often used, there are at least 2 nitrogen atoms per linker. Alternatively, there can be 3 nitrogen atoms per linker if the other isocyanate groups are reacted with an amine-functionalized polymer to form a urea. However, this linker chemistry has the potential to be easily characterized to determine graft density using elemental analysis to determine nitrogen content, only if the polymer backbone does not contain nitrogen. Since isocyanate moieties are moisture-sensitive, the presence of residual water has a negative impact on reaction yields. In this case, CNCs must either be solvent-exchanged through successive centrifugation steps [53,54] or freeze-dried and re-dispersed [55] in dry organic solvents in order to remove residual water. However, this preparative drawback is counteracted by the high reactivity of isocyanates towards CNC hydroxyl groups, often yielding high surface coverage compared to other grafting *to* chemistries.

Table 1. Summary of polymer grafting *to* CNCs including polymers (in alphabetical order), linker chemistry, reaction solvent, grafted polymer molecular weight (MW), and target application, if reported.

Grafted Polymer	Linker Chemistry	Solvent	Polymer MW [g/mol]	Graft Density [chains/nm^2]	Target Application	Ref.
amino-modified ssDNA	carbodiimide coupling	water	20-mer 78-mer	–	DNA/CNC hybrids	[56]
 Jeffamine	carbodiimide coupling	water, DMF	1000, 2070, 2005	1.2	stimuli responsive nanocomposites	[57]
			2000	1	stimuli responsive nanocomposites	[58]
 maleated poly(propylene)	esterification	toluene	3900	–	nanocomposite films	[59]
 poly(butadiene)	thiol-ene click	THF	–	–	nanocomposites	[60]
 poly(caprolactone)	isocyanate-mediated	toluene	10 000, 42 500	–	nanocomposite films	[61]
 poly(caprolactone-*b*-L-lactide)	isocyanate-mediated	toluene	6190, 10 500	–	nanocomposites	[49]
 poly(caprolactone) diol	Cu catalyzed azide-alkyne cycloaddition	DMF	–	–	nanocomposites	[62]
 poly(ethylene glycol)	carbodiimide coupling^a	water	1000	0.5	steric stabilization/ dispersion for liquid formulated products or nanocomposites	[48]
			400	–	nanocomposites	[50]

 poly(ethylene glycol) monoallyl ether	triazinyl chemistry	water	388	–	nanocomposites	[63]
 poly(ethylene oxide)	epoxy ring opening[b]	water	2086	–	steric stabilization/ dispersion for liquid formulated products or nanocomposites	[36]
 poly(lactide-*co*-glycidyl methacrylate)	epoxy ring opening[b]	dioxane	70 000	–	nanocomposites	[52]
 poly((*N*-3-(dimethylamino) propyl methacrylamide)-*co*-styrene)-SG1	SG1[c] capped polymer/glycidyl methacrylate-modified CNCs	water	2200, 4400, 5700	0.8-14.2	CO_2 switchable flocculants, stimuli-responsive Pickering emulsions, nanocomposites	[64]
 poly((*N*,*N*-(diethylamino)ethyl methacrylate-*co*-styrene)-SG1	SG1[c] capped polymer/glycidyl methacrylate-modified CNCs	water	4200, 7800, 19 700	0.8-14.2	CO_2 switchable flocculants, stimuli-responsive Pickering emulsions, nanocomposites	[64]
 poly(styrene)	carbodiimide coupling[a]	DMF	4840	0.14[d]	dispersion for liquid formulated products or nanocomposites	[51]

 poly(*tert*-butyl acrylate)	carbodiimide coupling[a]	DMF	10 530	0.14[d]	dispersion for liquid formulated products or nanocomposites	[51]
 poly(tetramethylene glycol)	isocyanate-mediated	DMF	1000	–	nanocomposites	[55]
 poly(urethane)	isocyanate-mediated	DMF	–	–	nanocomposites	[54]

[a] Carbodiimide coupling refers to an amine functionalized polymer grafting *to* carboxylic acid groups on the CNC surface.

[b] Epoxy ring opening refers to an epoxy terminated polymer reacting with CNC surface hydroxyl groups under alkaline conditions.

[c] SG1 – *N*-*tert*-butyl-*N*-(1-diethylphosphono-2,2-dimethypropyl) nitroxide

[d] Approximate grafting density was calculated from the % polymer reported based on calculations outlined in reference [65] and assuming CNC dimensions of 120 nm in length and 15 nm in cross-section.

3. Polymer grafting *from* CNCs

Grafting *from* CNCs provides a modification route where theoretically high grafting densities (hundreds to thousands of polymer chains per CNC) may be achieved, and tends to be more popular in the literature, with reports of both hydrophilic and hydrophobic polymers grafted from CNCs. Polymer grafting *from* CNCs is a rapidly growing research field, with all examples published in the past 10 years. The existing literature can be divided into three categories of grafting *from* techniques: free radical polymerization, ring opening polymerization (ROP), and controlled radical polymerization (CRP) which is further broken down into three subcategories: atom transfer radical polymerization (ATRP), reversible addition-fragmentation chain-transfer polymerization (RAFT), and nitroxide mediated polymerization (NMP).

The main advantage of grafting *from*, specifically with controlled polymerization techniques, is the ability to control grafting density as well as graft length [66]. However, grafting *from* can be a multi-step process, where in many cases the initiator must be immobilized on the CNCs prior to polymerization [67]. Moreover, most (but not all) of the grafting *from* polymerization reactions reported to date occur in organic solvents where CNC colloidal stability is not ideal. The tradeoff is that the dispersion of CNCs in organic solvents (and hydrophobic polymers) should improve as the polymerization proceeds, particularly when grafting hydrophobic polymers.

3.1 Free Radical Polymerization

Free radical polymer grafting *from* CNCs is a convenient method for grafting polymers on CNCs as it is carried out in water and does not require a pre-step to attach surface initiators. Instead, water soluble radical initiators react with the cellulose backbone or surface hydroxyl groups resulting in a free radical site from which the polymer can grow. These reaction conditions are favourable for CNCs and help to ensure that the modification occurs on individual nanoparticles as opposed to aggregates. Free radical polymer grafting *from* CNCs has been demonstrated with ceric ammonium nitrate (CAN), potassium persulfate (KPS), and ammonium persulfate (APS) initiators and a range of water soluble monomers (Table 2). Reaction conditions involve elevated temperatures, inert atmospheres to ensure radicals are not terminated early, and thorough mixing. Typical applications for CNCs grafted via aqueous free radical polymerization are for improved compatibility and incorporation into polymer nanocomposites, for *in situ* incorporation into polymer-CNC hydrogels, or to impart responsive behavior and control colloidal stability and interface stabilizing abilities of CNCs.

Free radical polymer grafting *from* CNCs with CAN was first demonstrated by Kan et al. who grafted CNCs with the hydrophilic, pH responsive polymer poly(4-vinylpyridine) (P4VP). Grafting P4VP from CNCs resulted in pH responsive CNCs that showed potential as reversible flocculants [68]. Pracella et al. [69] also used CAN to graft poly(glycidyl methacrylate) from CNCs in order to improve CNC compatibility in nanocomposites. Furthermore, Tang et al. showed that both poly(oligoethylene glycol) methacrylate (POEGMA – a thermally responsive polymer) and poly(methacrylic acid) (PMAA – a pH responsive polymer) could be grafted from CNCs by sequentially using CAN to graft POEGMA and then APS to graft PMAA [70]. CAN has also been used to graft hydrophobic PMMA from CNCs [71]. Similarly, ceric salt was used to graft poly(acrylamide) from CNCs resulting in nanocomposite hydrogels [72]. One slight complication in these water-based polymerizations is that the CNCs tend to aggregate as the polymer chains grow and entangle (and become less hydrophilic); to surmount this issue, sonication was found suitable to provide sufficient energy and mass transfer during polymerization to reduce the formation of locally aggregated regions [68,71].

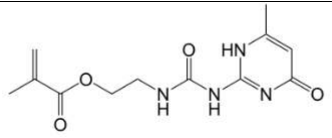
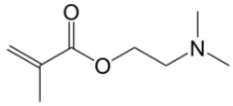
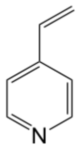
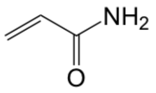
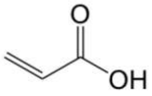
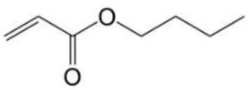
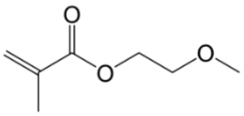
KPS has been used to graft hydrophilic polymers such as poly(acrylamide) [73–75], poly(acrylic acid) [76,77], poly(methacrylic acid-co-ethylene sulfonic acid) [78], the hydrogen bonding moiety 2-ureido-4[1H]-pyrimidone [79], and recently hydrophobic poly(styrene) (PS) [80] from CNCs. The reactions have all been performed in aqueous media and have typically been intended for CNC-polymer hydrogels [73,74,76,77,79] or improving the compatibility between CNCs and hydrophobic polymers [80].

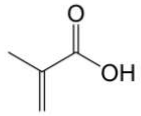
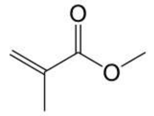
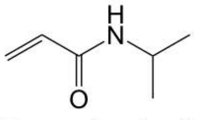
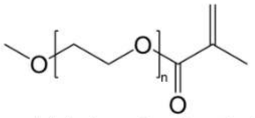
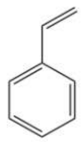
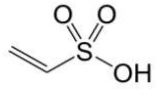
APS has only been used to graft hydrophilic polymers from CNCs. Tang et al. grafted poly[2-(dimethylamino)ethyl methacrylate] (PDMAEMA) from CNCs in order to prepare dual responsive Pickering emulsions, as PDMAEMA has both pH and thermoresponsive behavior [81]. Similarly, APS has been used to graft another thermoresponsive polymer, poly(*N*-isopropylacrylamide) (PNIPAM) to prepare thermoresponsive hydrogels [82].

Other methods of free radical polymer grafting *from* CNCs involve the use of a pre-attached bis(acyl)phosphane oxide photoinitiator [83], or using the Graftfast method [84]. The bis(acyl)phosphane oxide-modified CNCs were dispersed in ethanol and grafted with hydrophobic polymers such as poly(methyl methacrylate) (PMMA), poly(butyl acrylate) (PBA), and hydrophilic PNIPAM to achieve 300-477% polymer by mass [83]. The Graftfast method uses chemical reduction of diazonium salts by reducing agents in the presence of vinyl monomers and has been used to graft PS from CNCs in water [84].

The pitfalls of free radical polymer grafting *from* CNCs are the inability to control the grafted polymer length (and polydispersity) and the grafting density, leading to a heterogeneous modification that is typically difficult to characterize. Moreover, free radical polymerization in general is known to lead to high polydispersity due to the lack of control over termination reactions. Most papers on free radical polymer grafting *from* CNCs do not report the grafted amount, and if it is reported, it is typically under 20% by weight (Table 2). Additionally, a significant amount of free homopolymer (not grafted on the CNCs) is produced as a side reaction and can be difficult to separate from the modified CNCs, leading to impure products. For some applications (e.g. if the grafted CNCs are to be added to a bulk polymer to produce nanocomposites), producing “side” homopolymer may not be detrimental, however, the yield of polymer-grafted CNCs is low which may make it less suitable for scale-up despite the advantage of working in water under mild conditions.

Table 2. Summary of free radical polymerization grafting *from* CNCs including monomers (in alphabetical order), initiator used, amount of polymer grafted from the CNCs (where reported), and the target application discussed in the paper. All reactions were carried out in aqueous environment except reference [83].

Monomer	Initiator	Amount of Polymer Grafted (wt.%)	Target Application	Ref.
 2-(3-(6-methyl-4-oxo-1,4-dihydropyrimidin-2-yl)ureido)-ethyl methacrylate	KPS	7	cell adhesive hydrogels	[79]
 2-(dimethylamino)ethyl methacrylate	APS	11	responsive Pickering emulsions	[81]
 4-vinyl pyridine	CAN	–	pH responsive flocculants	[68]
 acrylamide	KPS	–	nanocomposite hydrogels	[73–75]
	ceric salt	60	nanocomposite hydrogels	[72]
 acrylic acid	KPS	–	nanocomposite hydrogels	[76,77]
 butyl acrylate	bis(acyl)phosphane oxide	300-477	–	[83]
 di(ethylene glycol) methyl ether methacrylate	CAN	11.5*	stimuli responsive colloids	[70]

 methacrylic acid	APS	11.5*	stimuli responsive colloids	[70]
	KPS	–	myoglobin separation	[78]
 methyl methacrylate	CAN	11	nanocomposites	[71]
	bis(acyl)phosphane oxide	300-477	–	[83]
 *N*-isopropylacrylamide	APS	–	wound dressings	[82]
	bis(acyl)phosphane oxide	300-477	–	[83]
 poly(ethylene glycol) methyl ether methacrylate	CAN	11.5*	stimuli responsive colloids	[70]
 styrene	KPS	15	nanocomposites	[80]
	Graftfast	–	–	[84]
 vinyl sulfonic acid	KPS	–	myoglobin separation	[78]

*Represents total amount of polymer, as two different polymers were grafted.

3.2 Ring Opening Polymerization

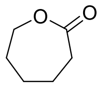
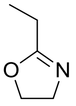
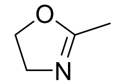
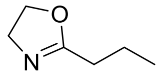
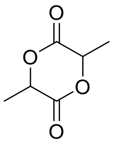
Given the abundance of hydroxyl groups present at the CNC surface, ROP is a common approach to graft polymers from CNCs [85–87]. ROP of cyclic monomers, such as ε-caprolactone (ε-CL) [86,87,96–98,88–95], *l*-lactide (*l*-LA) [90,98,107,108,99–106], and *d*-lactide (*d*-LA) [94,109–111] can be initiated directly from these –OH groups. The first synthetic pathways for grafting polymers from CNCs were, in fact, developed based on surface-initiated ROP from –OH groups [86]. The main interest in grafting such polyesters from CNCs is toward the development of biobased and biodegradable nanocomposites, which have great potential for biomedical devices and packaging [85]. Shown in Table 3 is a summary of published work on ROP from CNCs, including solvent, degree of polymerization (DP), contact angle, and reported target application (where provided). In all reported work, the grafting density is not reported, likely owing to the fact that there is no bond formation between the CNCs and polymer that can be distinguished from unmodified CNCs. The majority of the initial work in this area focused on ROP of ε-CL, which is conducted in organic solvents, such as toluene [86,89–95,98], or in bulk [87,88,96,97] due to the low moisture tolerance of the reaction. To work in toluene, CNCs are solvent exchanged from water to acetone to toluene via successive centrifugation, or dry CNCs are dispersed in toluene via sonication, however, even if separated initially, aggregation and sedimentation of CNCs in toluene is very fast (but can be partially mediated through constant stirring), and likely leads to non-uniform surface modifications. Polylactic acid (PLA) was also grafted from CNCs in DMSO [107]. In general, polyesters, such as poly-ε-caprolactone (PCL) and PLA, have most often been grafted from CNCs using tin(II) 2-ethylhexanoate ($Sn(Oct)_2$) as a catalyst, with temperature ranges of 80 to 130 °C [86,88,100–104,106,107,109,110,89,91–96,99]. Under such conditions, ROP proceeds via a coordination-insertion mechanism [85]. Other inorganic compounds, such as magnesium hydride (MgH_2) [105] and zinc oxide [107], and organic compounds, such as citric acid [97], tartaric acid [91], and 4-dimethylaminopyridine (DMAP) [91,112] have also been used to catalyze ROP from CNCs. Chang et al. reported bulk ROP of ε-CL catalyzed by $Sn(Oct)_2$ under microwave irradiation, which resulted in high PCL contents [88,96]. In one of these studies, the authors obtained PCL contents of 90-96%, yielding thermoformable one-component nanocomposites [96]. Given the relative hydrophobicity of such polyesters, the water contact angle of the resulting CNCs grafted with PCL typically falls within the range of 70-90° (Table 3).

The primary disadvantage of ROP of lactones and lactides from CNCs is the moisture sensitivity, which necessitates either drying and re-dispersing CNCs in organic solvents using high energy sonication or laborious solvent-exchange assisted by centrifugation. Moreover, the existence of ester functional groups along the polymer chains does not allow a straightforward means to cleave polymers off of CNCs and analyze them by standard techniques, such as gel permeation chromatography (GPC). Therefore, little is known regarding the molecular weight and polydispersity of the grafted polyesters themselves. The use of sacrificial initiators, such as benzyl alcohol [107], provides a method to estimate the physical properties of the grafted polyesters, although one must assume that the kinetics of the simultaneous solution ROP are analogous to those initiated from the CNC surface. This approach has also been utilized during the grafting of

PCL from other types of cellulosic nanoparticles [113]. This investigation determined the surface coverage of CNCs to be between 3-7% of anhydroglucose units (AGUs) with PCL molecular weights from 4-11 kDa (DP of 15-43) and polydispersities of 1.2-1.4. Luiz de Paula et al. used ^{1}H and ^{13}C NMR spectroscopy of PLA-*g*-CNCs to determine a DP of 12 for the grafted polymers [105]. Wu et al. estimated a DP of 24 for similar systems based on FTIR spectroscopy [111].

Most often, hydrophobic polyesters are grafted from CNCs via ROP, however a few hydrophilic polymer brushes have also been successfully synthesized, namely oxazolines [114,115]. Since the mechanism of oxazoline ROP is cationic, tosylation of hydroxyl groups is first necessary [115]. Here, tosylated CNCs were used for bulk ROP of 2-ethyl-2-oxazoline. 2-Methyl-2-oxazoline and 2-*n*-propyl-2-oxazoline were further grafted from poly(2-isopropenyl-2-oxazoline)-modified CNCs to give bottle brush-type polymer grafts [114]. Indocyanine green (ICG) was then immobilized on these bottle brush-modified CNCs via electrostatic interactions toward photothermal cancer therapeutic agents.

Table 3. Summary of ring opening polymerization grafting *from* CNCs including monomers (in alphabetical order), polymerization solvent, degree of polymerization (DP), contact angle, and target application, where reported.

Monomer	Polymerization Solvent	DP	Contact Angle	Target Application	Ref.
 ε-caprolactone	toluene	–	~78	nanocomposites	[86]
			–	nanocomposites	[89,90,93–95]
			70	–	[91]
			82	–	[92]
			–	–	[108]
	bulk monomer	–	–	–	[87]
			89	one-component nanocomposites	[96]
			~78	–	[97]
			–	nanocomposites	[88]
	bulk monomer (microwave)	–	89	one-component nanocomposites	[96]
			–	nanocomposites	[88]
 2-ethyl-2-oxazoline	bulk monomer (microwave)	–	–	post-polymerization modification	[115]
 2-methyl-2-oxazoline	acetonitrile	–	–	photothermal cancer therapy (bottle brushes)	[114]
 2-*n*-propyl-2-oxazoline	acetonitrile	–	–	photothermal cancer therapy (bottle brushes)	[114]
 lactide	toluene	–	–	shape-memory polymers	[98]
		–	–	nanocomposites	[90,94,110,99–101,103,104,106,108,109]
		–	–	–	[102]
		24	–	nanocomposites	[111]
	DMSO	–	76	nanocomposites	[107]
	bulk monomer	12	–	nanocomposites	[105]

3.3 Controlled Radical Polymerization

Controlled radical polymerization (CRP), also known as reversible-deactivation radical polymerization (RDRP), has given rise to an unlimited number of new polymeric materials with improved macroscopic properties resulting from a comprehensive understanding of structure-property relationships as well as guidelines based on theoretical predictions [116]. CRP is characterized by a combination of fast initiation and minimal termination, along with a dynamic equilibrium between propagating radicals and a given dormant species. Fast exchange among active and dormant species is required for good control over molecular weight, polydispersity, and chain architecture in all CRP systems. A growing species should ideally react only with a few monomer units before it is deactivated to the dormant state. In particular, surface initiated CRP provides a sophisticated method of tailoring the chemical and physical properties of interfaces and can be used to design better nanocomposites with improved properties owing to the enhanced interfacial interactions between matrix and filler [117]. To date, three types of CRP have been used to graft *from* CNCs including atom transfer radical polymerization (ATRP), reversible addition-fragmentation chain-transfer polymerization (RAFT), and nitroxide mediated polymerization (NMP) [118]. Each type of CRP allows for control over the polymer graft length, and the addition of initiating groups to the CNC surface prior to polymerization allows for control over the polymer grafting density.

Grafting density and graft length play an important role in the addition of polymer-grafted CNCs into hydrophobic polymers and organic solvents and are important properties that can be tuned for a desired application [118]. For example, improving compatibility between polymer-grafted CNCs and organic solvents may require steric stabilization where the critical grafting density would be below the point of entanglement between neighboring chains [65]. However, for some applications, such as incorporation into polymer latexes or polymer nanocomposites, the CNCs may only require a dense, short chain modification. It is therefore important to consider optimizing grafting density and graft length for a particular application such that the desired properties are achieved without exceeding steric stabilization or “overcompensating” with excess polymer that may not be necessary.

3.3.1 Atom Transfer Radical Polymerization

Transition metal-mediated controlled radical polymerization provides a method for grafting polymers from CNCs with excellent control over both graft length and grafting density. Of the various transition metals that have been used to catalyze CRP, Cu species are the most widely employed. Several variants of Cu-mediated CRP have been reported, which differ in the electron transfer mechanism [119]. Some examples include single-electron transfer living radical polymerization (SET LRP) [120] and activators (re)generated by electron transfer (A(R)GET) ATRP [121]. In the case of polymer grafting from CNCs, normal atom transfer radical polymerization (ATRP) is commonplace. The first report of using ATRP from a cellulose substrate (filter paper) was by Malmström and Carlmark [122], and since then, many examples of using surface initiated ATRP (SI-ATRP) from CNCs have been demonstrated (Table 4). In order to perform SI-ATRP from CNCs, an initiator grafting step is necessary in order to convert the CNC surface into a macroinitiator. This is typically done in organic solvents such as tetrahydrofuran (THF) or DMF, using triethylamine (TEA) and 4-(dimethylamino)pyridine (DMAP) to attach α-bromoisobutyryl bromide (BiBB) to the available hydroxyl groups on the CNC surface, with an example shown in Figure 3. While DMF has been shown to be an acceptable solvent for dispersing CNCs, preparing a proper dispersion of CNCs in THF (i.e., where the CNCs are not aggregated) is difficult. Most literature examples use sonication to disperse freeze dried CNCs in organic solvents, where it is assumed that sonication energy can break up the CNC aggregates into individual CNCs. The vast majority of reported examples of SI-ATRP from CNCs use the initiator attachment protocol involving TEA, DMAP, and BiBB, however bromoisobutyric acid with 1,1'-carbonyldiimidazole in dichloromethane has also been shown to be effective [123,124]. Furthermore, recent work has used a water-based approach (albeit still a multi-step process) to attach 2-bromoisobutanoic acid *N*-hydroxysuccinimide ester to CNCs that were oxidized and modified with ethylenediamine [125]. This is a significant step towards maintaining the "green" aspect of CNCs, whereby the initiator attachment and polymer grafting were performed in water. In another advancement, Boujemaoui et al. [126] used a functional acid (2-bromopropionic acid) during the hydrolysis of cellulose in order to prepare functionalized CNCs with SI-ATRP initiating groups, all in one step during CNC production. This is significant if controlled polymer grafting *from* CNCs is anticipated to be used at an industrial scale.

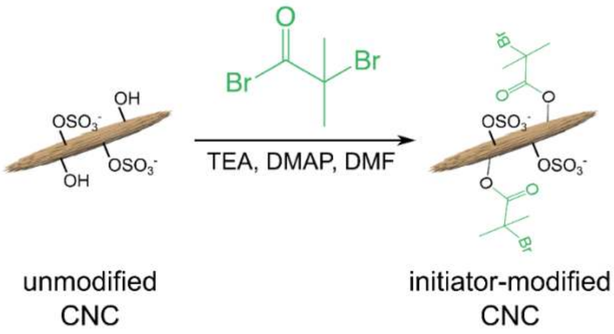


Figure 3. Schematic of the most common method for attaching ATRP surface initiators to CNCs, adapted from reference [127].

While there have been many reported methods of attaching ATRP initiator groups to the CNC surface, little is reported on the efficiency and reproducibility of these reactions. Zoppe et al. [128] studied the effect of CNC surface charge (i.e., sulfate half ester groups) on the initiator efficiency while grafting in aqueous media and found that CNCs with higher charge density had higher initiator efficiency at the expense of high polydispersity caused by inefficient deactivation. Morandi et al. showed that an increasing amount of Br content can be correlated to an increase in the volume of initiator introduced in the attachment step, but there was no report of reproducibility or efficiency of the reaction [67]. This remains a critical step in the SI-ATRP grafting *from* CNCs, as grafting density is directly related to the initiator attachment efficiency. Elemental analysis is the most common method to quantify the amount of initiating groups on the CNC surface (where Br can be detected and correlated to the number of initiating sites per CNC). Therefore, until a systematic study is performed and can predict the efficiency and reproducibility of the initiator attachment step, quantification through elemental analysis is critical. Furthermore, purification of the CNC starting material with methods such as Soxhlet extraction have been shown to result in more reproducible and efficient surface modifications [129] and may result in more consistent reports of polymer grafting density. This is critical, as some reports have indicated that adsorbed oligosaccharides are present on the surface of purified CNCs depending on the hydrolysis reaction conditions [130], which can hinder functionalization of CNC surface hydroxyl groups and grafting yields.

The first report of SI-ATRP grafting *from* CNCs was by Yi et al. [131] who grafted PS. A comprehensive list of polymers grafted from CNCs via SI-ATRP is shown in Table 4. Morandi et al. [67] also grafted PS from CNCs (Figure 4a) and showed a series of PS-*g*-CNCs with varying grafting densities. In their work, the grafted polymer was cleaved from the surface and characterized to show that good control over the SI-ATRP was achieved [47]. If a non-cleavable ATRP initiator is used, as in most cases, a sacrificial initiator (that is a free initiator in solution with similar properties to the initiating groups on the CNC surface) is added to the reaction in order to polymerize free polymer which is collected and characterized to measure the MW and polydispersity (PDI) of the grafted polymer. Most common for systems with BiBB as the surface initiator, ethyl α-bromoisobutyrate (EBiB) is used as sacrificial initiator. Although discrepancies between free polymer and polymer grafted from the CNCs are likely, until recently this has been reported to be the most accurate method of determining the MW and PDI of polymer grafted from the CNC surface, and Morandi et al. [47] showed that the MW and PDI of grafted polymer cleaved from the CNC surface was similar to that of homopolymer polymerized from sacrificial initiator. In a recent report by Zhang et al. [132], elemental analysis of initiator-modified CNCs was combined with thermal gravimetric analysis (TGA) and dynamic light scattering (DLS) of the polymer-grafted CNCs to calculate the weight average MW of the polymer grafted from CNCs, without the need to cleave the polymer chains from the CNC surface. The authors prepared PS-*g*-CNCs and compared the mass of grafted PS (deduced from the TGA curves) with the amount of initiating sites (determined by elemental analysis) and matched theoretical values calculated according to monomer conversion with the MW of the polymer prepared via sacrificial initiator. The MW matched that of the free polymer, and the combination of characterization methods has been proposed as a convenient method for characterizing polymer graft length.

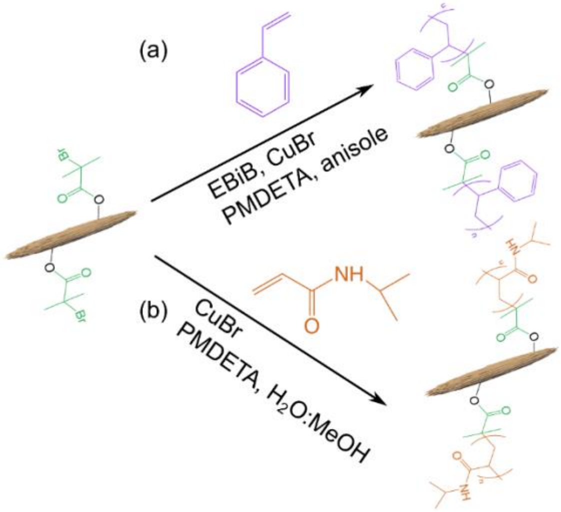
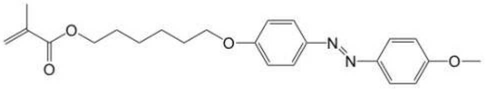
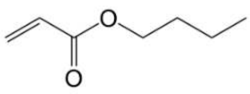
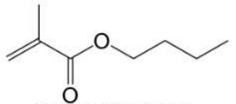
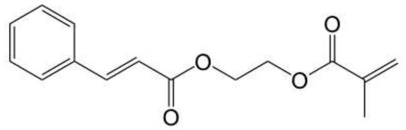
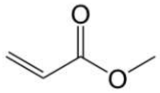
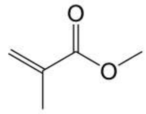
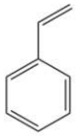
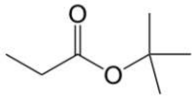
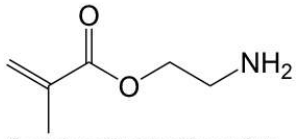
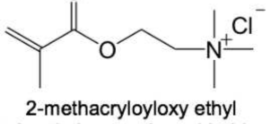
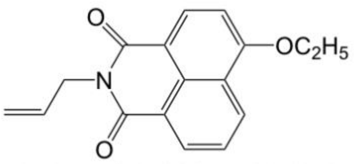
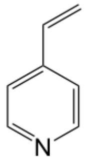
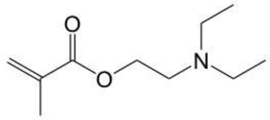
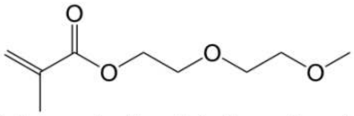
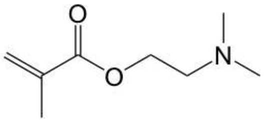
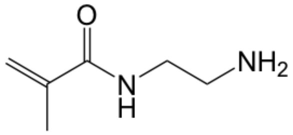
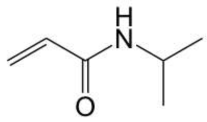


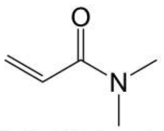
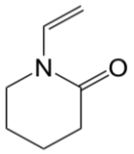
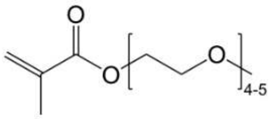
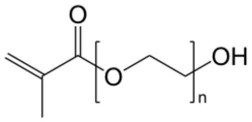
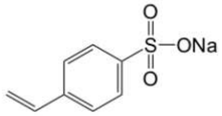
Figure 4. Examples of SI-ATRP grafting of (a) styrene [67] and (b) *N*-isopropylacrylamide [133] *from* initiator-modified CNCs.

Table 4. Summary of the literature on SI-ATRP grafting *from* CNCs, including monomers (in alphabetical order divided by hydrophobic and hydrophilic polymers), polymerization solvent, target degree of polymerization (DP), grafting density (calculated approximately here from Br content of initiator-modified CNCs, where reported), contact angle, and target application, where reported. All examples used CNCs grafted with BiBB in a pre-polymerization step except references [123,124] which grafted bromoisobutyric acid or 2-bromoisobutanoic acid [125], reference [47] which used a photo-cleavable initiator, and reference [126] where the initiator-modified CNCs were prepared during hydrolysis.

Monomer	Polymerization Solvent	Target DP	Grafting Density^{x} (chains/nm^2)	Contact Angle	Target Application	Ref.
			Hydrophobic polymers			
 6-[4-(4-methoxyphenylazo)phenoxy]hexyl methacrylate	chlorobenzene	100	–	–	–	[134]
 butyl acrylate	bulk monomer	1000	1-20	–	thermoplastic elastomer reinforcement	[135]
	toluene	50, 200	1	50-130°	nanocomposite latex particles[65]	[65]

 butyl methacrylate	toluene	–	–	90°	nanocomposites	[136]
 cinnamoyloxy ethyl methacrylate	DMF	10	–	67°	UV absorbent nanocomposites	[137]
 methyl acrylate	DMSO	50, 300, 600	–	90-126°	–	[127]
	DMSO	600	1.6	–	–	[123]
 methyl methacrylate	anisole	60-200	0.7	–	–	[126]
	bulk monomer	1000	1-20	–	thermoplastic elastomer reinforcement	[135]
 styrene	Bulk monomer	–	–	–	chiral nematic ordering	[131]
	anisole	100	1.5	–	drug delivery	[47]
	anisole	20-200	1.5-4	94°	pollutant removal	[67]
	DMF	–	–	–	–	[132]
 *tert*-butyl acrylate	DMF	100	0.3	–	–	[138]
Hydrophilic polymers						
 2-aminoethyl methacrylate	water/methanol	–	6-25	–	biomedical	[139]
 2-methacryloyloxy ethyl trimethylammonium chloride	10:1 water:DMSO	–	0.1	–	patchy nanoparticles	[125]

 4-ethoxy-9-allyl-1,8-naphthalimide	water/methanol	200	4	30-60°	–	[140]
 4-vinyl pyridine	DMF	100	–	–	catalysis	[141]
 diethylaminoethyl methacrylate	methanol	500	0.05	–	CO_2 responsive colloids	[124]
	DMF	10, 25, 50	2	–	Si nanorod template	[142]
 di(ethylene glycol) methyl ether methacrylate	water/DMF	25	–	–	tunable LCST	[143]
 dimethylaminoethyl methacrylate	methanol	500	0.05	–	CO_2 responsive colloids	[124]
	methanol	60	–	–	chiral nematic films	[144]
	DMF	500	1	–	high affinity virus binding	[145]
 n-(2-aminoethylmethacrylamide)	water/methanol	–	6-25	–	biomedical	[139]
 *N*-isopropylacrylamide	water/methanol	200	4	30-60°	–	[140]
	water/methanol	–	6-25	120° (above LCST)	–	[133]
	water/methanol	343, 361	0.07	–	–	[146]

 *N,N*-dimethylacrylamide	water	–	0.02 , 1	–	–	[128]
 *N*-vinylcaprolactam	water/DMF	–	2	–	–	[147]
 oligoethylene glycol methyl ether methacrylate	water/DMF	25	–	–	tunable LCST	[143]
 poly(ethylene glycol methacrylate)	DMF	–	–	–	films and biosensors	[148]
 sodium 4-vinylbenzenesulfonate	10:1 water:DMSO	–	0.1	–	patchy nanoparticles	[125]

[x] Approximate grafting density was calculated from the Br content (where reported) based on calculations outlined in reference [65] and assuming CNC dimensions of 120 nm in length and 15 nm in cross-section and that all Br sites were converted to polymer chains.

Since the initial reports of SI-ATRP grafting *from* CNCs, various functional polymers have been grafted including hydrophobic polymer such as PS [67,131,149], poly(methacrylate) (PMA) [123,127], PMMA [126], poly(6-(4-(4-methoxyphenylazo)phenoxy) hexyl methacrylate) [134], and copolymers of poly(MMA-co-BA) [135] and poly(butyl methacrylate) [136], among other (shown in Table 4). In most cases, hydrophobic polymers are grafted from CNCs to improve CNC compatibility with hydrophobic matrices. However, few reports go on to test the polymer-grafted CNC dispersion in composites. A notable example of hydrophobic polymer-grafted CNCs used in new applications is recent work by Kedzior et al. [65] who grafted PBA from CNCs at varying graft lengths. They found that above a critical graft length, the polymer-grafted CNCs were too aggregated to be incorporated inside polymer latex particles. This is an important factor to consider when altering the surface chemistry of CNCs with polymers – more polymer is not always better, especially when scale-up and industrial production of polymer-grafted CNCs are of interest.

Notably, there are more reported examples of hydrophilic polymers grafted from CNCs via SI-ATRP. Polymers such as poly(diethylaminoethyl methacrylate) [124], poly(ethylene glycol methylacrylate) [148], poly(oligoethylene glycol) methyl ether acrylate [143], poly([(2-methacryloyloxy) ethyl] trimethylammonium chloride) [125], poly(sodium 4-vinylbenzenesulfonate) [125], poly(dimethylaminoethyl methacrylate) [124,144,145], PNIPAM [125,133,146] (shown in Figure 4b), PNIPAM fluorescent copolymers [140], poly(N,N-dimethylacrylamide) [128], poly(2-aminoethylmethacrylate) and poly(2-aminoethylmethacrylamide) [139], poly(acrylic acid) through hydrolysis of poly(tert-butyl acrylate) [138], and poly(N-vinylcaprolactam) [147] have been grafted from CNCs, typically in polymerization solvents such as water, methanol, DMF, and DMSO, all of which are considered good solvents for proper CNC dispersion.

Since the initiator attachment occurs on available hydroxyl groups on the CNC surface, polymer grafting is expected to occur relatively uniformly across the CNC surface. However, work by Zoppe et al. [125] showed for the first time that site specific surface modification of CNCs with initiating groups could lead to polymer growth preferentially on the ends of CNCs, yielding patchy nanocrystals. NIPAM, [2-(methacryloyloxy)ethyl]trimethylammonium chloride, and sodium 4-vinylbenzenesulfonate were polymerized from the CNC ends, and the work proposed the use of CNCs with end-tethered polymer chains as an experimental platform to study the self-assembly of end-functionalized anisotropic nanohybrids.

In all SI-ATRP cases, purification of the products after polymer grafting is necessary to remove the Cu catalyst. Adsorbed Cu catalyst results in polymer-grafted CNCs with a blue or green appearance, depending on the Cu valency. Typical purification methods involve extensive centrifugation and washing steps and/or separation via Cu binding to ethylenediaminetetraacetic acid. One way to overcome the cumbersome purification needed to remove catalyst was shown by Wang et al. [123] who used Cu(0) (copper wire) as the catalyst. This allowed for a simple purification with only a few centrifugation steps. Another example of a SI-ATRP technique that uses significantly less initiator than traditional SI-ATRP used photo-induced ATRP with 50 times less Cu, resulting in significantly fewer centrifugation steps to remove the remaining Cu catalyst [127].

3.3.2 Reversible Addition-Fragmentation Chain-Transfer Polymerization

In comparison to ATRP, there are very few reports of using RAFT to polymerize *from* CNCs. In general, RAFT is known as one of the most successful CRP methods as it is applicable to a wide range of monomers and provides good control owing to the fast exchange reactions between RAFT agent and monomer. RAFT polymerization requires the appropriate selection of a RAFT agent, which is chosen based on monomer. Common RAFT agents are dithioesters, dithiocarbamates, trithiocarbonates, and xanthates [116]. Possibly owing to the more complex nature of RAFT or chain transfer agent attachment, there have been only eight reports of RAFT grafting *from* CNCs since 2014, all of which are reported in Table 5. The first report, by Zeinali et al. [150] attached 2-(dodecylthiocarbonothioylthio)-2-methylpropionic acid (DDMAT) in one step to the CNC surface and polymerized a random copolymer of poly(NIPAM-*co*-acrylic acid). The goal of this work was to control the lower critical solution temperature for the polymer by tethering from the surface of CNCs. The same authors have also prepared block copolymers of poly(NIPAM-co-acrylic acid) using the same technique [151].

Other examples of using RAFT to graft polymers from CNCs include the work of Anzlovar et al. [152] who attached 4-cyano-4-(phenylcarbonothioylthio)pentanoic acid (CPADB) to CNCs via esterification and grafted PMMA from the surface in order to better incorporate CNCs into a CNC/poly(vinyl acetate) composite. Additionally, work by Boujemaoui et al. [153] used either a one or two step process to attach chain transfer agent (CTA) to the CNC surface, and showed that the one step protocol yielded CNCs with more CTA than the two step procedure. Vinyl acetate was then polymerized from the CTA-CNCs (schematic shown in Figure 5) in order to prepare polymer-grafted CNCs that were used to prepare nanocomposites with improved mechanical properties compared to unmodified CNC nanocomposites [153].

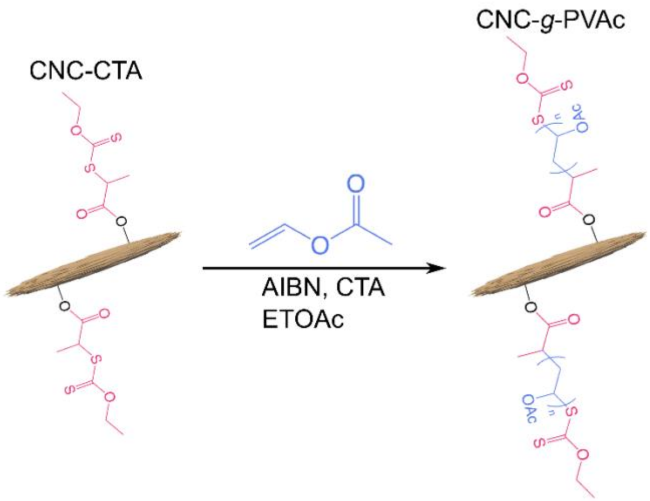
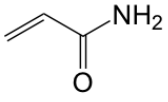
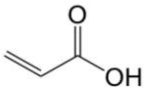
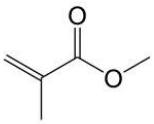
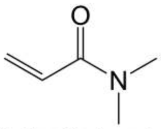
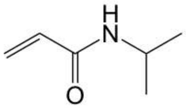
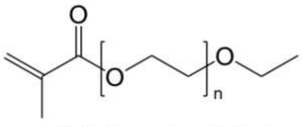
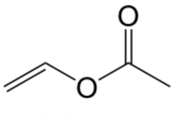


Figure 5. An example of using RAFT to graft vinyl acetate *from* chain transfer agent-modified CNCs (CNC-CTA) using 2,2’-azobis(2-methylpropionitrile) (AIBN) initiator, free chain transfer agent, in ethyl acetate (ATOAc), adapted from reference [153].

Hu et al. [154] used a multi-step process to perform both RAFT and ATRP from the surface of CNCs. The authors grafted poly(poly(ethylene glycol)ethyl ether methacrylate) via RAFT (Table 5) and poly(2-(dimethylamino)ethyl methacrylate) via ATRP (Table 4). Unmodified CNCs were first functionalized with ATRP initiating sites, followed by functionalization with primary amino groups which were then functionalized with RAFT initiation sites by attaching 4,4’-azobis(4-cyanovaleric acid) was to the amino groups. RAFT and ATRP were then carried out sequentially. The target application for this work was the use of polymer-grafted CNCs to conjugate Au nanoparticles for biomedical applications, and to date this is the only report of using multiple CRP techniques to graft CNCs with two different polymers.

Other work used a free macroRAFT agent in an attempt to control the propagation of free radicals generated at the CNC surface. Liu et al grafted water soluble polymers (poly(acrylamide) [155,156] and poly(*N,N*-dimethylacrylamide) [157]) from CNCs using this method. However, the degree of control was affected by the macroRAFT agent adsorption, concentration, and suspension viscosity.

Table 5. Summary of the literature involving RAFT polymerization grafting *from* CNCs including monomers (in alphabetical order), polymerization solvent, target degree of polymerization (DP), grafting density, and target application, where reported.

Monomer	**Polymerization Solvent**	**Target DP**	**Grafting Density[x] (chains/nm^2)**	**Target Application**	**Ref.**
 acrylamide	water	–	–	–	[155,156]
 acrylic acid	dioxane	–	–	stimuli responsive nanocomposites	[150,151]
 methyl methacrylate	THF	–	–	nanocomposites	[152]
 *N,N*-dimethylacrylamide	water	–	–	–	[157]
 *N*-isopropylacrylamide	dioxane	–	–	stimuli responsive nanocomposites	[150,151]
 poly(ethylene glycol)ethyl ether methacrylate	DMF	–	–	theranostics	[154]
 vinyl acetate	ethyl acetate	57, 230	0.1	nanocomposites	[153]

[x] Grafting density was calculated based on the S content (where reported) based on ref [65] and assuming CNC dimensions of 120 nm in length and 15 nm in width and that all S sites were converted to polymer.

3.3.3 Nitroxide Mediated Polymerization

Nitroxide mediated polymerization (NMP) is a form of CRP that relies on a reversible termination equilibrium between growing propagating macroradicals and the nitroxide moieties that act as control agents. This allows for the synthesis of well-defined polymeric structures from a variety of monomers such as styrene, acrylates, and methacrylates [116,158]. NMP is a simple polymerization method as it does not involve reversible redox processes or chain transfer reactions and is convenient to use in grafting *from* reactions with CNCs, as the purification does not require the removal of transition metals. The major disadvantage is the typically lower polymerization rates, higher temperatures needed, and monomer limitations compared to other CRP techniques. To date, only a few examples of using NMP grafting *from* CNCs exist in the literature and are reported by Cunningham and coworkers who have grafted both hydrophilic and hydrophobic polymers.

Roeder et al. were the first to use NMP from CNCs to produce CNC-*g*-PMMA and CNC-*g*-PMA [159], shown in Figure 6. CNCs were treated with 4-(chloromethyl)styrene in DMSO, followed by *N*-(2-methylpropyl)-*N*-(1-diethylphosphono-2,2-imethylpropyl)-*O*-(2-carboxylprop-2-yl) hydroxylamine (BlocBuilder®, BB) in *t*-butanol, then polymerized with methyl methacrylate or methacrylate. The polymer-grafted CNCs showed improved dispersion in organic solvents such as methanol, acetone, THF, and toluene.

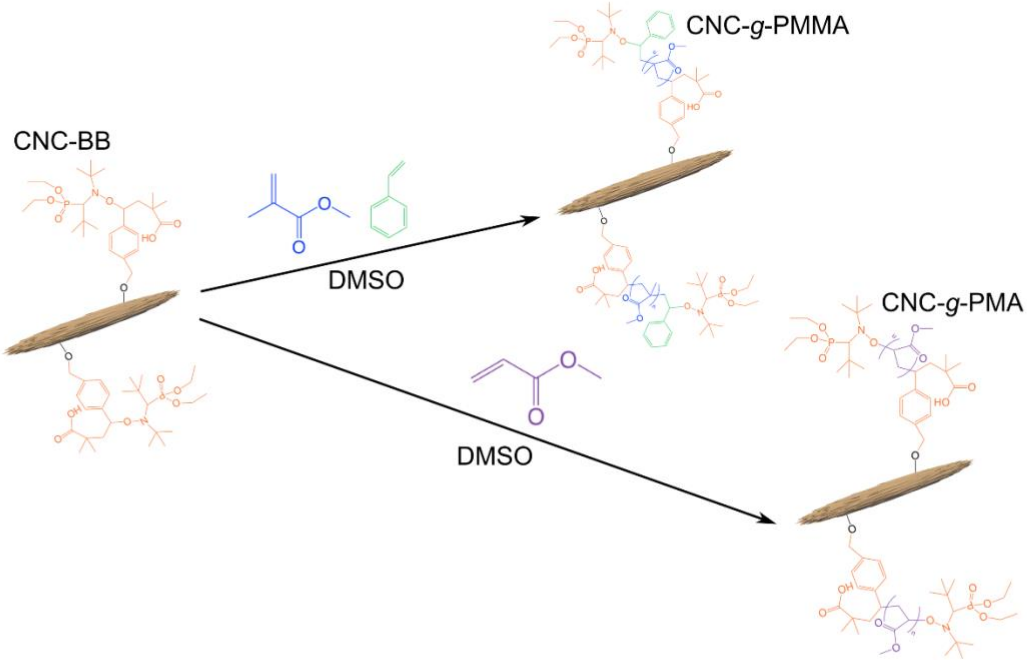


Figure 6. Example of using NMP to graft methyl methacrylate or methacrylate *from* BlocBuilder®-modified CNCs (CNC-BB), adapted from reference [153].

NMP has also been used to graft CO_2-responsive polymers from CNCs. This was first reported by Garcia-Valdez et a. [160] who prepared BlocBuilder®-modified CNCs using the same protocol as Roeder et al. [159]. They dispersed the initiator-modified CNCs in DMSO and polymerized switchable monomers such as 2-(dimethylamino)ethyl methacrylate, 2-(diethylamino)ethyl methacrylate, and *N*-[3-(dimethylamino)propyl] methacrylamide with a small amount of styrene to improve control. The resulting polymer-grafted CNCs showed reversible CO_2-responsiveness in water.

4. Purification and Characterization of Polymer-grafted CNCs

In order to fully understand the properties of polymer-grafted CNCs, the reaction product must be thoroughly purified before characterization in order to avoid characterizing excess reagents or free polymer that may be leftover or adsorbed to the CNC surface. Regardless of grafting method, purification is commonly done through centrifugation (where the modified CNCs are collected in the pellet and washed with solvent), dialysis to remove unreacted small molecules, stirred cell ultrafiltration, or Soxhlet extraction. These techniques become critical in the case of polymer grafting where homopolymer is present, since most characterization techniques cannot distinguish between covalently bound and adsorbed/trapped polymer. Furthermore, characterization difficulties arise when trying to distinguish between organic polymers and cellulose as they often have similar chemical moieties [129].

While a comprehensive list of suggested characterization methods for unmodified CNCs has recently been reported, with one section dedicated to characterizing functionalized cellulose nanomaterials [12], the list does not specifically address polymer-grafted CNCs. Important properties to characterize include polymer grafting density, graft length, polymer PDI, and initiator efficiency. The most common characterization techniques for polymer-grafted CNCs are water contact angle, elemental analysis, Fourier-transform infrared spectroscopy (FTIR), X-ray photoelectron spectroscopy (XPS), X-ray diffraction (XRD), nuclear magnetic resonance spectroscopy (NMR), thermal gravimetric analysis (TGA), and differential scanning calorimetry (DSC). To characterize free homopolymer, polymer synthesized from sacrificial initiator or polymers cleaved from CNCs, traditional polymer characterization methods such as gel permeation chromatography (GPC) or NMR spectroscopy can be used.

The main methods to infer CNC surface modification after grafting is to examine the water contact angle of a dried CNC film or powder [65,67,133,136,140,71,86,91,92,96,97,107,127] and to test colloidal stability of CNCs in non-aqueous solvents [65,127]. This provides indirect evidence that the grafting has been successful and that the hydrophilicity of CNCs has been changed. In order to probe the chemical composition, elemental analysis, FTIR, and XPS have been used extensively. Elemental analysis is a useful technique when the polymer-grafted CNCs contain an element different than carbon, hydrogen, or oxygen, which are found in unmodified CNCs. For example, if nitrogen containing monomers such as 4-vinylpyridine are grafted from CNCs, nitrogen is present in the polymer grafts such that elemental analysis to determine nitrogen content can be used to calculate the amount of polymer present. Similarly, if new chemical bonds are introduced, FTIR can play a useful role in identifying the presence of these new bonds [67]. For example, when grafting acrylate monomers from CNCs, the presence of a carbonyl peak implies that polymer is present. XPS is another technique that can be used to confirm the presence of new elements, and furthermore can be used to collect high resolution carbon (C1s) or nitrogen (N1s) spectra. With high resolution carbon, the C1s spectra can differentiate between four typical carbon bonding environments: C1 (C-C, carbon bonded to only carbon), C2 (C-O-C, carbon bonded to one oxygen), C3 (O-C-O, carbon bonded to two oxygen), and C4 (O-C=O, carbon with three bonds to oxygen), which have different binding energies. Unmodified CNCs should only contain C2 and C3 (though C1 is always present due to contamination, so samples should be as pure as possible [161,162]), therefore the presence of C4 or an increase in C1 is often used to quantitatively determine the amount of polymer present [71].

XRD can be used to determine changes in crystallinity upon polymer grafting *to* or *from* CNCs. When CNCs are grafted with amorphous polymer, the % crystallinity is expected to decrease for polymer-grafted CNCs, which has been shown in previous work [127]. The maintenance of the characteristic cellulose I peaks confirms that the CNC crystalline structure is retained during the modification reaction [67,133] and that the decrease in crystallinity is due to the presence of amorphous polymer. Although the effects of preferred orientation of cellulose crystallites during sample processing must be taken into consideration when using XRD to quantify the amount of amorphous polymer in grafted CNCs, as the orientation of CNCs influences the calculation of % crystallinity.

While NMR is the conventional “workhorse” of the synthetic polymer chemist, challenges arise when trying to analyze the chemical composition of CNCs and their derivatives. As CNCs cannot be dissolved in traditional NMR solvents (such as deuterated DMSO and deuterated chloroform), to the best of our knowledge there is only one report of using solution state NMR to characterize polymer-grafted CNCs. King et al. [163] used ionic liquids to dissolve PMMA-*g*-CNCs (prepared via free radical polymer grafting) and determine the polymer grafting density, after which methanolysis was performed in order to isolate the polymer grafts and determine their molecular weight through NMR self-diffusion measurements. This technique shows promise for quantifying polymer graft length and grafting density even for samples prepared via free radical polymerization that typically lack control over the polymerization kinetics [163].

Solid state NMR such as ^{13}C-cross polarization magic angle spinning (CP-MAS) NMR shows potential for quantitative characterization of polymer-grafted CNCs and is performed on dried samples. In the 1980s, ^{13}C CP-MAS NMR was first used to determine the structure and crystallinity of native cellulose I [164,165], and in the 1990s, Heux et al. used the technique to study CNC structural aspects [166] and lateral dimensions [167]. It has recently been used to determine the degree of substitution of CNC modifications such as TEMPO oxidation [168], esterification [169], and polymer grafting [57,170], amongst others.

Polymer-grafted CNCs often display differences in thermal stability, which can be measured by TGA and DSC. TGA measures sample mass as a function of temperature and is used to determine the temperature at which a sample thermally degrades. Unmodified CNCs display a significant mass loss (and therefore thermal degradation) around 300°C [171]. A shift in thermal degradation temperature can be correlated to the presence of polymer or other small molecules. For example, after the attachment of ATRP initiators, the thermal degradation temperature of the CNCs decreases. This is attributed to the presence of the Br groups which may accelerate the degradation of the CNCs [126,127]. However, upon grafting polymer, the samples exhibit a secondary degradation peak that is shifted towards the onset of thermal degradation of the pure homopolymer, confirming the presence of polymer [133,138]. TGA can be used to determine the weight percent of polymer grafted based on the ratio of the secondary degradation peak attributed to the grafted polymer [127].

DSC is often used to determine the melting point and glass transition temperature (T_g) of semi-crystalline or amorphous polymers, respectively, so in the case of polymer-grafted CNCs, DSC is a way to characterize the polymer, but not the CNC itself. The T_g is the temperature above which a hard “glassy” polymer transitions into a soft or rubbery polymer as the polymer chains have increased mobility [172]. An increase in the T_g can imply a reduced mobility of the polymer, and in the case of polymer grafting, this implies that the polymer chains have been tethered to a surface. As such, an increase in the T_g of the polymer has been used to support the covalent binding of polymers to the CNC surface [127,133,173]. Although DSC is beneficial in confirming the polymer is grafted on the CNC surface, it is typically qualitative and cannot determine specific polymer properties such as molecular weight.

5. An Industrial Perspective of Polymer-grafted CNCs

There is significant value in the academic work to date on polymer grafted-CNCs which, in general, is closely followed by industrial producers and potential end-users of cellulose nanomaterials. While the richness of scientific understanding that can be gained in the fields such as polymer chemistry, colloidal science, carbohydrate chemistry, and materials science is expansive, there are obvious concerns related to implementation costs that in many cases are restrictive for commercialization. In some of the best-case scenarios, costs of polymer-grafted CNCs reach hundreds of dollars per kilogram, which is high compared to commodity polymers and unmodified CNCs on their own. This, of course, would limit the use of polymer-grafted CNCs to specialized high value applications, such as pharmaceutical and biomedical products, or applications where extremely small amounts of material would be used, such as in retention or drainage aids for papermaking. Articulating the current limitations are not intended to limit the academic community but spur creativity and innovation by asking researchers to think about surface modification routes, scale-up and suitable applications in new ways (and to consider industrial consequences at earlier stages in the experimental design). One way to effectively use the "fine tuning" abilities of polymer grafting methods is in the design of model systems: for example, CRP grafting *from* CNCs can be used to systematically change CNC properties in order to link the effects such as hydrophobicity, colloidal stability, particle coverage, and surface roughness to compatibility/functionality in a given application. Once the critical surface properties have been identified and optimized through polymer grafting, researchers can look for alternative (lower cost) routes to achieve the same properties, such as through adsorption, small molecule modifications, or minor changes to the CNC production process.

The industrial interest in polymer-grafted CNCs is partially reflected by the fact that during this research and development stage, a number of international and US patents have been filed on their preparation and use. Cellulose nanomaterial producers watch for intellectual property generated by other companies, however, to date the patents remain primarily illustrative or defensive. Hamad and co-workers hold a number of early patents related to CNCs grafted with PLA via ROP (US 2011/0196094) [174], and CNCs grafted with hydrophobic vinyl monomers via free radical polymerization with CAN (US 8,349,948) [175] and the application of these materials in nanocomposites with enhanced gas barrier, rheological and mechanical performance. The preparation of thermoplastic and thermoset composites with polymer-grafted CNCs has also been patented for use as packaging materials, structural composites for automotive and construction applications, sandwiched foam composites or combined with biocompatible polymers in medical applications (WO 2013/037041 A1) [176]. Additionally and complementary to their published paper, Carlmark et al. patented the preparation of functional CNCs via acid hydrolysis which notably included attaching ATRP initiator functional groups during CNC production (WO 2014/070092 A1) [177]. More recently, Castro et al. patented adding CNCs grafted with polyacrylamide and poly(acrylic acid) to paper substrates for increased retention, wet and dry strength (WO 2015/050806 A1) [178] and Moghadam et al. patented polymer-grafted CNCs for use as rheological modifiers (WO 2017/066540 A1) [179]. As alluded to above, a patent does not imply that product development will follow, but it does support that those working in this field are interested in assessing possible value in such materials and proposing novel processes and applications.

5.1 Manufacturing Considerations

This section discusses key industrial considerations related to new process development, such as the scale up and implementation of polymer-grafted CNCs. Bringing a process to manufacturing readiness is a step that is often little considered initially in bringing a new process to fruition. It is frequently a significant challenge to find the reaction conditions that can allow a new product to be formed industrially. In the end, however, a process will remain of academic interest only if it is not taken through the steps needed for industrialization.

So what are the steps? It will depend on the particular process that is being considered but in this review the focus is on modifying the surface of CNCs to make them compatible with a wider range of media. The high level steps in this case are:

1. Determine the value of the proposed modification in the targeted application
2. Determine if the cost of the production will maintain the value in the application
3. Assess the safety, environmental and regulatory requirements of the new product

Step 1 requires identification of the value proposition for the modification. In which system or systems will a given modification be used? What will the improvement in properties be? Does the improvement address the need of an industrial partner at an acceptable cost? Is there a committed industrial partner? Answers to these questions will allow the move to Step 2.

Step 2 at first glance seems simple in that it is taking the reaction that is being done on the bench and using the same process, conditions and larger equipment to make larger quantities. In most instances, however, it would immediately fail Step 1. At the beginning it is essential to choose between competing processes for achieving the goal and consider the potential for integration into present manufacturing processes. How many steps does the process have? What solvents are being used in the process? What temperatures and times are being used in the process? What purification steps are required? What is the toxicology of the materials used in the manufacturing process? In the best of situations, the answer to these questions would be one, water, room temperature, instant, no purification and toxicologically benign. In addition, control of the process to provide a uniform product is essential. In the majority of proposed reaction schemes, many of these preferred parameters are not met and therefore the requirement in Step 1 becomes ever more challenging and the discussion with the industrial partner becomes more critical.

Even if Steps 1 and 2 are passed, Step 3 is essential. Many dollars were spent on the regulatory assessment of unmodified CNCs. Every modification to the surface represents a new material and a toxicological evaluation is needed with each type of modification. As well, impurities such as solvent and catalyst traces can remain that add further challenges to the eventual acceptance of the material by an industrial partner and the end-user. Included in Step 3 is the safety and environmental elements of the process. This consideration is married to the toxicological requirement and choices can be made, if solvents are required, as to the toxicological class to which they belong.

The principle of Occam's razor (that the simplest solution tends to be the best one) is often properly applied to hypotheses, but it can equally well be applied to processes and manufacturing, simpler is more likely to be successful!

6. Conclusions and Outlook

Polymer grafting *to* and *from* CNCs are sophisticated methods to prepare functional CNCs with novel properties, as evidenced by the many reports in the literature over the past decade. The wide variety of techniques provide a range of benefits and pitfalls, and when deciding on a technique to use, the reader is encouraged to consider the type of polymer (hydrophilic vs. hydrophobic), number of reaction steps, purification requirements, and control and tunability of polymer properties needed.

Polymer grafting *to* is useful when a pre-formed polymer with known molecular weight is of importance or the end-functionalized polymer is available commercially (and cheaply) or is straightforward to synthesize. However, high grafting density is difficult to achieve, and extensive purification is required to remove unreacted polymer. Additionally, quantification of graft density is difficult to characterize and rarely reported. This method is best used for niche applications where high grafting density is not crucial.

Polymer grafting *from* via free radical polymerization is a facile technique to modify CNCs with both hydrophilic and moderately hydrophobic polymers. The reactions are performed in aqueous environments where CNCs are colloidally stable, and there is no need to attach initiators, making this a one-step, and potentially more industrially feasible process. Free radical polymerization from CNCs also provides the opportunity to prepare CNC-polymer nanocomposites *in situ*, where purification to remove homopolymer can be omitted.

Finally, polymer grafting *from* CNCs using CRP provides control over both the polymer graft length and grafting density. This is the most complicated technique of grafting *from* CNCs and is often a multi-step process with lengthy purification. Reactions are always performed in solvents in which dispersing CNCs is a known issue, and as of yet, the uniformity of individual nanoparticle modification has not been determined experimentally. This technique should likely be reserved for model studies and specialty applications, recognizing that there are various set-backs when it comes to scale-up and cost feasibility. However, CRP allows for the systematic evaluation of graft length and grafting density, initiator efficiency, and polymer kinetics and can therefore be optimized to suit a range of academic/industrial needs. Furthermore, for high value application (such as biomedical applications) precise control and purity are crucial factors and cost may be less of a concern.

As fundamental and applied cellulose nanomaterial research continues to grow, grafting polymers *to* or *from* CNC surfaces remain one promising method amongst a “toolbox” of modification routes for providing improved compatibility between CNCs and their environments. For application-driven research we stress that it is important to consider the challenges of industrialization at early stages, specifically scale-up, toxicology and costs. While strong scientific foundations have been laid in this field, good industrial interaction is essential to advance the development of modified cellulose nanomaterial-based products.

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