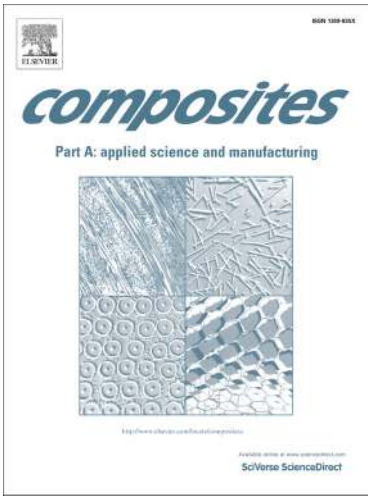

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Review of the recent developments in cellulose nanocomposite processing

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Abbreviations: A-CNC, acetylated cellulose nanocrystals; AFM, atomic force microscopy; BC, bacterial cellulose; CA, cellulose acetate; CAB, cellulose acetate butyrate; CMC, carboxymethyl cellulose; CNC, cellulose nanocrystals & cellulose nanowhiskers; CNF, cellulose nanofibers & nanofibrillated cellulose & microfibrillated cellulose; B-CNC, tert-butanol cellulose nanocrystals; DMAc, dimethylacetamide; EP, epoxy; GO, graphene oxide; GMA, glycidyl methacrylate; GTA, glycerol triacetate; HPC, hydroxypropyl cellulose; IL, ionic liquid; LDPE, low density polyethylene; LiCl, lithium chloride; LPEG, linear unsaturated polycondensate (oxyethylene); MAPP, maleated polypropylene; MCC, micro crystalline cellulose; MF, melamine formaldehyde; NR, natural rubber; PA6, polyamide; PCL, polycaprolactone, PE, polyethylene; PF, phenol formaldehyde; PAH, polyallylamine hydrochloride; PAN, polyacrylonitrile; PANI, polyaniline; PDMS, polydimethyl siloxane; PEDOT, poly(3,4-ethylenedioxythiophene); PHBV, polyhydroxy butyrate hydroxy valerate; PHO, poly-b-hydroxyoxanoate; PLA, polylactic acid; PP, polypropylene; PS, polystyrene sulfonic acid; PTFE, polytetrafluoroethylene; PVA, polyvinyl alcohol; PVAc, polyvinyl acetate; PVOH, polyvinyl alcohol; PU, polyurethane; SEM, scanning electron microscopy; S-MA, styrene maleic anhydride copolymer; THF, tetrahydrofuran; TS, thermoplastic starch; TEC, triethylene citrate; TEM, transmission electron microscopy; TOC, tempo oxidized cellulose; WF, wood fibers.

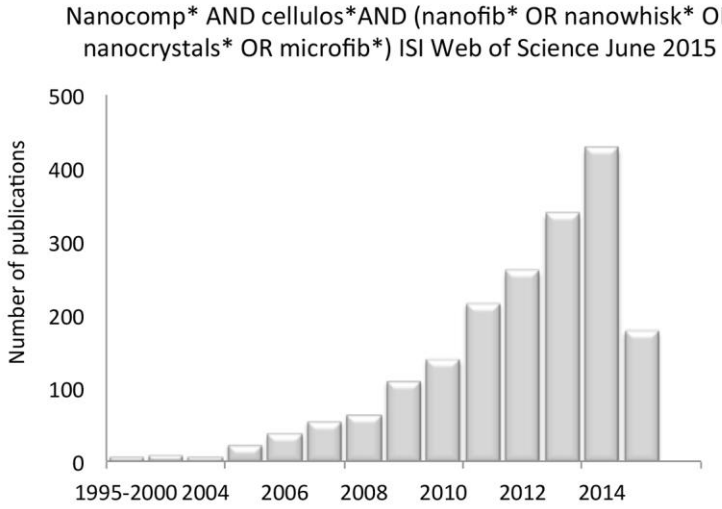
Abstract

This review addresses the recent developments of the processing of cellulose nanocomposites, focusing on the most used techniques, including solution casting, melt-processing of thermoplastic cellulose nanocomposites and resin impregnation of cellulose nanopapers using thermoset resins. Important techniques, such as partially dissolved cellulose nanocomposites, nanocomposite foams reinforced with nanocellulose, as well as long continuous fibers or filaments, are also addressed. It is shown how the research on cellulose nanocomposites has rapidly increased during the last 10 years, and manufacturing techniques have been developed from simple casting to these more sophisticated methods. To produce cellulose nanocomposites for commercial use, the processing of these materials must be developed from laboratory to industrially viable methods.

Keywords: A. Cellulose, Nanocomposites; E. Casting, Extrusion, Liquid Composite Molding, Spinning

1. Introduction

The research subject of cellulose nanomaterials started in the mid-90s. The pioneering group led by Chanzy and Cavaille at CERMAV in Grenoble, France [1], published the first paper on cellulose nanocomposites. This group led the research in this area until the beginning of 2000, by which time many researchers had joined the field. Cellulose nanocomposites are manufactured using different processes, and these processes affect the composite properties, such as the dispersion, distribution and alignment of the reinforcing phase. Thus, the research and development of the manufacturing process of celluloses nanocomposites is an essential part of the development of cellulose nanocomposites. The processing of nanocomposites initially involved solvent casting of water-soluble or water-dispersive polymers, which were mixed with cellulose nanomaterials [1-5] because both nanofibers and nanocrystals are easily dispersed in water. In 2005, Yano and co-workers in Japan made another breakthrough, developing cellulose nanopapers and their impregnation with thermoset polymers [6-9], thus producing composites that showed much higher mechanical properties than those based on starch and latex, i.e., biopolymers used in solvent casting. During the same time period, Oksman and co-workers started the processing development of cellulose nanocomposites in which different thermoplastic polymers were mixed with cellulose nanocrystals and nanofibers using twin-screw extrusion [10-15]. Since that time, the research on cellulose nanocomposites has grown exponentially, and this growth is reflected in the increase in the number publications. At the time of writing, there are almost 6000 publications on nanocellulose materials. However, many of these publications address the isolation of nanocelluloses from different raw material sources and the nanomaterial structure and properties rather than nanocomposites and their processing. A Web of Science search performed in June 2015 on nanocomposites (*see* ***Fig. 1***) resulted in 1700 journal publications.



Countries		Sources		Subjects	
China	381	Carb Hydr Polym	181	Casting	253
USA	313	Cellulose	174	Extrusion	133
Sweden	173	Biomacromol	104	Foams	82
France	156	J Appl Polym Sci	86	Fiber spinning	46
Canada	136	ACS Appl Mater & Inter	57	Impregnation	30
Japan	130	Compos Sci Technol	51	Compression molding	30

Fig. 1 *Number of publications on cellulose nanocomposites, showing the country, most publishing journals and popular subjects dealing with processing.*

The countries with the highest number of publications on this subject are China, followed by the USA, Sweden, France, Canada and Japan, showing for example that currently China is very active on this field and has over taken that role from USA. It is also seen that solvent casting is the traditional and simplest way to make lab-scale nanocomposites and has been the most popular method to prepare nanocomposites, with 253 articles in the search using this method. The use of extrusion or melt processing has increased, especially in recent years. Impregnation of prepared paper is also a common way to prepare nanocomposites, however, it was difficult to estimate the number of impregnation studies because only a few studies have focused on processing. Therefore, these articles lack keywords associated with this method of processing. Interest in foaming and fiber spinning of cellulose nanocomposites has also increased in recent years.

The number of publications on cellulose nanocomposites in composite and polymer material journals is lower (317), but the trend is similar, with the first article published in 1996 by Helbert et al. [16], increasing to 58 publications last year (2014).

The aim of this review is to provide an overview of the processing techniques of cellulose nanocomposites, including new development areas, such as nanocomposite foams and fibers. The main focus is on casting, melt-processing and resin impregnation, which are the most important processes of cellulose nanocomposites.

2. Pre-treatment of nanocelluloses prior to composite processes

In nanocomposites, the surface properties of nanocellulose determine the fiber-fiber bonding within the cellulose network and the interfacial adhesion between the fiber and matrix, which ultimately dictates the structure and properties of the composites. [17] The critical challenge to achieve the transfer of exceptional mechanical properties of nanocellulose of single fiber level to the macroscale properties of the bulk nanocomposites is not only the ability to obtain well-dispersed hydrophilic reinforcing nanocellulose in the polymer matrices but also to optimization of the fiber-matrix interface [18] Although nanocomposites have been successfully prepared from water suspensions of nanocellulose or from an organic medium (*N,N*-dimethylformamide) suspension [19], the hydrophilic nature and low thermal stability of nanocellulose limits the choice of polymer matrices and processing technologies for composites [2]. Since cellulose has a glass transition temperature in the range of 200-230°C and thermal decomposition starts at ca. 260°C, the compounding temperature is commonly restricted to about 200°C in the extrusion of thermoplastic composites reinforced with cellulosic fibers. Previous study showed that the thermal stability of CNFs decreased due to the homogenization and drying process and CNCs obtained by acid hydrolysis also showed decreased thermal stability due to the charge groups on the surface. To increase the surface hydrophobicity while maintaining the thermal stability, the surface pretreatment and chemical functionalization of CNCs and CNFs is a challenging and important pre-processing step in nanocomposite preparation. There are generally two approaches: covalent coupling of hydrophobic moieties directly on the surface of cellulose nanoparticles and covalent coupling of moieties directly on the surface of cellulose nanoparticles. ***Table 1*** shows examples of chemical functionalization methods that have been used for nanocellulose applications in nanocomposite preparation.

Table 1 *Examples of surface functionalization of nanocellulose in nanocomposites preparation.*

Type of modification	Functionalization method	NC	Polymer matrix	Composite processing method	Year & Ref
Non-Covalent	Anionic surfactant	CNC	PLA	Extrusion	2007 [12]
	Nonionic surfactant	CNC	PS	Solvent casting	2009[29]
	Ionic exchange	CNF	PLA	Solvent casting	2013[30]
Covalent	Silylation	CNC	PLA	Solvent casting	2010[24]
	Acetylation	CNF	PLA	Extrusion	2012 [15]
	Acetylation	TOC-CNF	PLA	Casting	2012 [20]
	Acetylation	BC	Acrylic	Impregnation	2007[31]
	Pol. grafting	CNC-PEG	PS	Extrusion	2013[32]
	Esterification	BC	PLA	Extrusion	2009 [21]
	Alkylation	MCC	PLA	Solvent casting	2015[33]
	Silanization	CNF	PLA	Solvent casting	2012[23]
	Pol. grafting	CNC-PCL	PCL	Extrusion	2011[34]

Glyoxalization	BC	PLA	Impregnation	2012[25]
Silylation	CNC, CNF	PLA	Extrusion	2015[22]
Esterification	CNC, CNF	PLA	Extrusion	2015[22]

The surface functionalization by acetylation [15,20], esterification [21,22], silanization [23], silylation [22,24], glyoxalization [25] or grafting of PCL [26], PEG [27] or GMA [28] on cellulose nanocrystals (CNCc) has, in some cases, improved the mechanical properties of PLA nanocomposites.

Upon coating with an anionic surfactant, cellulose nanocrystals have been effectively dispersed in PLA [12] (***Fig. 2***), but the use of surfactant had a negative effect on the mechanical properties of the PLA, which were improved by the addition of CNC.

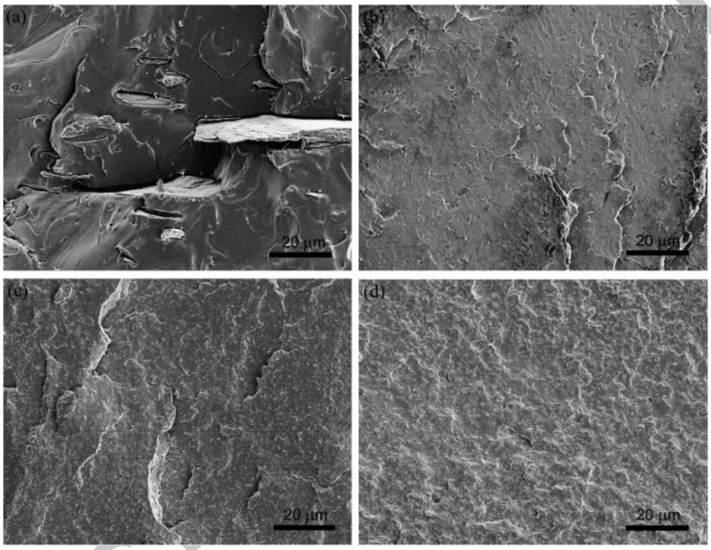


Fig. 2 *Improved dispersion of CNC in the PLA matrix as the surfactant content increases. Fractured surfaces of (a) PLA-CNC without surfactant show agglomerated CNC (b) PLA-CNC with 5% surfactant (c) PLA-CNC with 10% surfactant (d) PLA-CNC with 20% surfactant. (Copyright permission Taylor & Francis [12]).*

Non-ionic surfactant has also been utilized to improve the dispersion properties of cellulose nanocrystals in polystyrene [29]. Cellulose nanocrystals [35] and nanofibrils [36] modified with quaternary ammonium salts have shown high degrees of nanodispersion in organic solvents, and nanocomposites of modified cellulose nanocrystals with PVAc have been prepared.

To obtain surface-functionalized CNF, it is more efficient to perform the corresponding chemical reaction on micrometer-scale wood pulp fibers before the final mechanical disintegration step. In this fashion, TEMPO-mediated oxidation [37], carboxymethylation [38,39], cationization, and pegylation reactions [27] have been performed on WF and CNF. However, the major drawback in covalent functionalization to increase the hydrophobicity of nanocellulose is the tedious solvent exchange process and the use of organic solvents in these reactions. Recently, a solvent-free, one-pot process for surface esterification of cellulose nanocrystals was developed using carboxylic acids that act not only as a grafting solvent but also as a solvent media above their melting point [40]. Such green processes for surface hydrophobization of nanocellulose have the potential for application in large volume or even online composite processing.

3. Solvent casting

Solvent casting is the most commonly used method to produce cellulose nanocomposites. Solvent-casted nanocomposites were first reported by the French research group [1-3], and the first studies focused on tunicin-based nanocrystals in a latex matrix of poly(styrene-co-butyl acrylate, where an interesting reinforcing effect was demonstrated, especially above the polymer relaxation temperature [1,2]. Generally, the literature concerning the preparation of cellulose nanocomposites involves the solvent casting method as the processing approach [1-3,5,41-45]. When water-soluble polymers are used as matrices, the interactions between the nanocellulose and the respective matrix are strong due to the polar nature of both constituents. After mixing the aqueous suspension containing the two components, a solid nanocomposite film can be obtained by solvent evaporation (casting) ***(Fig. 3).*** The reinforcing effect of

CNC, leading to enhanced mechanical properties of different matrices, has recently been reviewed in the literature [46,47], and different solvent-casted composites, including material combinations, and some properties are listed in Table 2. It has been demonstrated that the reinforcing effect of CNC is due to the formation of a rigid percolating filler network caused by hydrogen bond interactions of CNC [48]. The formation of a percolating network is favored by slow processing, which allows self-organization of the CNC. Preventing aggregation in non-water soluble polymers is not trivial, especially when dispersing the CNC into hydrophobic matrices, such as PP, PE, PCL and PLA, due to the lack of compatibility between the hydrophilic nanocellulose and the hydrophobic matrix. To improve the dispersion of CNC in non-aqueous polymers, several strategies have been adopted, including the use of surfactants having one part compatible with the polymeric matrix and another with the CN [10,11,45,49] and chemical modification via reaction of the hydroxyl groups to tune the interface between the matrix and CNC and enhancing their interaction [34,50-54].

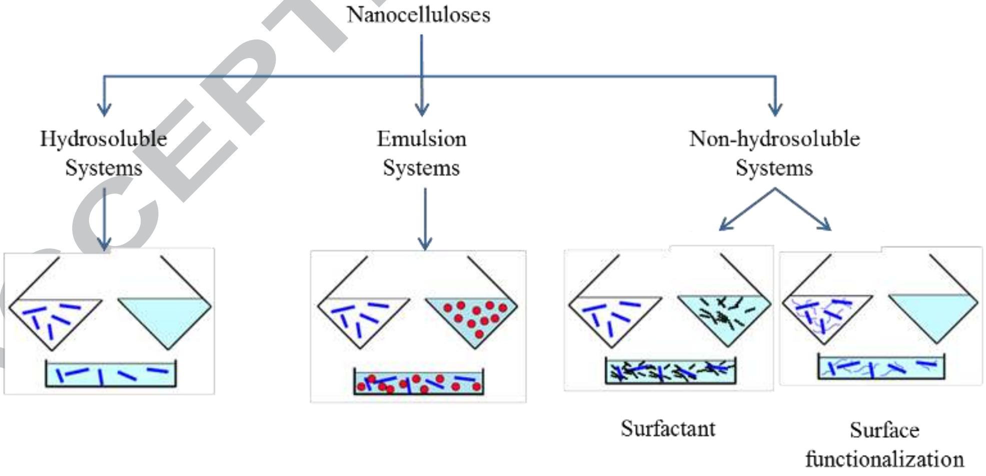


Fig. 3 *General scheme of the strategies used for the preparation of cellulose-based nanocomposites by solution casting.*

Solvent-casted CNC nanocomposites have been aligned using magnetic fields, electric fields and flow [55], but recently, a high CNC content, together with carboxymethylcellulose (CMC), has been reported by Wang et al. [56]. The alignment of CNC-CMC wet films was demonstrated, and improvement of the stiffness, strength, and work-to-fracture as a function of the degree of alignment was observed (see Table 2). Decreased hydrophobicity of nanocellulose to enhance the interface has been reported [44,51], as well as a sol-gel process to improve the dispersion of nanocellulose in non-water-soluble polymer [57].

Solvent casting has also been extensively used to process CNF-based nanocomposites with different matrices. Similar to the CNC, the first studies dealing with CNF nanocomposites concentrated on water-soluble or dispersible polymers [58,59] and were performed by Zimmermann et al., who later expanded to the non-water-soluble PLA matrix [51]. The good dispersion and distribution of cellulose nanomaterials into polymer is a key step to produce cellulose nanocomposites, and solvent casting is a simple and widely used technique to prepare nanocomposites.

__Table 2__ Examples of cellulose-based nanocomposites prepared by solution casting.

Polymer type		Type NC	Raw material source	NC content (wt%)	E (GPa)	σ (MPa)	ε (%)	Year&Ref.
Emulsion polymers	Poly(S-coBuA)	CNC	Tunicin	0-6	-	-	-	1995 [1]
	PHO	CNC	Tunicin	0-50	-	-	-	1999[60]
	Poly(S-coBuA)	CNC&CNF	Sugar beet pulp	6	0.2-144*	0.18-6.3	32-300	2004[61]
	PVA	CNF	Wood pulp	0-10	0.4-3	20-60	18-170	2004[58]
	HPC	CNF	Wood pulp	0-20	0.6-3	5-40	5-22	
	PVAc	CNC	Sisal fibers	0-10	-	-	-	2006[62]
	PVA	CNC#	MCC	2	Aligned crystals, improved modulus			2007[55]
	PVA	CNC	Cotton	0-12	1.8-2.9	100-140	9.1-29.5	2008[63]
	PU	CNC	Whatman filter paper	0.5-5	8-45*	7-50	751-1110	2011[18]
	Natural rubber	CNC&CNF	Palm tree	0-15	0.5-233*	0.5-12.2	3.95-575	2010[64]
	PVA	CNF	MCC	5	48% increase in storage modulus			2015[65]
Water soluble/ dispersible	Starch/Glycerol	CNF	Bleached sulfite pulp	0-100	-	-	-	2010[66]
	PEO	CNC&CNF	Wood pulp	0-10	0.8-1.7	12.8-26.9	86-526	2013[67]
	CMC	CNC#	Whatman filter paper	0-70	2.5-15	82-187	3.5-12	2015[56]
Non-water soluble polymers	aPP	CNC	Tunicin	0-6	0.4-18.5*	0.026-0.58	0.07-0.7	2005[68]
	PLA	B-CNC	MCC	5	Improved dispersion and thermal prop.			2007[45]
	PCL	CNC	Ramie	0-40	0.23-0.58	7.6-21.0	4-640	2008[50]
	PCL	CNC&CNF	Sisal	0-12	0.26-0.60	18.0-25.5	20-600	2009[44]
	PLA	A-CNF	Sulfite pulp	0-17	Acetylation improved dispersion			2010[51]
	CAB	CNC	MCC	0-9	1.3-2.2	29-57	5-9	2011[57]
	PLA	Al-CNC	MCC	0-1.5	2.3-2.4	25-27	3-3	2015[33]
	Epoxy	CNC	MCC	0-8	0.3-0.8	7-15	29-3.6	2015[69]

#Aligned
* MPa

5. Melt processing technologies

Melt processing of nanocomposites is very important and is expected to be the key processing method to get these materials to market where high volume products are targeted. Melt processing is traditionally used for many types of biocomposites; it is a cheap and fast processing method. In melt processing, cellulose nanomaterials are dispersed in a thermoplastic polymer melt. Our group started the processing development around 2003 and published the first paper on melt processes [10]. Melt processes are either batch or continuous, and the most common way to make nanocomposites is batch processing using Brabender or micro-extruders, where small amounts of materials are added into a closed processing chamber, melted and mixed for a relatively long time. Continuous methods, where the materials are continuously fed into the processing unit, melted and mixed, are less common because a larger amount of materials is needed to make test materials, and usually, only a small amount of nanomaterials are available. Continuous processes are preferred for scaling up because this type of extruder has better mixing and venting compared to the batch-wise equipment. The interest in melt processing has increased in recent years, and attempts at processing development to improve the process for industrialization have been made [10,11,13,70-75]. However, many studies focus on nanocellulose from different sources mixed with different polymers, where more attention is paid to chemical functionalization, coating of nanocellulose, and grafting to improve the dispersion of nanomaterials [28,34,76-83]. A master-batch approach, where a polymer is used as a carrier for nanocellulose, has been used by several researchers and involves PVOH [11], PEO [84], PLA [14,39,71,85], PVA [86-88], PA6 [75], alginate [89], NR [90,91] and PCL [92].

5.1 Batch processing

A number of studies on cellulose nanocomposites prepared using micro-extruders [12,28,32,34,76-79,81,88,93-96] and batch mixers [71,74,80,82-85,93,97] have been reported in recent years. These batch-wise processes are convenient on the small scale but are not easily converted to industrial compounding. However, they are a good way to test a small amount of materials (few grams). The drawback is that a long processing time is needed, which leads to discoloration and degradation of the polymer or the cellulose. Furthermore, there are no atmospheric or vacuum vents for the removal of volatiles, moisture or entrapped air/gas; thus, it is difficult to process materials that are not dry. ***Fig. 4*** shows a photograph of a DSM micro-extruder and a schematic of a similar Haake micro-extruder, both of which are very commonly used in the studies on cellulose nanocomposites.

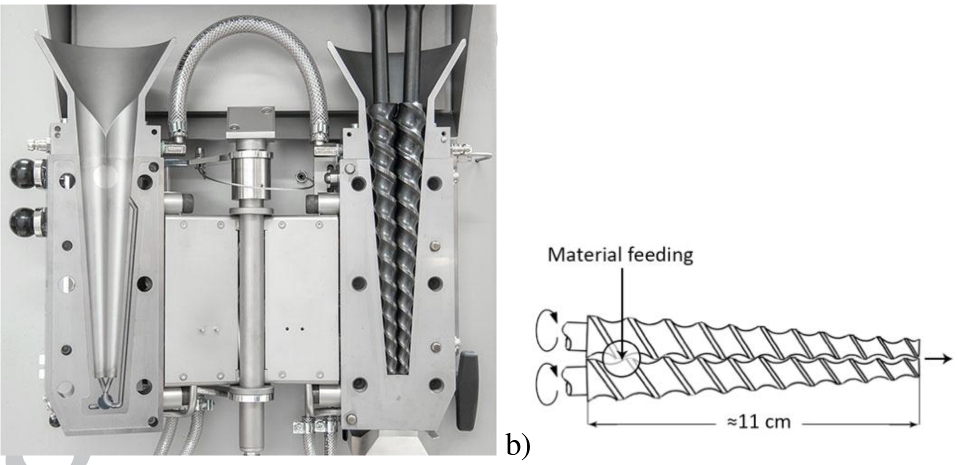


Fig. 4 *a) DSM micro-extruder (DSM) showing the processing chamber and conical screw design; only 5 or 15 ml is needed for one batch, depending on the size. b) Schematic of a Haake micro-extruder with similar conical screw design.*

Batch processed nanocomposite material combinations, as well as the main results, are presented in the ***Table 3***.

Table 3 *Processing of cellulose nanocomposites with batch processing, micro-extrusion and Brabender type mixing.*

Pre-process	Nanocellulose	Matrix	NC content (wt%)	Dispersion	Findings	E (GPA)	σ (MPa)	ε (%)	Year, Ref.
Surfactant 5,10,20 % & freeze dried	CNC	PLA	5	TEM, 10, 20% surfactant	Best prop. with 5% surfactant	2.6>3.1	35>52	1.8>3.1	2007[12]
Premix & dried	CNF	PLA	5	SEM	Improved strength	3.4>4.3	56>66	<	2008[85]
Premix & dried	CNF	PLA powder	1, 2	Yes SEM	Improved strain energy 200%	3.5>4.8	45>54	-	2009[71]
Grafting PCL Drying	CNC-g-PCL	PCL	2,4,8	Yes AFM	Thermal properties				2011[34]
Encapsulation CNC & CNF	CNC & CNF	Ecoflex	2,5,10	Poor dispersion	No improvements				2011[89]
Acetylation, drying of BC	BC	PLA	1,4,6	SEM	Increased moisture uptake	3.6>5.2	65>84	1.9<0.8	2011[83]
Master-batch CNF-PCL	CNF	PCL/PP -MAPP	1	SEM, AFM	Improved toughness	0.9> 1.2	30	200>450	2011[92]
Surface mod. freeze dried	CNC-g-PEG CNC-PEO	PS	2-20	SEM & AFM	All films strongly colored				2013[32]
Master-batch CNF10	Freeze dried CNF	PHBV	2,5,10	Not well dispersed	-	1.7>3.2	32>34	8.8<3.9	2013[80]
Surface coated CNC	CNF-PEO & MAPP10	PP	10	-	-	0.5>0.7	21>32	1067<352	2014[84]
PLA-g-GMA freeze dried	CNC	PLA+PLA-g-GMA	1	Dispersed SEM	Facilitated crystallinity	2>2.4	44>62	17<5	2015[28]
Surface mod. ATBC as plasticizer	Freeze dried CNC	PLA	5	Partially TEM	High flexibility	0.6< 0.5	13>19	90>148	2015[81]
Premix freeze dried	PEO-CNC	PLA	1,3	SEM	-	3.4>3.9	61<38	2.7<1.1	2015[82]

* > improved and < decreased properties

Many of the reported studies are about different material combinations, and the nanocellulose is usually CNC that has been freeze-dried. CNC, together with surfactants, surface coatings, grafting and chemical modifications, has been tested to improve the interface and dispersion of cellulose nanomaterials in polymers, as discussed previously. Lin and Dufresne [32] compared chemical grafting of PEG to PEO coating on CNC and used PS as a matrix. The modified CNC was freeze-dried and added into the DSM micro-extruder together with PS pellets; the processing was performed at 200°C and 150 rpm for 10 min. The photographs showed strongly discolored films; the chemical grafting of PEG decreased the discoloring and improved the thermomechanical properties, especially after the relaxation of PS. Similarly, a PEO coating on cellulose nanofibers was tested by Iwamoto et al. [84]. They used PP as a matrix polymer and reported improved mechanical properties with the coating and with MAPP as compatibilizer. Another attempt to develop nanocomposites processing was reported by Lemahieu et al. [89], who encapsulated CNC and CNF with alginate and mixed the capsules with the starch-based biopolymer Bioplast GF 106/02 using a DSM micro-extruder. The results were disappointing; the capsules were not well-dispersed in the extrusion process and resulted in poor mechanical properties. However, the idea is interesting because it addresses the issues of the difficultly in handling and feeding the dry nanomaterials into the extruder. Recently, Yang et al. [28] prepared a coupling agent by grafting GMA into PLA and used the coupling agent to prepare a master-batch with CNC, which was diluted with PLA to 1% CNC content. The results were interesting; the use of PLA-g-GMA improved the CNC dispersion and with only 1 wt% addition of CNC, the mechanical properties were improved.

Brabender-type batch mixing is a traditional method to make polymer blends on the lab scale. Iwamoto et al. [85] made cellulose nanofiber-reinforced PLA with different nanofiber contents, from 3 to 20 wt%, by first preparing a suspension mixture of CNF, PLA, acetone and water. The liquid phase was removed using vacuum, and the mixture was mixed in a Brabender type mixer for 12 min at 40 rpm. The results were promising: good dispersion was achieved, and the mechanical properties, both modulus and strength, were improved without decreasing the strain with a 10 wt% CNF content.

Roll-milling is another batch process and is usually used in rubber processing and to mix carbon-black and other additives into rubbery material. Roll-milling is effective in mixing and has been used by researchers to make cellulose nanocomposites [71,74,91]. Okubo et al. [71] showed that the dispersion of cellulose nano- or microfibers was improved with decreased gap distance in roll-milling and that the dispersion of 1 wt% CNF improved the energy absorption before failure by almost 200%. Visakh et al. [74,91] used roll-milling for the preparation of natural rubber nanocomposites with CNC and showed that latex-based master-batch preparation followed by mill-compounding was a viable route to produce rubber-based nanocomposites, which can potentially be scaled-up to a commercial process.

5.2 Continuous melt processing

In continuous melt mixing processes, there are two types of twin-screw extruders, namely, co-rotating and counter-rotating, for compounding purposes. For the processing of nanocomposites, the co-rotating twin-screw extruders (***Fig. 5***) are preferred because they are better for mixing and dispersing compared to the counter-rotating ones. Co-rotating extruders can also effectively remove volatiles and moisture, which is important if liquids are used as processing aids.

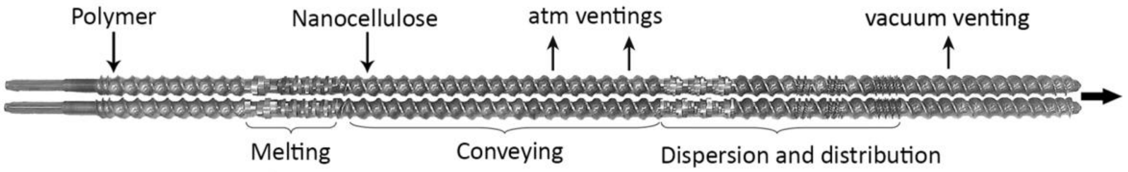


Fig. 5 *Twin-screw extruder screw configuration showing the feeding inlets for polymer and liquid nanocellulose, atmospheric venting as well as vacuum venting at the end. This screw configuration is designed for dispersive and distributive mixing.*

Co-rotating, twin-screw extruders have flexible modular designs, and the screw configuration can be changed from gentle melt mixing of sensitive materials to dispersive mixing with high shear forces. The materials can be fed continuously using gravimetric feeding systems or by pumping the materials as a liquid. Liquid-assisted feeding is a promising method for nanocomposites processing, and it has been shown to be an effective way to produce nanocomposites [10,11,70,98,99]. Nanocomposites prepared by the continuous extrusion process are listed in ***Table 4***, showing the materials, main findings and mechanical properties.

In a review of the water-assisted production of thermoplastic nanocomposites by Karger-Kocsis et al. [98], they listed the benefits of using liquid feeding of nanomaterials into the extruder, including the following: a) surface modifications are not necessary, b) there is no degradation of the surface modifiers, c) health risks are reduced because the nanomaterials are in a slurry, and d) dispersion is improved because of the “blow-up” phenomena caused by pressurized liquid evaporating from the melt, particularly in cases where water is used in the process. In a first study on PLA as a matrix in cellulose nanocomposites, DMAc/LiCl swelled cellulose nanocrystals were dispersed in water and fed as a liquid into the extruder [10]. The results were promising; all mechanical properties were improved compared to PLA with DMAC/LiCl used as the control, as seen in ***Table 4***. The use of PEG as a processing aid also led to increased strain, up to 17%. The same authors also prepared CAB-CNC composites, where the cellulose nanocrystals were mixed with plasticizer (which was required due to the brittle CAB) with the aim of assisting the feeding of CNC into the extruder and also to facilitate dispersion [13]. Recently, Herrera et al. [70] used a similar approach and prepared nanocomposites with PLA and CNF with interesting properties and well-dispersed nanofibers. The addition of only 1 wt% CNF together with a plasticizer improved the ductility of PLA. Another study by Herrera et al. [99] on PLA with cellulose and chitin nanocrystals showed that 1 wt% nanocrystals of both cellulose and chitin improved the mechanical properties of plasticized PLA.

The first attempt to prepare a master-batch using a carrier polymer for nanocellulose with the aim of being able to feed the material into the extruder in a dry form and to improve the dispersion was reported by Bondeson and Oksman [11]. PVOH-coated CNC was dry-fed into an extruder and mixed with PLA. This process was compared with liquid feeding of the same materials, and it was shown that better dispersion was obtained with the liquid process [11]. Corrêa et al. [75] used PA6 as a carrier polymer for CNC in the PA6 matrix and showed well-dispersed nanocrystals and improved thermal stability, but only a moderate improvement of the modulus, and no change of the strength was shown.

Iyer et al. [101] showed that cellulose nanocrystals can be dispersed with LDPE and PP using solid-state pulverization, which is a type of continuous twin screw extrusion process in the solid state, using cooling instead of heating during mixing. They showed well-dispersed CNC in the LDPE and PP and slightly improved properties. However, in this method, the CNC is first freeze-dried and premixed with the polymer prior to the process, which can be risky because free nano-sized particles must be handled.

Table 4 *Continuous compounding using twin-screw extrusion.*

Pre-process	Nanocellulose	Matrix	NC content (wt%)	Dispersion	Findings	E (GPA)	σ (MPa)	ε (%)	Reference
PLA-g-MA & PEG	Liquid CNC	PLA PLA-PEG	5	Yes TEM	Improved toughness	2.9>3.9	41>78	1.9 >2.7	2006[10]
Master-batch PVOH/CNW, freeze dried	Liquid CNC Dry CNC	PLA	5	Yes PVOH TEM	Improved toughness	3.3>3.6 3.4>3.7	56>68 54>67	2.0>2.4 1.8>2.3	2007[11]
-	Liquid CNC	CAB-TEC	5	Yes, TEM	Thermal properties	0.8>3.2	21>40	13<2	2008[13]
Master-batch CNF5	Solvent ex. CNF	PLA	1, 3, 5	Only partly SEM	Thermal properties	2.9>3.6	59>71	3.4<2.7	2010[14]
Master-batch CNF20	CNF	PVAc	1, 5, 10	Partly SEM	Improved creep	1.7>2.7	39>47	4.3<2.4	2011[87]
Master-batch CNC20	CNC	PVAc	1, 5, 10	Partly SEM	Fracture toughness				2011[86]
Acetylation, master-batch	Ac-CNF	PLA	1,3,5	Partly SEM	Thermal properties	2.9>3.6	58>71	3.4<2.9	2012[15]
Master-batch CNF50	CNF-s	PLA	2.5, 5 7.5	SEM, not dispersed	No improvements in mechanical properties				2012[39]
TEC plasticizer	Liquid CNF	TS	5, 10, 15, 20	Partly SEM	Toughness	0.3>1.2	4>21	305<262	2013[100]
-	Liquid CNC	PLA	1	SEM	Toughness	0.7>0.9	28	6 < 3.9	2015[99]
PA6 coated CNC 33	Freeze dried CNC	PA6	1	SEM dispersion	Thermal stability	1.4>1.8	52<50	73<33	2015[75]
Plasticized PLA	Liquid CNF	PLA-GTA	1	SEM	Toughness	1.2<0.8	28>29	18>31	2015[70]
Solid-state pulverization	Freeze dried CNC	PP, LDPE	5, 7, 10	SEM	Creep	1.2>1.8 0.2>0.3	36>38 10>13	700<12 510<460	2015[101]

* > improved and < decreased properties

Another development is extrusion where the fibrillation of cellulose is performed in the same process as the nanocomposites. Hietala et al. [100] attempted to separate and disperse nanofibers of wood pulp in a one-step process, where the preparation of thermoplastic starch (TS) and the compounding of fibers and matrix was performed. Unfortunately, the results did not show good fibrillation of the pulp. Suzuki et al. [73,102] tested a similar approach but with several steps: first fibrillating the cellulose in the presence of PP powders in the solid state (at 0°) and then compounding the polymer and cellulose nanofibers. This approach is promising for the future industrial preparation of cellulose nanocomposites in large-scale processing.

6. Nanofiber preforms and their impregnation

6.1 Nanofiber preforms

CNF networks or nanopaper have been frequently used as reinforcing sheets or preforms in composites and are made using filtration and a drying process akin to papermaking [6,103-105]. CNF are physically entangled in the wet gel after vacuum filtration from a water suspension. As the water evaporates, fiber-fiber bonding due to secondary attraction forces, including hydrogen bonds, develops between the CNF. The resulting cellulose nanopaper in themselves has an interesting combination of E-modulus (13.2 GPa), tensile strength (214 MPa), and strain-to-failure (10%) despite a porosity of 28%. Good mechanical properties of these nanopapers are important to the composites made from them as it has been shown that these composites rely heavily on the properties of the CNF network rather than of the individual nanofibers [48]. Sehaqui et al. made the first attempt to develop nanopaper preparations using a semiautomatic sheet former, Rapid Köthen [106], for making CNF papers and found it to rapidly produce nanopaper with high mechanical properties (see ***Table 5***). A standard British hand sheet maker has also been used [107].

Table 5 *Properties of nanopapers obtained by different preparation methods, STD in brackets. (Ref.* [106] *Copyright ACS).*

Preparation method	Dia. (mm)	Thickness (μm)	Prep. time (h)	σ (MPa)	ε (%)	E (GPa)
Suspension casting	80	40	120−144	180 (10)	5.9 (0.8)	10.3 (0.16)
Filtration, drying at 55°C	72	45	48−72	211 (26)	6.6 (1.5)	12.1 (0.29)
Filtration, hotpress at 105°C	72	55	2−3	178 (17)	6.3 (1.4)	10.3 (0.31)
Rapid-Köthen sheet former	200	40	1−2	232 (19)	5.0 (1.1)	13.4 (0.25)

Increasing the orientation of the CNF can greatly improve the mechanical properties of nanopaper [27,105,108]. In a fiber network mechanics context, increased out-of-plane orientation lowers the in-plane modulus. The high modulus and ultimate strength indicate that constrained drying leads to good in-plane orientation of the nanofibers and possibly also higher density [106]. However, producing cellulose nanopapers in a fast and continuous fashion similar to classic papermaking has yet to be achieved. To control the porosity of the resulting nanopaper, the drying process for the nanocellulose hydrogel obtained by filtration is essential. By exchanging the solvent of the hydrogel from water to ethanol, methanol, or acetone before drying, the porosity can be increased from 19% (drying from water) to 40% (drying from acetone) [105]. A further increase in nanopaper porosity can be achieved by solvent exchange either to tert-butanol followed by freeze-drying or to ethanol and then to CO_2, followed by super-critical drying [109]. The porosity range is 40−86%, and wood-based nanopaper with an exceptionally high specific surface area (up to 480 m^2g^{-1}) has been obtained. The high-porosity nanopaper also has interesting mechanical properties that are comparable to those of commodity thermoplastics but with much lower density.

6.2 Resin impregnation of CNF preforms

Resin impregnation of CNF was one of the first methods of producing CNF composites with high strength and stiffness [104]. The process forms a nanocellulose network then impregnates the network with a low-viscosity resin under vacuum, as shown in ***Fig. 6***.

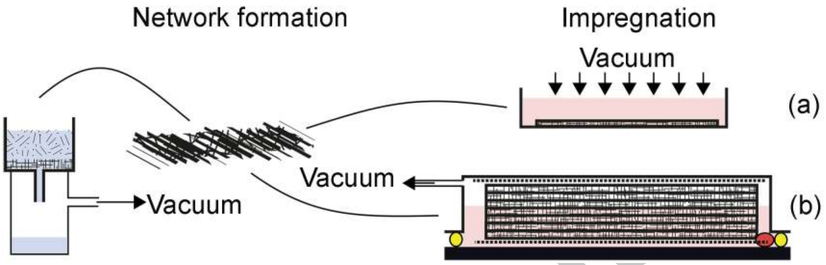


Fig. 6 *Schematic depicting two different approaches to impregnation (a) through immersion in resin, typically in a reduced pressure atmosphere, and (b) vacuum infusion of stacks of nanocellulose networks.*

The resin flowing into the dry network is initially driven by the capillary action of the wetting of the network by the resin. The flow is then assisted by the expansion of gases (air) remaining in the network due to the reduced atmospheric pressure, causing bubbles to rise due to the increased buoyancy force of the surrounding liquid, in this case, the resin. The process is therefore enhanced if there is a positive capillary effect between the resin and the CNF network, if the liquid is of low viscosity to permeate through the network and if there is sufficient time for the network to be fully impregnated. ***Table 6*** summarizes the different nanocomposites made using this technique, some of the important processing parameters and the resulting composite properties. Vacuum pressure is not always used [113,114,118,120], but almost all processes have long impregnation times. A high consolidation pressure has been found to increase the properties [104,110] because of the increase in the fiber volume fraction.

Table 6. *Overview of the nanocomposites manufactured using resin impregnation.*

	Matrix	Type	E	σ	ε	NC content		Impregnation time	P	Process	Year Ref.
			(GPa)	(MPa)	(%)	wt. %	vol. %	(hours)	(MPa)		
Dense networks	PF	CNF	19*	370*	2.5	78		12(vacuum)+96	100	Solvent: methanol Several layers	2005 [104]
	PF	BC	27*	370*	2.2	78		12(vacuum)+96	50	As above	2005 [110]
	MF	CNF	16	108	0.8	87		20(vacuum)+96	0	Solvent - not specified thin film	2007 [111]
	EP	BC	21	325	>2	65		12(vacuum)	0	UV cured, thin film	2005 [7]
	TCDDMA	CNF	7	-	-	62		24 (vacuum)	0	UV cured, thin film	2005 [6]
Network treated to improve impregnation	PF	CNF	10.5	145	4.2	78		12(vacuum)+96	100	Alkali treatment of CNF reduced stiffness	2008 [112]
	PVA	CNF	3.8	71	-	20		12	-	Oven dried network, impregnated -left to dry	2009 [113]
	CAB	CNF	7	71	3.9		54	12(vacuum)		Solvent: acetone thin film	2014 [114]
	PHD	BC	15.5	142	1.4	75		<12	0	Solvent: chloroform Impregnated -left to dry	2011 [115]
	EP	CNF	9.8	138	8.4		50	12	0	Cured 80°C 3 h+120°C 2 h, thin film	2014 [116]
	Acrylic	BC	0.4	20	15	5		12(vacuum)		Solvent: ethanol, UV cured	2008 [117]
Other strategies	PU	BC	12	151	6.2		43	0.02	0	UV cured, thin film	2012 [118]
	EP	CNF	9	96	5.9		58	<6 (gel-time)	0.1	Vacuum infusion, several layers, cure 20°C 24 h+50°C 16 h	2012 [119]
	EP	BC	7	102	5.3		49	<6 (gel-time)	0.1	As above	2012 [119]
	PF	CNF	4.9	248	14.7	92		22	30	TOC-CNF, freeze-dried, water swollen	2013 [120]
	EP 'in situ'	CNF	4.8	54	2		18	12	0	Cured 93°C 1 h+90°C 2 h+120°C 2 h, thin film	2014 [121]

* from bending tests, E modulus, σ strength, ε strain at failure, P consolidation pressure

The flexural modulus of the nanocomposites was similar to that of paper pulp (micro-sized fibers) produced by the same method, but the flexural strength increased by 80% from 210 to 380 MPa. Bacterial cellulose-based composites showed both higher stiffness (28 GPa) and higher strength (400 MPa) than the CNF and pulp fiber networks due to the higher crystallinity of the BC networks [119] or because the BC networks are more homogeneous [110], which would result in lower stress concentrations. These networks also have high porosity, allowing good impregnation of the resin [48]. One method of increasing the porosity and thus the impregnation in both CNF and BC networks is the use of solvents to reduce the nanofiber cohesion in drying, thus opening the structure of the network [114,115,122]. This opening of the structure and reducing of the nanocellulose network stiffness, which was found to be an issue in MF and PF impregnated CNF [103,104,111], has been used to maintain a high strain to failure in nanocomposites manufactured using resin impregnation. This has been achieved by applying alkali treatments to the CNF network before impregnation [112] or by using ductile resins combined with increasing the porosity of the mat using solvent exchange [116,123].

Fig. 7 shows a flexible, transparent composite produced in this way (5 wt% BC fiber mat impregnated with an acrylic resin) [117]. Transparent cellulose nanocomposites have been the subject of a number of studies, particularly by Yano's group at Kyoto University in Japan [6-8,117,123-125]. An interesting result of this group and others shows that although poor transparency can indicate poor impregnation [118], high transparency does not necessarily reflect good impregnation, as shown by the optical transparency of dense CNF networks that have only been polished [123].

Fig. 7 *Transparent, foldable, impregnated nanocomposite based on BC and UV cured acrylic resin*[117] *(Copyright permission Wiley).*

Further work on the impregnation of CNF networks has shown that a larger amount of waterborne resin, in this case, PF, was taken up by freeze-dried networks that had been water-swelled compared to networks that were solely freeze-dried [120]. The authors suggested that the reason for this is that the good compatibility of the PF and the CNF results in the CNF forming a barrier at the initial contact of the resin and the CNF, thus restricting the flow of resin to the rest of the network. By water-swelling the network, more of the bonds are taken up by the water, allowing the resin to more easily move into the network's now opened structure. The resin impregnation described previously forms prepreg nanocellulose that is then consolidated. Another more traditional composite manufacturing technique was applied to these nanocomposites, i.e., the use of vacuum infusion in stacks of CNF and BC networks [119]. In this study, the stacks were impregnated with a low-viscosity epoxy and were consolidated by vacuum pressure. In a later study by other authors, swelling of the CNF fibers was shown to occur upon impregnation with epoxy, which may affect the wetting of fibers in the liquid composite molding manufacturing methods [126]. An interesting concept tested by Ansari et al.[121] was impregnating nanocellulose 'in situ' in the pulp. In this study, pulp was bleached and oxidized, leaving the pulp composed of little else than bundles of nanocellulose fibers. These fibers were then impregnated with an epoxy, and the final composite had a modulus and yield strength similar to that of epoxy reinforced with CNF with a similar fiber content. In these nanocomposites, the high plasticity was lost and, with it, the high ultimate strength of the CNF-epoxy composite. The resin impregnation route has successfully been used to manufacture functional CNF-composites, for example, in the formation of flexible magnets and reduced water uptake [127-129].

Film-stacking to introduce a polymer phase between nanopapers is an easy approach to produce nanocomposites using thermoplastic matrices where the nanofiber network structure is retained. Seydibeyoglu and Oksman [130] prepared PU nanocomposites by stacking PU films with CNF mats and compression molding. A significant improvement in tensile strength and modulus was observed using the nanofiber network in the film stacking process compared to matrix alone or the micro-scaled fiber network. Cherian et al. [131] also used film stacking of PU films with CNF networks. The film stacking process was easy and resulted in a layered structure. The disadvantage is the limited filling of the pores in the nanopaper with polymers, resulting in limited interaction between the matrix and the reinforcement.

6.3 All-cellulose nanocomposites

Partial dissolution of cellulose nanopaper (or non-woven cellulose networks) to convert amorphous cellulose regions to matrix phase forming an all-cellulose composite has been studied extensively [132-145]. Although the concept of all-cellulose composites was first developed and discussed by Nishino [133] (kraft fibers dissolved completely and regenerated in the presence of ramie fiber), it was Gindl et al.[134] who pioneered partial dissolution, also termed surface selective dissolution, of cellulose I.

Fig. 8 shows the processing route for all-cellulose nanocomposites, as described by Staiger and co-workers[132]. The partially dissolved cellulose is regenerated in situ, usually in water or methanol, to form the matrix, which is then consolidated or welded together under pressure. Filter paper, dissolving grade beech pulp, microcrystalline cellulose ramie fibers and regenerated cellulose have all been used to obtain all-cellulose composites. Some of the studied materials are listed in ***Table 7***, showing the material combinations used and the mechanical properties achieved. LiCl/DMAc and ionic liquids are the most commonly used solvent systems, although NMMO and NaOH/urea have also been used with limited success [137-142,145]. In these nanocomposite processing approaches, the non-dissolved regions of cellulose, usually the crystalline regions, act as the reinforcement in a matrix of dissolved cellulose regions, resulting in cellulose nanocomposites with excellent compatibility between the matrix and the reinforcing phase.

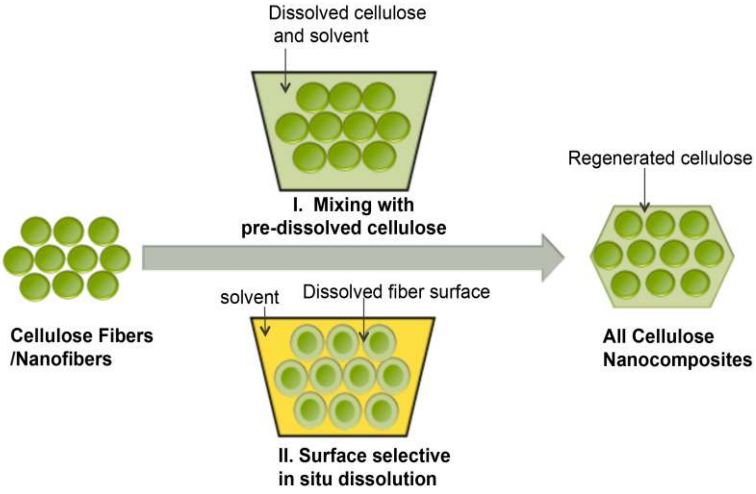


Fig. 8 *Schematic representation of the processing of all-cellulose nanocomposites via i) two stage and ii) one stage cellulose dissolution processes, adapted from* [132] *(Permission from M Steiger).*

The use of a cellulose nanopaper network to process all-cellulose nanocomposites following the in situ approach was first reported by Duchemin et al.[139], where the ionic liquid 1-butyl-3-methylimida-zolium chloride was used as the solvent. The cellulose I crystalline structure was retained after the partial dissolution, and high mechanical properties were achieved. They also showed that penetration of the ionic liquid was limited to the surface, forming a skin-core structure. Soykeabkaew et al. [141] used bacterial cellulose (BC) networks for surface selective dissolution with LiCl/DMAC and prepared composites with high strength and modulus, as shown in ***Table 7***.

Table 7 *Process development of all-cellulose nanocomposites by cellulose dissolution.*

Raw material	Solvent	E (GPa)	σ (MPa)	ε (%)	Year, Ref
Dissolution					
Kraft pulp	LiCl/DMAc	25	400	3.0	2004[133]
Cellulose powder	NMMO	1.8	29	21	2009[138]
Cotton pulp	NaOH/Urea	5.1	124	-	2009[137]
Partial dissolution					
MCC	LiCl/ DMAc	13.1	243	8.6	2005[134]
Filter paper	LiCl/DMAc	8.2	211	3.8	2007[135]
Ramie fiber	LiCl/DMAc	26	480	3.7	2008[136]
BC	LiCl/DMAc	18	411	4.3	2009[141]
MCC	LiCl/DMAc	6.9	106	3.3	2009[140]
CNF	Ionic liquid	10.8	124	3.2	2009[139]
CNF	Ionic liquid	6.8	118	12.8	2012 [143]
CNF	Ionic liquid	2.2	110	11	2014 [144]
CNF	LiCl/DMAc	17.5	188	11.8	2015 [145]

Mathew et al. also used ionic liquids to partially dissolve the cellulose nanofiber network for ligament applications [143]. The partially dissolved networks were regenerated in water and were cleaned by extensive washing with distilled water and consolidation at 60°C. Ligament-type prototypes were prepared by rolling the nanopaper sheets into tubules after the surface selective dissolution and regeneration in water. ***Fig. 9*** shows the ligament prototypes prepared and the microstructure with nanofibers embedded in the cellulose matrix.

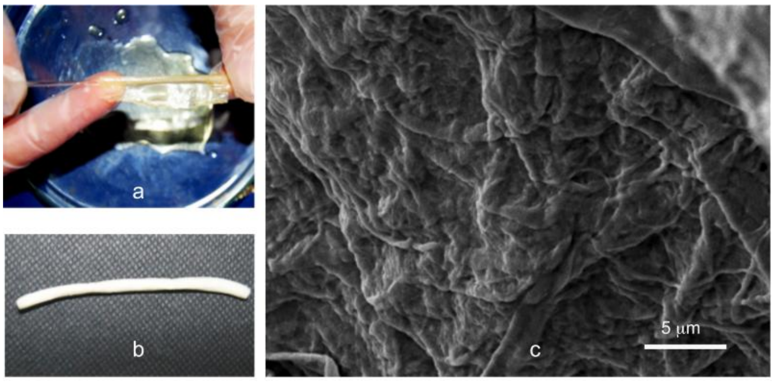


Fig. 9 *Photograph showing the a) ligament prototype processing using ionic liquid dissolution b) the prototype in tubule form c) the microstructure of the prototype walls after partial dissolution.*

Recently, Mashkour et al. [144] developed strong magnetic cellulose nanocomposites prepared by partial dissolution. The process resulted in flexible, anisotropic and super magnetic nanocomposite films that are expected to have advanced applications as storage devices, magnetic micro-robots and micro switches.

7. Porous nanocomposite materials

The nanocelluloses CNF and CNC have been used to prepare composite foams with various polymers. Foams with high porosity, small pore size and superior mechanical properties have been obtained with the addition of a small amount of nanocellulose compared to neat polymer foams [146-152] because the size of the nanocellulose is small enough to strengthen the cell walls in the foams [153]. ***Fig. 10*** compares the morphology of poly(ε-caprolactone) foams with and without nanocellulose, showing that an increase of the porosity and density was observed with a higher content of CNC, but a reduction of the pore diameter was reported [154].

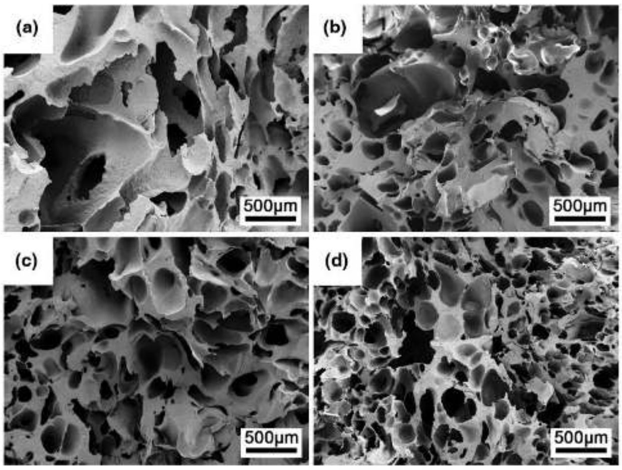


Fig. 10 *Morphology of poly(ε-caprolactone) foams with (a) 0 % CNC, (b) 0.5 % CNC, (c) 1% CNC and (d) 5% CNC prepared by injection molding with an* $scCO_2$ *supply system* [154] *(Copyright permission Springer).*

Generally, the conventional processes, such as extrusion, compression molding or injection molding, have been developed to produce porous materials with nanocellulose [151,154-158], as shown in ***Table 8***. The physical blowing agents, such as supercritical carbon dioxide ($scCO_2$) and nitrogen (scN_2), are injected into the compound during the process to create pores [152,154,155]. The poor dispersion of the nanocellulose in a polymer matrix has been shown to be the main problem for these methods because these materials tend to form aggregates [159]. Researchers have developed a procedure to introduce water as a blowing agent into the compounding process because water is non-toxic, freely available and environmentally friendly [155,157,158]. PLA and CNF were first mixed using a micro-extruder, and CNF (suspension) acted as both the reinforcement and the blowing agent [158]. Furthermore, the release of water as a byproduct caused by the chemical reaction in the extrusion is another approach to obtain porous materials [157,160]. The use of water as a blowing agent has gained attention due to environmental concerns; however, it is difficult to produce uniform cell structures and high-cell-density foams, and water may erode the screw [150,155,158]. Compared to the conventional techniques described above, foaming in the high-pressure chamber can create foams with greater cell density and distributed nanocellulose [161]. This process can be utilized after nanocomposites are made by extrusion, injection molding, compression molding or solvent casting [150,151,159,162]. Nanocellulose-reinforced composites are first prepared and are then placed in a high-pressure vessel filled with gas, such as $scCO_2$. After the nanocomposite is completely saturated with gas, cell nucleation and growth are initiated by thermodynamic instability caused by depressurization [150,151,162]. However, this process is more time consuming and is currently only performed at the laboratory scale [161]. Recent studies have attempted to diminish the use of blowing agents and steps of processing to fabricate foams. Freeze-drying has been found to be a simple and promising approach to prepare engineered porous structures with nanocellulose. The foam structure prepared by this approach depends on various key factors, such as the suspension concentration and the freezing rate [151,163-165]. However, the main downsides of this method are that it is a discontinuous and time-consuming process and that the solvents that can be used to dissolve polymers are limited [148,166].

The processing of foams with nanocellulose is in its infancy and is far from mass production. This may be due to the limited availability and high cost of nanocellulose.

7.1 Polyurethane foams

Polyurethane (PU) foams are widely used in many applications, and biobased PU foams have gained interest during the recent years. However, the properties of the bio-PU foams need to be improved to reach the level of petroleum-based PU-foams. Therefore, nanocellulose has been tested as an additive in PU foam preparation by several authors [167-174]. During the preparation of PU nanocomposite foams reinforced with nanocellulose, freeze-dried or dehydrated nanocellulose has been directly incorporated and dispersed in the polyol [171-173,175]. To improve the dispersion of CNC in the PU, the nanocrystals have been first dispersed in organic solvents and subsequently added to the polyol with sonication [167,170,174]. In this method, freeze-drying causes agglomeration of CNC, and the removal step of the solvents increases the cost and pollutes the environment. Therefore, the CNC suspension directly incorporated into polyol resin is considered a good solution, and the water can be removed under high vacuum pressure [169]. Then, the catalyst, surfactant, blowing agent and isocyanate are added with vigorous stirring. The nanocomposite foam is obtained within a few seconds. A small amount of nanocellulose can significantly improve the mechanical properties and thermal stability of the PU nanocomposite foams [167,169-173,175]. Thus, the incorporation of nanocellulose in the synthesis of rigid PU nanocomposite foams is desirable and promising. Some examples of PU foams are listed in ***Table 8***.

7.2 Aerogels

Nanocomposite aerogels are ultra-high-porosity foams and have gained large interest in recent years [109,176-185]. Conventionally, the term "aerogels" has been used to designate liquid-containing gels synthesized by the sol-gel process and dried under supercritical conditions. Recently, gels dried by freeze-drying have also been termed as aerogels [186]. Aerogels are non-periodic porous nanostructured materials, which exhibit unusual properties, such as high porosity up to 99%, surface areas between 100 and 1000 m^2/g, densities in the range 0.004-0.005 g/cm^3 and low heat conductivity [177]. The first study on aerogels based on nanocellulose was reported by Kuga et al. [182] using an aerogel from BC hydrogel, where solvent exchange was used followed by freeze-drying. Freeze-drying of aqueous CNF and CNC gels is a "greener" alternative to other methods, such as solvent exchange. The schematic representation of aerogel formation from an aqueous dispersion of CNF is shown in ***Fig. 11**,* adapted from Isogai et al. [183]. Recently, this approach has been used to prepare composite aerogels consisting of nanocellulose and polymers. The morphology and the mechanical properties can be modified by varying the freezing speed and type of crosslinking used [180]. The combination of nanocellulose and polymers results in aerogels with enhanced properties. The addition of 30 wt% xyloglucan increased the modulus and strength of CNF aerogels [184]. Electrically conducting nanocellulose composite aerogels have also been prepared using electrically conducting polymers, such as PANI [176] and PEDOT:PSS [176,185].

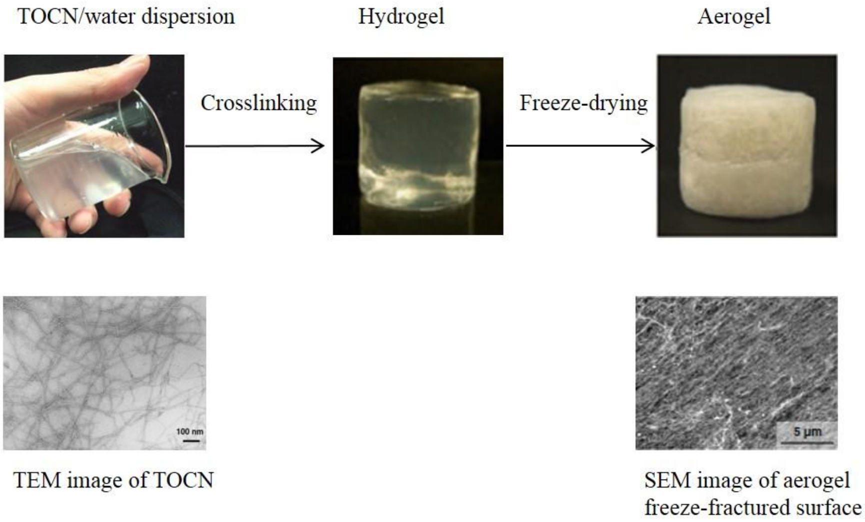


Fig. 11 *Conversion from TOC-CNF/water dispersion to aerogel, adapted with permission from Prof. A Isogai.*

The unidirectional freeze-drying process is a promising and novel technique for creating oriented porous structures. PVA/CNF aerogels filled with PDMS were produced using this method [181]. These methods and results are summarized in ***Table 8***.

Table 8 *Porous cellulose nanocomposite foams and preparation procedures.*

Foaming processing	Type polymer	Type NC	NC (wt%)	Blowing agent	Improvement E (%)	Improvement σ (%)	Year & Ref
Thermoplastic foams							
Micro-extrusion	PLA	CNF	1-2	Water	-	-	2011 [158]
Freeze-drying	PVA	CNF	20-60	-	75	62	2012 [149]
Freeze-drying	PVA	CNF	1 - 5	-	33	70	2012 [147]
Extrusion, injection molding	PCL	CNC	0.5-5	$scCO_2$	70	60	2014 [154]
Freeze-drying	Acrylic	CNC	1-8	-	149	66	2015 [166]
PU-foams							
CNC dispersed in DMF	Sucrose polyol	CNC	0.75	Pentane	180	143	2010 [167]
CNC dispersed in THF	Castor oil polyol	CNC	0.5-3	-	42	13	2011 [174]
CNC dispersed in water	Lignin PU	CNC	0.25-5	Pentane	212	160	2012 [169]
Freeze dried CNF	Soy polyol	CNF	1	Water	39	49	2014 [172]
Freeze dried CNC	Palm oil polyol	CNC	1-8	Water	216	117	2015 [171]
Mixing CNC	Rapeseed oil polyol	CNC	1-3	Water	9	-	2015 [173]
Aerogels					Porosity (%)		
Mixing/ freeze-drying/ impregnation	PANI	CNF	2	-	95-98		2008 [176]
Mixing, freeze-drying	Xyloglucan	CNF	0.5	-	98.5		2010 [184]
Mixing, freeze-drying	Soy protein isolate	CNF	0-100	-	92-92.7		2013 [179]
Mixing, freeze-drying, annealing	PVA	CNF, CNC	2-10	-			2015 [180]
Mixing, cross-linking, freeze-drying	PVA	CNF, CNC	(0.8-1.0)				
Mixing, unidirectional freeze-drying, pore filling with PDMS	PVA	CNF	0.74	-	>98		2015 [181]

8. Fiber spinning

Continuous fibers based on cellulose have gained interest in recent years because natural fibers are usually short, and if the fibers are made into yarn, some of the properties are lost because of twisting. Several spinning techniques, listed in ***Table 9***, have been tested, including common melt-spinning of biopolymers reinforced with nanocellulose with PLA and CAB as matrix materials [187-190], wet-spinning of polymer nanocellulose [191-196] or only nanocellulose [197-200] to a bath and dry-spinning of CA-CNC and pure nanocellulose [201,202]. Melt-spun nanocomposite fibers, in which cellulose nanocrystals (CNC) were used as reinforcements, were first introduced by John et al. [187]. The dispersion of CNC was performed using solvent exchange of aqueous CNC to acetone, followed by master-batch preparation and its dilution in extrusion. However, the addition of CNC did not lead to significant improvement in the mechanical properties because of the poor dispersion of CNC. Hoooshmand et al. [188,189] achieved better dispersion using the sol-gel technique and subsequently improved the mechanical properties of melt-spun fibers with the addition of CNC. Surface modification has been used to prepare composite spheres, which were melt-spun to composite fibers, and slightly improved mechanical properties were reported [190]. Further, alignment of the nano-reinforcements along the fiber axis by drawing is another way to improve the mechanical properties of the nanocomposite fibers. Hooshmand et al. showed that solid-state drawing, even with a low draw ratio (1.5), significantly increased both the modulus and the strength of the fibers [189]. Studies of melt-spinning of nanocomposite fibers are listed in ***Table 9***, showing the enhanced properties, material combinations and draw ratios.

The use of single filaments for wet-spinning is a promising method to produce strong nanocomposite fibers. Araki et al [197] used a similar approach, as described in the section on partially dissolved cellulose. Partially dissolved MCC fiber was prepared, with a nanocomposite-like structure and with non-dissolved oriented cellulose nanocrystals along the fiber axis. Another technique involves adding CNC as a reinforcement in the solution dope, which was reported for first time in 2010 by Urena-Benavides et al. [191]. They spun CNC-reinforced alginate fibers and reported improved strength and modulus compared to pure alginate. Several studies with different matrix materials, such as silk and PVA, have been reported [192-195,203,204] to prepare wet-spun nanocomposite fibers.

The latest development on continuous fiber spinning is fiber spinning of only cellulose nanofibers (CNF) without the use of a matrix or binder polymer. Pioneering work on simply wet-spinning tempo-oxidized CNF through a syringe into a bath containing organic liquid (***Fig. 12***) was reported by Iwamoto et al. and Walther et al. [198,199]. For these fibers, the alignment of CNF was reported as a key factor to achieve high mechanical properties. Torres-Rendon et al. [200] also developed a specific wet stretching device, as shown in ***Fig. 12***, to increase alignment.

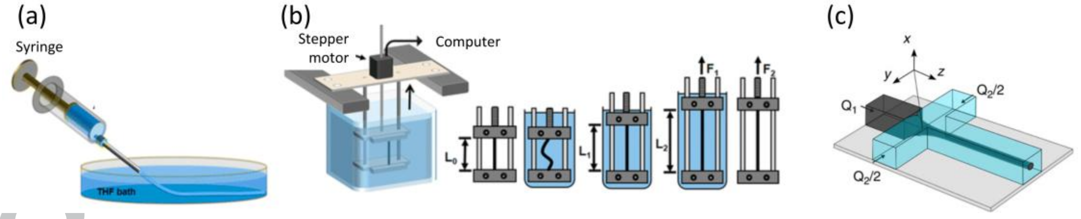


Fig. 12 *(a) Overview of the wet spinning process, (b) schematic illustration of the computer-controlled wet stretching device, adapted with permission from* [200]**.** *Copyright permission from American Chemical Society and (c) schematic drawing of the flow focusing channel. Q1 is the CNF core flow, and Q2 is the NaCl sheath flow adapted from* [205]*, Copyright permission from Nature Publishing Group.*

Dry-spinning of CNC-reinforced nanocomposite fiber was performed using cellulose acetate (CA) as the matrix. The CNC was solvent exchanged to DMAc using a rotary evaporator, and improvements of 600% and 150% for the modulus and strength were reported

[201]. The first dry-spun matrix-free cellulosic fibers were later prepared using piston-driven extrusion (capillary rheometer) to spin CNF suspensions [202]. By lowering the aqueous CNF concentration and increasing the spinning rate, a better aligned and denser structure fiber with higher mechanical properties was formed.

Table 9. *Overview of the cellulose-based nanostructured fibers, process and enhanced properties.*

Pre-processing	**Matrix**	**NC type & content (wt%)**	**Enhancement of mechanical properties****		**Draw ratio**	**Spinning process**	**Year & ref.**
			E (%)	*σ* (%)			
Melt-spun fibers							
Solvent-ex, master-batch	PLA	CNC 1, 3	8	-12	SSD: 2	Extruder	2013 [187]
Solvent-ex, master-batch	CAB	CNC 2	17	-6		Extruder	2014 [188]
Sol-gel, master-batch	CAB	CNC 2,10	90 (135)	23 (45)	SSD: 1.5	Extruder	2014 [189]
Preparation of spheres	PLA	BC, CNC 2, 7	-6	11	MD: 17-47	Extruder	2014 [190]
Wet-spun fibers							
Partially dissolved MCC		CNC	47	42		Syringe	2006 [197]
Dispersion in dissolved SA		CNC 2-50	123	38	WD: 2.4-4.6	-	2010 [191,192]
Dispersion in dissolved PVA		CNC 5-30	86	28	HD: 20-38	Syringe	2011 [204]
TOC, dispersion in dissolved PVA		CNF 1	31	-	HD: 10-20	Wet spinning	2013 [193]
TOC, dispersion in dissolved silk		CNF 1, 2.5, 5	-	-	WD: 1.5	Syringe	2013 [194]
Dispersion in dissolved PAN		CNC 0.5, 1, 2	100	21	WD: 8	-	2013 [203]
Dispersion in dissolved PVA		*CNF 1, 2, 3,6	220	58	WD: 2 HD: 13.5	Syringe	2014 [195]
TOC-CNF spun to coagulation bath		CNF 100	180	350		Syringe	2011 [199]
CNF spun to coagulation bath		CNF 100		-		Syringe	2011 [198]
As above		TOC-CNF 100	(310)	(145)		Syringe	2014 [200]
CNF pumped through channel		CNF 100	40	66		Flow-focusing channel	2014 [205,206]
Dry-spun fibers							
Solvent-exchange	CA	CNC 1-49	637	137		Capillary viscometer	2014 [201]
CNF suspension	-	CNF 100	65	70		Capillary rheometer	2015 [202]

*phr

** Numbers in brackets show the effect of fiber drawing

SSD: solid state draw ratio; MD: melt draw ratio; WD: wet draw ratio; HD: hot draw ratio

9. Conclusions

This review addresses the recent developments of the processing of cellulose nanocomposites, focusing on the most common techniques, including solution casting, melt-processing of thermoplastic cellulose nanocomposites and resin impregnation of cellulose nanopapers using thermoset resins. Important techniques, such as partially dissolved cellulose nanocomposites, nanocomposite foams reinforced with cellulose nanocrystals and nanofibers, as well as long continuous fibers or filaments, are also addressed, which have great potential as future reinforcing fibers for use in biocomposites. Some of the conclusions drawn are as follows:

- Solution casting is by far the most common method to produce nanocomposite films because of its simplicity, but the development of the methodology for large-scale use or for industrialization has not been achieved.
- Melt processing using extrusion has increased rapidly in recent years, and some attempts at large-scale processing have been conducted, for example, the development of a process where fibrillation and composites are made in one step during extrusion or where solid-state pulverization is used for dispersion followed by melt-processing.
- Resin impregnation is the process by which composites with the best mechanical properties are obtained. Until now, the focus has been on high mechanical properties and additional functionality rather than process development efficiency and upscaling.
- Light materials, such as foams, are important for future lightweight biocomposite structure development and can be produced using cellulose nanomaterial. Some of the most promising results are based on freeze-drying.

- The development of continuous native cellulose fibers is an emerging technology and is believed to be important when biocomposites with light weights and targeted properties are required.

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Figure captions:

Fig. 1 *Number of publications on cellulose nanocomposites, showing the country, most publishing journals and popular subjects dealing with processing.*

Fig. 2 *Improved dispersion of CNC in the PLA matrix as the surfactant content increases. Fractured surfaces of (a) PLA-CNC without surfactant show agglomerated CNC (b) PLA-CNC with 5% surfactant (c) PLA-CNC with 10% surfactant (d) PLA-CNC with 20% surfactant. (Copyright permission Taylor & Francis [12]).*

Fig. 3 *General scheme of the strategies used for the preparation of cellulose-based nanocomposites by solution casting.*

Fig. 4 *a) DSM micro-extruder (DSM) showing the processing chamber and conical screw design; only 5 or 15 ml is needed for one batch, depending on the size. b) Schematic of a Haake micro extruder with similar conical screw design.*

Fig. 5 *Twin-screw extruder screw configuration showing the feeding inlets for polymer and liquid nanocellulose, atmospheric venting as well as vacuum venting at the end. This screw configuration is designed for dispersive and distributive mixing.*

Fig. 6 *Schematic depicting two different approaches to impregnation (a) through immersion in resin, typically in a reduced pressure atmosphere, and (b) vacuum infusion of stacks of nanocellulose networks.*

Fig. 7 *Transparent, foldable, impregnated nanocomposite based on BC and UV cured acrylic resin*[117] *(Copyright permission Wiley).*

Fig.8 *Schematic representation of the processing of all-cellulose nanocomposites via i) two stage and ii) one stage cellulose dissolution processes, adapted from* [132] *(Permission from M Steiger).*

Fig.9 *Photograph showing the a) ligament prototype processing using ionic liquid dissolution b) the prototype in tubule form c) the microstructure of the prototype walls after partial dissolution.*

Fig. 10 *Morphology of poly(ε-caprolactone) foams with (a) 0 % CNC, (b) 0.5 % CNC, (c) 1% CNC and (d) 5% CNC prepared by injection molding with an* $scCO_2$ *supply system* [154] *(Copyright permission Springer).*

Fig. 11 *Conversion from TOC-CNF/water dispersion to aerogel, adapted with permission from Prof. A Isogai.*

Fig. 12 *(a) Overview of the wet spinning process, (b) schematic illustration of the computer-controlled wet stretching device, adapted with permission from* [200]**.** *Copyright permission from American Chemical Society and (c) schematic drawing of the flow focusing channel. Q1 is the CNF core flow, and Q2 is the NaCl sheath flow adapted from* [205], *Copyright permission from Nature Publishing Group.*