

Review article

Recent development of plant-derived nanocellulose in polymer nanocomposite foams and multifunctional applications: A mini-review

Supachok Tanpichai^{1,2*} 

¹Learning Institute, King Mongkut's University of Technology Thonburi, 10140 Bangkok, Thailand.

²Cellulose and Bio-based Nanomaterials Research Group, King Mongkut's University of Technology Thonburi, 10140 Bangkok, Thailand

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Abstract. Since last decades, nanocellulose has gained much attention in nanocomposite foams owing to high stiffness and strength, renewability, sustainability and biodegradability. Nanocellulose is hydrophilic, and could be easily dispersed in hydrophilic polymer matrices; however, there are challenges to introduce nanocellulose in less hydrophilic polymers. This review addresses the development of polymer nanocomposite foams with plant-based nanocellulose (cellulose nanofibers and cellulose nanocrystals), and the chemical modification and mechanical approaches to enhance the dispersibility of nanocellulose in hydrophobic polymer matrices. The combination of nanocellulose and other nanoparticles such as graphene nanoplatelets, montmorillonite clay, carbon nanotubes and zeolites to yield multifunctional porous nanocomposite materials with promising features such as self-extinguishment, dye adsorption, microwave absorption, conductivity and biocompatibility is also discussed in this paper.

Keywords: nanocomposites, nanocellulose, foam, surface modification, mechanical properties

1. Introduction

With growing environmental awareness, attempts have been made to replace fossil oil-based materials with biodegradable materials. Cellulose-based materials such as wood, cotton, hemp and so on are the most ubiquitous natural polymer in the world, and are renewable, biodegradable, sustainable, non-toxic and environmental friendly [1–4]. Cellulose could be derived from many parts of cellulosic sources such as seed (cotton), wood, bast (flex, hemp, kenaf, ramie and jute), fruit (coir, lemon and banana), leaf (pineapple, sisal and banana) and stalk (sugarcane, bamboo, rice, wheat and water hyacinth) [5–9], and cellulose has been greatly used in our daily lives such as textiles, paper and housing for thousands of years.

During last decades, the growth in nanocellulose has tremendously increased. Nanocellulose extracted from plants has two generic forms: cellulose nanofibers (CNFs) and cellulose nanocrystals (CNCs), as shown in Figure 1. CNFs, sometimes called nanofibrillated cellulose (NFC), with widths of less than 50 nm and lengths up to several μm , are disintegrated from a dilute pulp suspension using mechanical treatment with high shear forces such as grinding, homogenizing, refining and microfluidizing [7, 10–17]. It should be noted that these mechanical approaches consume large amounts of energy owing to repetitious mechanical treatment cycles. Therefore, chemical or enzymatic pretreatment is facilitated prior to mechanical fibrillation to reduce the energy consumption [6, 12, 18, 19]. On the other hand, CNCs or cellulose

*Corresponding author, e-mail: supachok.tan@kmutt.ac.th

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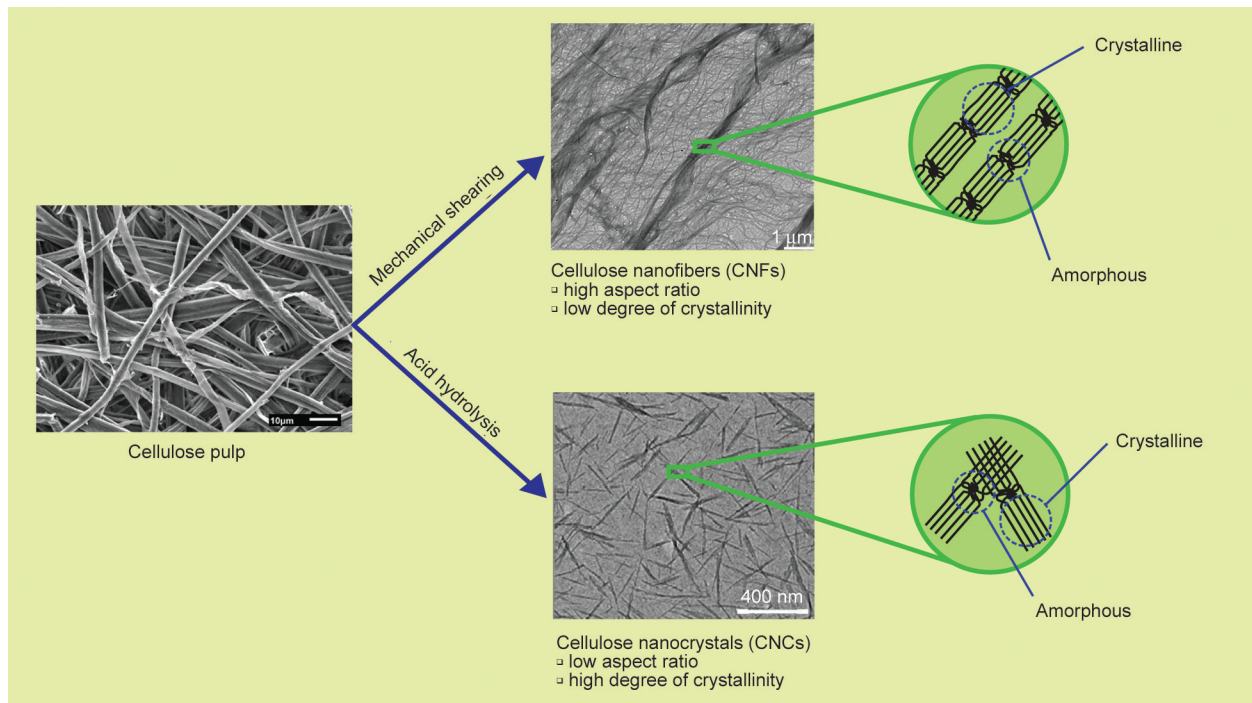


Figure 1. Schematic of production of cellulose nanofibers (CNFs) and cellulose nanocrystals (CNCs) from cellulose pulp. Reprinted and adapted from Tanpichai and Witayakran [24] with permission of John Wiley and Sons, Jonoobhi *et al.* [25] with permission of Elsevier and Favier *et al.* [26] with permission of John Wiley and Sons.

nanowhiskers (CNWs), rod-like particles with widths of less than 20 nm and lengths of lower than 500 nm, are produced from cellulosic sources using acid hydrolysis such as hydrochloric acid, sulfuric acid or maleic acid in order to remove disordered cellulose regions and followed by sonication treatment [20–23]. This results in a higher degree of crystallinity of CNCs while CNFs contain both amorphous and crystalline regions. The CNC morphology depends on the acid concentration, treatment time, and temperature applied during the hydrolysis treatment.

Plant-derived nanocellulose was initially introduced as a reinforcing agent in a polymer to prepare nanocomposites in 1995 [26]. The shear modulus of the latex with 6 wt% CNCs extracted from tunicates was a thousand times higher than that of the neat latex when the materials were measured at the rubbery state (above the glass transition temperature of the matrix). Since that time, many researchers have prepared nanocellulose reinforced nanocomposites, and nanocellulose is becoming a topical field because of its unique properties such as high mechanical properties, renewability, biocompatibility, biodegradability, and chemical stability [27–29]. Young's modulus of the single crystal of cellulose has been measured to be ~138 GPa using Raman spectroscopy [30] and X-ray diffraction [31]. When the density is taken into account, the specific Young's modulus of the crystalline

Table 1. Moduli of materials [2, 44, 45].

Material	Modulus [GPa]	Density [$\text{g}\cdot\text{cm}^{-3}$]	Specific modulus [$\text{GPa}\cdot\text{g}^{-1}\cdot\text{cm}^3$]
Sisal	28	1.3	22
Flax	28	1.6	18
Hemp	35	1.1	32
E-Glass	69	2.5	28
S-Glass	86	2.5	34
Aluminum	69	2.7	26
Steel	200	7.8	26
Crystalline cellulose	138	1.5	92

cellulose is significantly higher than that of glass fibers, aluminium and steel, as shown in Table 1.

Over the past few years, a large number of review articles have been published in many aspects of nanocellulose, including nanocellulose production, characterization, modification and applications [5, 21, 32–43]. However, the use of plant-derived nanocellulose in polymeric porous materials has not been addressed enough. Therefore, this review focuses on the recent development in preparation of the nanocomposite foams with nanocellulose and the multifunctional applications of these porous materials. At the time of writing, there are around 170 articles on nanocomposite foams with nanocellulose published in the Web of Science database, and the number of publications in this research field has been increasing annually, as shown in Figure 2.

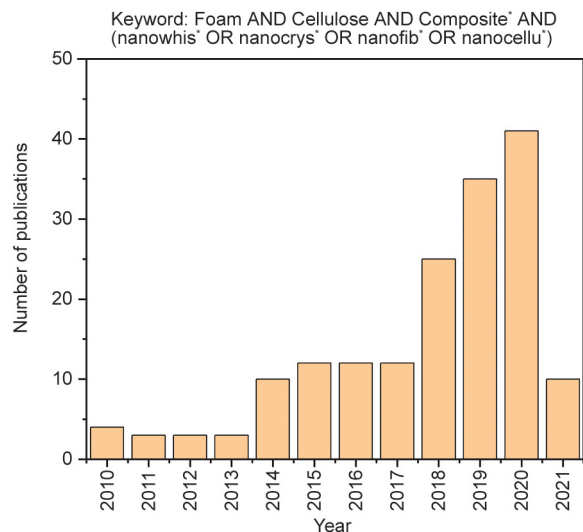


Figure 2. The number of annual publications on nanocomposite foams with nanocellulose between 2010 and 2021. The data was obtained from the Web of Science database using keywords of Foam AND Cellulose AND Composite* AND (nanowhis* OR nanocrys* OR nanofib* OR nanocellu*) (01-08-2021).

2. Plant-derived nanocellulose reinforced nanocomposite foams

Foam is generally prepared by dispersing gases into a liquid, solid or hydrogel using various approaches such as freeze-drying, supercritical drying, oven drying and melt-processing, and porous foam materials have a wide range of applications such as packaging, absorption and tissue engineering owing to light weight, low density and heat and sound insulation [40, 46–48]. Due to superior mechanical performances and size in the nanoscale, nanocellulose has attracted more attention as reinforcement to improve mechanical properties of petroleum and bio-based polymer foams such as polyurethane (PU), poly(vinyl alcohol) (PVA), poly(lactic acid) (PLA), tannin and xylan [48–61]. Mechanical properties of foams depend on cell structure (close and open cell) and cell wall properties. When the foam is under compression deformation, linear elasticity corresponding to the bending of cell walls initially begins, followed by a plateau-like region due to the bucking of cell walls. The densification regime caused by the collapse of cells subsequently takes place at a higher strain, presenting a significant increase in stress [62, 63]. Zhou *et al.* [49] have found that the presence of CNCs had an effect on cell size, dimension stability, mechanical properties, water uptake, and thermal properties of the PU foams. An increase in compressive strength, modulus, and water uptake was observed with increasing

CNC loadings. With 4 wt% of CNCs, the compressive strength and modulus of the nanocomposite foams were two and four times higher than those of the neat PU foams. This increase was due to the higher cell wall rigidity induced by CNCs. However, with the addition of more than 4 wt% of CNCs, the compressive strength and modulus of the nanocomposite foams significantly decreased owing to poor dispersion of CNCs in the PU matrix. Moreover, the reduction in volumetric shrinkage of the nanocomposite foams was found with increasing CNC contents. Moreover, the maximum tensile strength of 0.73 MPa was observed for natural rubber latex foams with 15 phr of CNFs; however, the rubber latex foams with 20 phr of CNFs presented the lower tensile strength of 0.26 MPa [64]. This reduction in the tensile strength of the nanocomposites at 20 phr of CNFs was caused by poor dispersion of CNFs in the rubber matrix. Similarly, the mechanical properties of the PVA foams prepared by the freeze-drying approach were enhanced with the introduction of CNFs up to 30 wt%. With the incorporation of more than 30 wt% CNFs, the compressive stress and modulus of the nanocomposite foams decreased. The good dispersion of CNFs in the PVA matrix was observed when loadings of CNFs were low because the amorphous PVA acted as a glue to combine these nanofibers. Nevertheless, macroporous open cells with a large distribution of CNFs were observed from the nanocomposite foams at a high loading of CNFs [48]. It is worth noted that the incorporation of nanocellulose in hydrophilic polymer matrices plays a vital role in mechanical properties of the nanocomposite foams. At low loadings of nanocellulose, the improvement in mechanical properties of the nanocomposite foams would be observed owing to good dispersion and interaction between the matrix and fillers, which results in the efficient stress transfer from the matrix to nanocellulose. In contrast, a decrease in mechanical properties of the nanocomposite foams is possibly noticed when a high loading of nanocellulose is applied. This reduction is caused by aggregates of nanocellulose particles, which affects their reinforcing efficiency. Although the promising mechanical performances of the nanocomposite foams with nanocellulose could be estimated, the precise nanocellulose concentration used to obtain the nanocomposite foams with the optimum mechanical properties is hardly predicted because mechanical properties of the nanocomposite foams are dominated by various

parameters such as the processing route, polymer properties, nanocellulose architecture and properties, dispersion and alignment of nanocellulose particles, adhesion between the nanocellulose and polymer matrix and foam density, porosity and pore size.

The development of cross-linking would be an attractive route to improve interaction between the cellulose particles and polymer matrix to yield nanocomposite foams with higher mechanical properties [63, 65–69]. Song *et al.* [63] have presented a significant increase in mechanical properties of the CNC reinforced PVA nanocomposite foams with the use of formaldehyde as a cross-linker. With the introduction of 1.5 wt% CNCs, the compressive strength at 70% strain and modulus of the cross-linked foams were 58.2 and 43.2 kPa, while the neat foams had the compressive strength and modulus of 6.7 and 7.5 kPa, respectively. The introduction of the cross-linker to bond CNCs and PVA to obtain well-organized structured foams with small pores connected through cell walls has been studied by Wang *et al.* [68]. Results showed low values of strength and modulus were obtained for the uncross-linked CNCs/PVA foams due to poor bonding between the matrix and CNCs, which hindered stress transfer between the matrix and fillers. With the addition of the cross-linker, mechanical properties of the cross-linked PVA foam at the same CNC contents, however, were significantly improved, attributed to 3D chemically cross-linked networks of the matrix and CNCs. Moreover, cross-linking has also been applied to stabilize foams in a swollen state. The cross-linked CNF/wheat gluten (WG) protein foams did not show any improvement of mechanical properties when the foam samples were tested in a dry condition compared with the uncross-linked WG and uncross-linked WG/CNF foams [70]. But, when conditioned in water for 16 h, the uncross-linked CNF/WG foam could not perform the test as it was fragmented in water. The cross-linked CNF/GA foam showed high stability and could be repeatedly deformed to a value of 80% strain without showing any damage, while the uncross-linked WG and cross-linked WG foams showed a small recovery with damage after compression. A similar finding has been reported by Liang *et al.* [71]. The cross-linking of CNCs and CNFs with the poly(methyl vinyl ether-*co*-maleic acid) (PMVEMA) and poly(ethylene glycol) (PEG) matrix could develop the nanocomposite foams which were stabilized in high humidity and water environment. Although cross-linking can enhance

the mechanical properties of the nanocomposite foams with nanocellulose, the availability of functional groups on cellulose and polymer is mandatory to form cross-linking between these two phases. The degree of improvement in mechanical properties of the nanocomposite foams depends on the cross-linking density and compatibility between the polymer and cellulose. With a high degree of cross-linking, the material becomes more rigid, and this improvement in mechanical properties would be more pronounced when a cross-linked porous material with nanocellulose is deformed in water or high relative humidity.

3. Modification of nanocellulose for hydrophobic polymers

Nanocellulose efficiently improves mechanical properties of hydrophilic polymer matrices; however, the dispersion of nanocellulose in hydrophobic polymers such as polypropylene (PP), polyethylene (PE), and PLA is challenging owing to poor interfacial adhesion between nanocellulose and these polymers [54, 66, 72–74]. This leads to the occurrence of nanocellulose aggregation, resulting in the reduction in mechanical properties of the nanocomposite foams [63, 75]. The surface modification to lessen the hydrophilicity of nanocellulose would be discussed in this section, and the mechanical approach to disperse nanocellulose in hydrophobic polymer matrices would also be mentioned. Table 2 summarizes results and methods to develop nanocomposite foams with nanocellulose.

3.1. Chemical modification

Surface modification of nanocellulose such as acetylation, grafting, esterification, TEMPO-mediated oxidation and silylation has been widely studied to solve the usage limitation of nanocellulose in hydrophobic polymers [54, 66, 72–74, 78]. Wang *et al.* [72] modified CNFs with alkenyl succinic anhydride (ASA) to reduce the hydrophilicity of CNFs, and the PP foams with modified CNFs were produced. The better dispersion of the modified CNFs in the PP matrix contributed to the higher cell density and smaller cell sizes than the foams with unmodified CNFs. The yield stress and tensile modulus of the PP foams with the unmodified CNFs were 43.4 MPa and 1.22 GPa, while the addition of modified CNFs at the same loading improved the yield stress and modulus to 44.3 MPa and 1.35 GPa, respectively. This improvement was attributed to the better interaction between

Table 2. Results and preparation of nanocomposite foams with cellulose nanocrystals (CNCs) and cellulose nanofibers (CNFs).

Matrix	Reinforcement	Processing	Results	References
Acrylic latex	CNCs (0–8 wt%)	Mixing and freeze-drying	Mechanical properties ↑ Density ↓	[56]
Epoxy resin	TEMPO-oxidized CNFs (0–60 vol%)	Freeze-drying and impregnation	Glass-transition temperature ↑ Water absorption ↑ Porosity ↑ Density ↓	[76]
Natural rubber latex	CNFs (0–100 wt%)	Mixing and freeze-drying	Mechanical properties ↑ Absorption capacity ↑	[77]
Poly(butylene succinate)	CNCs (0–0.5 phr)	Compounding, compression molding and supercritical CO ₂ injection	Crystallinity ↑ Meting properties ↑ Cell density ↑ Cell diameter ↓	[78]
Poly(butylene succinate)	Acetylated CNCs (0–0.5 phr)	Compounding, compression molding and supercritical CO ₂	Crystallinity ↑ Meting properties ↑ Cell density ↑ Cell diameter ↓	[78]
Poly(ethylene-co-vinyl acetate)	CNFs (0–3 wt%)	Compounding and compression molding	Mechanical properties ↑ Density ↓ Cell diameter ↓	[79]
Poly(ethylene-co-vinyl acetate)	Acetylated CNFs (0–3 wt%)	Compounding and compression molding	Mechanical properties ↑ Density ↓ Cell diameter ↓	[79]
Poly(lactic acid)	CNCs (0–3 wt%)	Solvent casting and leaching	Mechanical properties ↑ Density ↑	[80]
Poly(lactic acid)	CNCs (0–3 wt%)	Solvent casting, melt extrusion and compression molding	Mechanical properties ↓	[81]
Poly(lactic acid)	Acetylated CNCs with the degree of substitution of 0.58 (0–3 wt%)	Solvent casting, melt extrusion and compression molding	Mechanical properties ↓	[81]
Poly(lactic acid)	Acetylated CNCs with the degree of substitution of 1.26 (0–3 wt%)	Solvent casting, melt extrusion and compression molding	Mechanical properties ↑	[81]
Polypropylene	Alkenyl succinic anhydride-modified CNFs (0–15 wt%)	Compounding and injection molding	Mechanical properties ↑ Cell density ↑ Cell diameter ↓	[74]
Polypropylene	Alkenyl succinic anhydride-modified CNFs (0–5 wt%)	Kneading, melt-extrusion, materbatch preparation and foam injection molding	Mechanical properties ↑ Cell density ↑ Cell diameter ↓	[72]
Polypropylene	CNFs (0–10 wt%)	Extrusion and injection molding	Mechanical properties ↑ Cell diameter ↑	[82]
Polystyrene	CNFs (0–1 wt%)	Compounding, melt extrusion, injection and expansion	Mechanical properties ↑ Density ↑ Glass-transition temperature ↓ Average cell diameter ↓	[83]
Polystyrene	TEMPO-oxidized CNCs (0–1 wt%)	Compounding, melt extrusion, injection and expansion	Mechanical properties ↑ Density ↑ Glass-transition temperature ↓ Cell diameter ↓	[83]
Poly[styrene-(ethylene-co-butylene)-styrene]	CNFs (0–0.005 phr)	Solvent casting	Mechanical properties ↓	[84]
Poly[styrene-(ethylene-co-butylene)-styrene]	TEMPO-oxidized CNFs (0–0.01 phr)	Solvent casting	Mechanical properties ↑	[84]
Poly(vinyl alcohol)	CNFs (0–60 wt%)	Freeze-drying	Mechanical properties ↑ Porosity ↑ Density ↓	[48]

Table 2. Continuous.

Matrix	Reinforcement	Processing	Results	References
Poly(vinyl alcohol)	TEMPO-oxidized CNCs (0–2 wt%)	Solvent casting (cross-linking with formaldehyde)	Water uptake ↓ Mechanical properties ↑	[63]
Poly(vinyl alcohol)	CNCs or CNFs (0–1 wt%)	Mixing and freeze-drying (cross-linking with borax)	Mechanical properties ↑ Density ↑ Thermal stability ↑ Porosity ↓	[69]
Poly(vinyl alcohol)	CNFs (0–0.1 wt%)	Extrusion and supercritical CO ₂ injection	Crystallinity ↑ Cell density ↑ Cell diameter ↓	[85]
Polyurethane	Carboxymethylated CNFs (0–4 wt%)	Mixing	Mechanical properties ↑	[86]
Polyurethane	CNCs (0–6 wt%)	Mixing	Mechanical properties ↑ Thermal conductivity ↓ Cell diameter ↓	[87]
Polyurethane	CNCs (0–0.8 wt%)	Mixing	Mechanical properties ↑ Density ↑ Thermal conductivity ↑	[60]
Polyurethane	CNCs (0–1 wt%)	Mixing	Mechanical properties ↑ Water absorption ↑	[88]
Poly(ϵ -caprolactone)	CNCs (0–1 wt%)	Solvent casting and leaching	Mechanical properties ↑ Water absorption ↑ Cell viability ↑ Crystallinity ↓ Water contact angle ↓	[89]
Starch	CNFs (0–70 wt%)	Solvent casting and freeze-drying	Mechanical properties ↑ Density ↓	[51]
Wheat gluten	CNFs	Solvent casting and freeze-drying	Mechanical properties ↑ Cell diameter ↓ Density ↓ Water uptake ↓	[70]
Xylan	CNCs (0–1.25 wt%)	Freeze-drying	Mechanical properties ↑	[55]

↑ indicates that property of the nanocomposites foams was higher than that of the neat foams.

↓ indicates that property of the nanocomposites foams was lower than that of the neat foams.

the polymer matrix and modified CNFs, which allowed stress to transfer from the soft matrix to the stiff modified CNFs. Effects of various modification levels of acetylation on CNC surfaces on properties of the PLA nanocomposite foams have been studied [81]. Results showed that CNCs with the moderate degree of substitution (1.26) could better improve the interfacial adhesion between the matrix and cellulose, leading to higher mechanical properties of the nanocomposite foams in comparison with those of the nanocomposite foams with unmodified CNCs and acetylated CNCs with the low degree of substitution (0.58). Tensile strength and modulus of the nanocomposite foams with moderate substituted CNCs were 10.7 and 203.9 MPa, while the nanocomposite foams with unmodified CNCs and CNCs with the degree of substitution of 0.58 had similar inferior tensile strength (~8 MPa) and modulus (~130 MPa). Effect of the degree of functionalization

of CNCs via methacryloxypropyltrimethoxysilane on mechanical properties of poly(styrene-*co*-divinylbenzene-*co*-2-ethylhexyl acrylate) nanocomposite foams has also been reported [90]. Furthermore, the surface modification approach of acetylation on CNC surface has been applied to improve the dispersion of CNCs in poly(butylene succinate) (PBS). A decrease in the cell size within the foams (27.7 μm) was observed for the PBS foams with modified CNCs, while the unmodified CNC/PBS foams had a bigger cell size of 33.2 μm [78]. The higher cell density caused by more cell nucleation sites was attributable to the well-dispersed acetylated CNCs in the PBS foams. The small cell size and high cell density allowed less heat to penetrate through the material. This resulted in the lower thermal conductivity of the modified CNC/PBS foams (0.027 $\text{m}\cdot\text{K}^{-1}$) in comparison with that of 0.063 $\text{m}\cdot\text{K}^{-1}$ for the neat PBS foam. It is worth noted that the chemical modification

could provide the good dispersion of nanocellulose and strong interfacial interaction between nanocellulose and hydrophobic polymers, which could offer the great stress transfer from the matrix to stiff nanocellulose; nevertheless; the time-consuming chemical approach associated with complex chemical reactions and chemical expense would be taken into consideration.

3.2. Mechanical approach

The good dispersion of hydrophilic nanocellulose particles in hydrophobic polymer matrices could be successfully achieved by the Pickering emulsion approach without any chemical modification [89, 91, 92]. The Pickering emulsion process has been proved to be a straightforward way to fabricate nanocomposite foams with organized nano or microstructures [93–95]. Nanocellulose particles acting as an emulsifier at the oil-water or air-water interface to stabilize emulsions could control porosity, pore size and

mechanical properties of the foams [95–97]. Recent works on the use of CNFs to stabilize nonwater-soluble polymer droplets such as poly(carbonate) (PC), poly(methyl methacrylate) (PMMA), polystyrene (PS), and PLA have been reported [93]. Nonwater-soluble polymers dissolved in 1,2-dichloroethane (DCE) to form the oil phase were stabilized by CNFs through the Pickering emulsion pathway, and the emulsion was lyophilized to develop a nanocomposite foam. Figure 3 presents the fabrication of the nanocomposite foams prepared from the hydrophobic polymers and CNFs via Pickering emulsion technology. Results showed that the stabilization of Pickering emulsions could hardly be affected by polymer types and concentrations. This could confirm the universality of this processing route. The formation of a dense network of nanocellulose was noticed at the oil/water interface when a high concentration of nanocellulose particles was applied. This led to the prevention of the flocculation of droplets and improvement

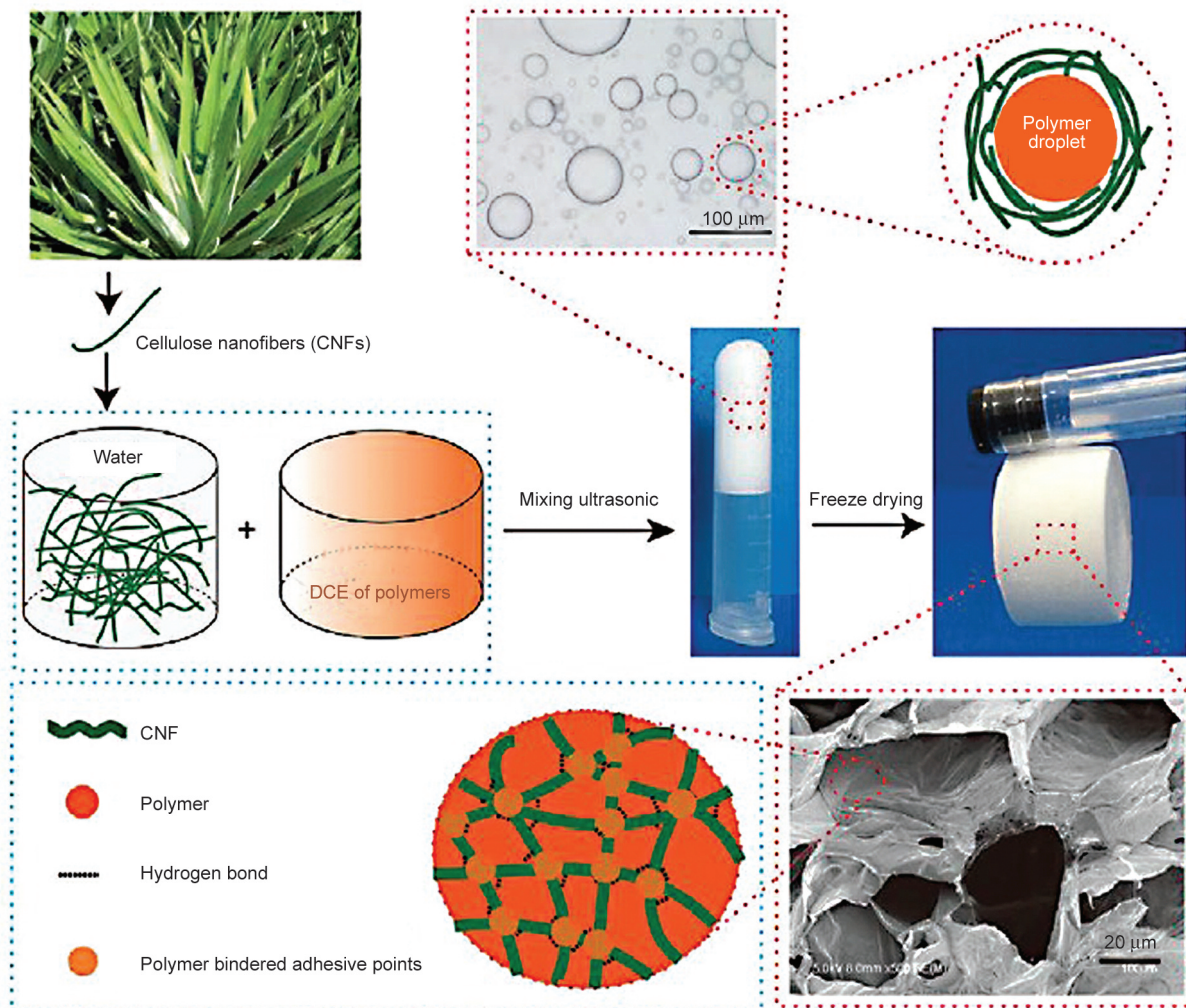


Figure 3. Formation of the polymer nanocomposite foams between cellulose nanofibers (CNFs) and nonwater-soluble polymers. Reprinted from Li *et al.* [93] with permission of John Wiley and Sons.

of the emulsion stability. Furthermore, the effects of various charge densities on CNF surfaces at the air-water interface on the stability of the aqueous foams have been investigated by Cervin *et al.* [98]. The fiber aggregations and number of fiber contact points at the interface and complex viscoelastic modulus of the air and water interface could be dominated by the charge density of CNFs. The modified CNFs with increasing the charge density led to an increase in the complex viscoelastic modulus, attributed to the accumulation of the modified CNFs and gel formation at the air-liquid interface. The complex viscoelastic modulus had a correlation with foam stability. Notably, it was found that CNFs with a higher aspect ratio could enhance the higher foam stability than foams stabilized by low-aspect-ratio nanocellulose owing to the formation of networks at air-water interfaces, which increased the complex viscoelastic modulus. The Pickering emulsion approach would be favorable to fabricate a scaffold for biomaterial applications such as cartilage, bone, nerve, and cardiovascular tissue regeneration because of less toxicity and no chemistry use. The issues that might hinder the scalability of this Pickering emulsion method are low productivity, batch processing, and material size limitation.

Dip-coating is the facile technique to introduce nanocellulose on hydrophobic polymeric foams [99, 100]. Although nanocellulose could not form chemical interaction with hydrophobic polymeric materials, the physical interlocking of cellulose nanoparticles on the foam structure would play an important role. The three-dimensional (3D) porous hydrophobic PU foam was dipped in a CNC aqueous suspension to form the CNC-coated PU foam [100]. This altered the hydrophobicity to the hydrophilic feature. With increasing CNC concentrations, the hydrophilic character of the CNC-coated PU foams was more pronounced. The neat PU foams had a water contact angle of 126.6° while the water contact angle values of the PU foams coated with CNCs were 92.8° (0.25 wt% CNCs), 80.73° (0.50 wt% CNCs), 74.0° (0.75 wt% CNCs), and 49.9° (1 wt% CNCs). Similarly, the melamine nanocomposite foams coated with CNFs were developed using a dip-coating method, and the formation of CNF films on the foam skeleton was observed [101]. The formation of the thin film of CNFs on the surface of the porous silica foam has also been reported when the silica foam was dipped in a CNF suspension. This simple dip-coating

approach has been adapted to coat porous materials with a mixed suspension of nanocellulose and other nanoparticles such as silver nanowires [99] and graphene nanoplatelets [102]. Vice versa, a hydrophilic nanocellulose porous material could be dipped in a hydrophobic polymer solution to yield a nanocomposite foam. A polypyrrole-coated CNF sponge was prepared by immersing a sponge of CNFs in a polymerized pyrrole solution [103]. In addition, a freeze-dried CNF aerogel was immersed in an epoxy solution to develop a CNF reinforced epoxy nanocomposite foam [76]. With the addition of the epoxy resin, the mechanical properties of the nanocomposite foams were significantly higher than those of the CNF aerogels. With increasing an epoxy resin content, the CNF aerogel was covered by larger amounts of the resin. The higher dispersion of the resin in the CNF aerogel provided a better stress transfer process from the resin to stiff CNFs, which could enhance the mechanical properties of the nanocomposite foams. It should be mentioned that the main purpose of dipping polymeric foams in a suspension of nanocellulose is not to enhance the mechanical properties but to add specific features induced by nanocellulose, such as water absorption or sound absorption. On the other hand, higher dimensional stability and mechanical properties are expected for dipping a nanocellulose aerogel or sponge in a polymer solution. Therefore, the straightforward dip-coating process could be applied for mass preparation to adapt the surface of foams owing to the quick process and less complex preparation steps.

4. Recent applications of nanocomposite foams with nanocellulose

Although nanocellulose has been greatly used as reinforcement to improve the mechanical properties of polymer foams, the final application of these foams is still limited. Therefore, the introduction of nanofillers with specific features such as clay, carbon nanotube or zinc oxide associated with nanocellulose would possibly offer further multifunctional characteristics to the porous materials for instance, flame retardancy, absorption and conductivity [100, 104–106]. Table 3 presents recent applications of the nanocomposite foams with nanocellulose and nanofillers.

4.1. Flame retardancy and thermal insulation

Flame retardancy and thermal insulation are the main features that could expand the applications of

Table 3. Recent applications of the nanocomposite foams with nanocellulose (cellulose nanofibers (CNFs) or cellulose nanocrystals (CNCs)) and nanofillers.

Application	Material	Method	References
Flame retardant foam	Poly(vinyl alcohol)/CNFs/montmorillonite clay	CNFs and montmorillonite clay were mixed together, and a poly(vinyl alcohol) solution was added to the mixed suspension. The mixed suspension was subsequently freeze-dried.	[104]
Flame retardant foam	TEMPO-oxidized CNFs/graphene oxide/ sepiolite nanorods	Graphene oxide and sepiolite nanorods were added to a CNF suspension, and boric acid was introduced to the mixed suspension. The as-prepared suspension was then freeze-dried.	[107]
Microwave absorber	Poly(lactic acid)/CNFs/carbon nanotubes/ ferroferric oxide nanoparticles	A uniform CNF and carbon nanotube aqueous suspension was mixed with an oil phase of poly(lactic acid) and ferroferric oxide nanoparticles to form a Pickering emulsion, and the emulsion was then freeze-dried.	[108]
CO ₂ absorbent	Gelatin/ CNFs/silicate particles	A suspension of CNFs, silicate particles, and gelatin was freeze-dried.	[109]
CO ₂ absorbent	Gelatin/TEMPO-oxidized CNFs/zeolitic imidazolate particles	A zinc nitrate hexahydrate was mixed with a suspension of TEMPO-oxidized CNFs. Then, this hybrid material was added to a gelatin solution, and the suspension was freeze-dried.	[110]
Oil/water absorbent	Polyurethane/CNCs/graphene	A polyurethane foam was dipped in a mixed suspension of CNCs and graphene.	[100]
Oil/water separator	Polyurethane/CNFs/graphite	Spray-dried CNFs and graphite were firstly mixed with polyols, and isocyanate was further added. Then, the mixture was cured in a vacuum oven.	[111]
Sound absorbent	Melamine/CNFs	A melamine foam was immersed in a suspension of CNFs, and the melamine foam coated with CNFs was cyclic-freeze-dried.	[101]
Electronic device	Polyurethane/CNFs/silver nanowires	A polyurethane was coated with CNFs and silver nanowires using a dip-coating method.	[99]
Electronic and telecommunication device	Silica/CNFs	A silica foam synthesized from a carbon foam was coated with a thin layer of CNFs.	[112]
Energy conversion and storage	Polypyrrole/poly(ethylene glycol)/CNFs	A freeze-dried CNF sponge was immersed in pyrrole, and the polymerization occurred. The polypyrrole-coated CNF sponge was dipped in a molten poly(ethylene glycol).	[103]
Energy conversion and storage	Melamine/CNFs/graphene nanoplatelets/poly(ethylene glycol)	A melamine foam was dipped in a mixed suspension of CNFs and graphene nanoplatelets. Then, the coated foam was immersed in a hot poly(ethylene glycol) solution.	[102]
Supercapacitor electrode	Polypyrrole/CNFs/graphene	Graphene was dispersed in a CNF suspension, and pyrrole was gradually added to this mixed suspension. This suspension was polymerized, and dried.	[113]
Bone tissue engineering	Hydroxyapatite/CNCs	A heterogeneous mixture of CNCs and hydroxyapatite was freeze-dried.	[114]
Bone tissue engineering	Bioactive glass scaffold/CNCs	A bioactive glass scaffold was coated with CNCs.	[115]

the nanocomposite foams with nanocellulose [107]. An attempt has been made to prepare nanocomposite foams of PVA, CNFs, and montmorillonite clay (MTM) with the same flame retardancy as phenolic foams [104]. Results showed that the CNF/PVA nanocomposite foams with 35 and 42.5 wt% MTM self-extinguished in less than 2 s while the nanocomposite foam with an MTM weight content of 27.5 could not stop flame propagation, and the neat CNF foam was completely carbonized, as shown in Figure 4a.

The self-extinguishment of the nanocomposite foams was attributed to the brick-and-mortar structured cell walls in which clay was dispersedly aligned in the mixed CNF and PVA matrix. Flame-retardant and highly compressible nanocomposite foams have also been introduced by Li *et al.* [116] using CNFs and aramid nanofibers (ANFs) through the freeze-drying approach. When the nanocomposite foam samples were heated at 90 °C for 180 s, the lower thermal conductivity was observed for the CNF/ANF

nanocomposite foams (~39 °C) in comparison with that of the CNFs (43.7 °C) and ANFs (52.6 °C) foams, as shown in Figure 4b. The higher heat distribution of the nanocomposite foams was attributed to the hierarchical porous structure in an axial direction. Moreover, the complete recovery to an original state after 50 compressing-releasing cycles at a strain of 50% with no deformation was found for the CNF/ANF nanocomposite foams owing to the compact

network of CNFs and ANFs, which distributed stress over the entire framework without any stress concentration (Figure 4c). Silica has also been introduced to decrease the thermal conductivity of the nanocellulose reinforced nanocomposite foams for thermal insulating materials [117]. Silica particles were mixed with TEMPO-oxidized CNFs (TOCNFs) to yield silica-TOCNF nanocomposite foams using freeze-drying. The addition of silica particles could significantly

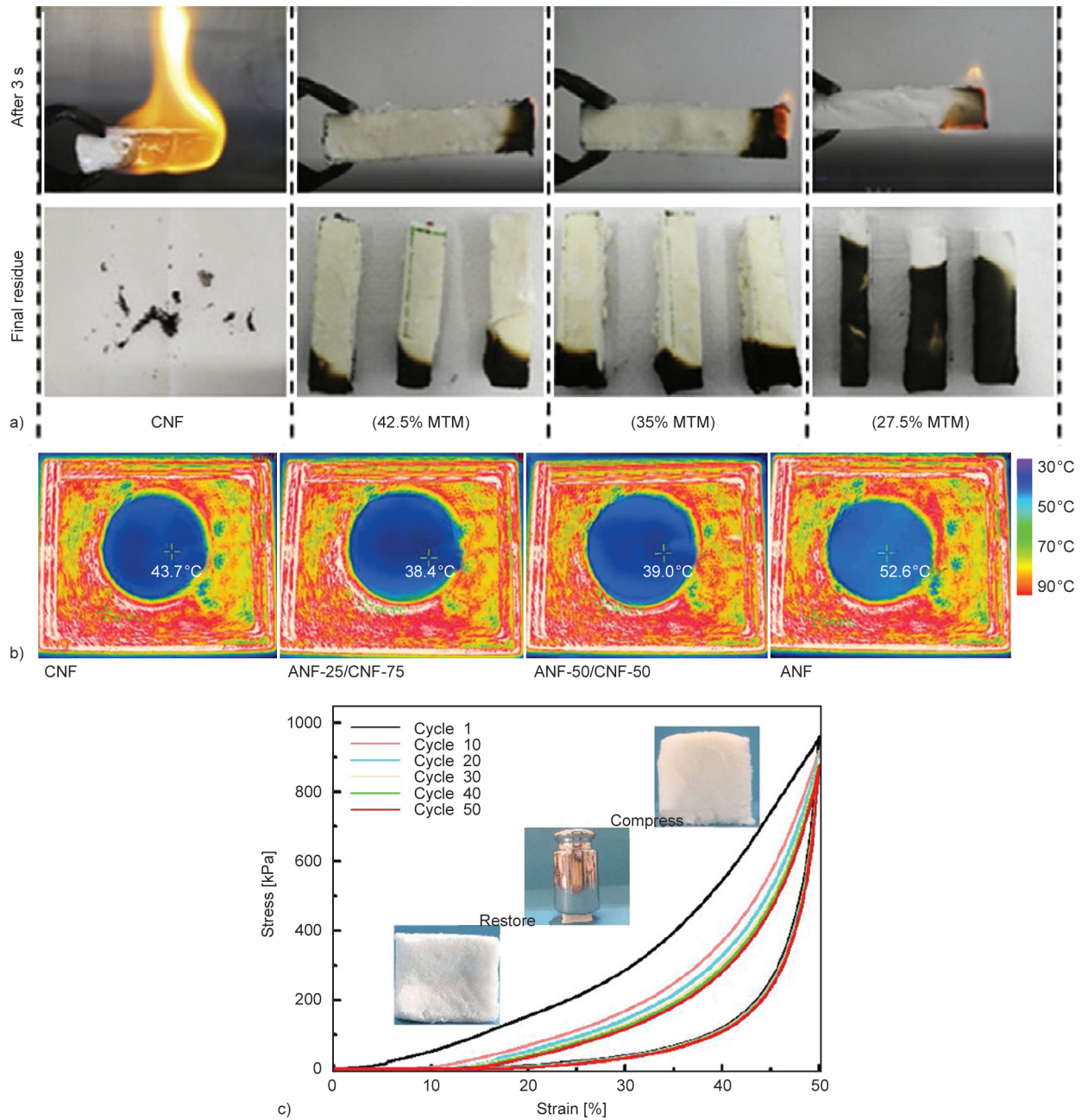


Figure 4. (a) Images of poly(vinyl alcohol) (PVA) with cellulose nanofibers (CNFs) and montmorillonite clay (MTM) after fire testing for 3 s and flame removal. Reprinted and modified from Medina *et al.* [104] with permission of Elsevier. (b) Infrared images of the nanocomposite foams prepared from CNFs and aramid nanofibers (ANFs) placed on a heating source with a temperature of 90 °C for 180 s [116] and (c) compressive stress-strain curves of the CNF/ANF nanocomposite foams after various compressing-releasing cycles at a strain of 50%. Reprinted and modified from Li *et al.* [116] with permission of Elsevier.

provide a 3.5-fold foam toughness higher than that of the neat TOCNF foams and yielded a lower thermal conductivity than that of air at a relative humidity of below 35%. This improvement resulted from an increase in the surface area and pore volume associated with a decrease in the pore size. Wicklein *et al.* [107] have fabricated super-thermal insulating and fire-retardant porous material with CNFs, graphene oxide and sepiolite nanorods with a thermal conductivity of $15 \text{ mW}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$, which was significantly lower than that of expanded polystyrene by $\sim 50\%$, and this nanocomposite foam presented good fire retardant properties.

4.2. Gas, liquid, and sound adsorption/absorption

Due to the porous structure, nanocomposite foams with nanocellulose have been possibly used to adsorb dyes, metal ions, and carbon dioxide (CO_2) with the presence of other nanoparticles such as zeolites. Nanocellulose particles were functionalized with zeolitic imidazolate framework-8 (ZIF-8), which possessed excellent chemical stability and flexible structure [118]. The formation of ZIF-8 nanocrystals on cellulose surfaces was attributed to electrostatic and hydrogen interaction, and the nanocomposite foams were fabricated by freeze-drying with the aids of CNFs. CNFs were introduced to entrap ZIF-8 nanocrystals within the foams. The porous structure of the foams was strengthened by hydrogen bonding and the physical entanglement of CNFs with cellulose fibers. It resulted in a dense porous structure and better mechanical properties. The compressive strength of the nanocomposite foams without CNFs was 0.68 MPa, and with the introduction of 10 wt% CNFs, the compressive strength increased to 1.08 MPa. With increasing CNF concentrations, the compressive strength of the nanocomposite foams continuously increased. Furthermore, the nanocomposite foam presented a great adsorption ability for fluorescent dyes, heavy metals, and organic solvents (Figure 5a). The high adsorption ability of the nanocomposite foams was because of the large specific surface area and abundant adsorption sites of the ZIF-8 nanocrystals. Interestingly, after pressing the nanocomposite foams, the deformed nanocomposite foams could be mostly returned to its original volume by immersion in water. Moreover, zeolite particles were mixed with nanocellulose and gelatin to form the nanocomposite foams for selective capture of CO_2 . The CO_2

adsorption and mechanical performances were linearly dependent on the zeolite loadings in the nanocomposite foams [109, 110].

The nanocomposite foams with nanocellulose could also remove metal ions from environments. Carboxymethylated cellulose nanofibers (CMCNFs) were embedded in PU foams, offering higher mechanical properties and metal removal efficiency in comparison with the neat PU foams [86]. The increase of CMCNF contents in the foams improved adsorption efficiency for removal of Cu^{2+} , Cd^{2+} , and Pb^{2+} . The metal ion accumulations on the porous surface was evidence of the adsorption of metal ions with CMCNFs dispersed in the matrix [109]. Superamphiphilic porous materials for oil and water absorbents could be easily developed by a facile dip-coating approach. The PU foams were dipped in a suspension of CNCs and graphene nanoplatelets (GNPs) [100]. The water contact angle (WCA) of the uncoated PU foams was 126.55° . With the introduction of GNPs (1 g) and CNCs (0.25–1 wt%), the wetting properties of the coated PU foams could be altered. The nanocomposite foam sample (0.25 wt% CNCs and 1 g of GNPs) showed the WCA value of 113° , representing strong hydrophobicity. When the CNC content in a GNP suspension increased to 0.50 and 0.75 wt%, the hydrophobic characteristic was immediately adjusted to hydrophilic feature with the WCA value of $\sim 0^\circ$. This unexpected change was attributed to the roughness of the coated PU surface. However, the foams dipped in the mixed suspension of GNP and 1 wt% CNCs showed the superhydrophobicity with the WCA value of 104° owing to the deposition of larger amounts of GNPs adsorbed with CNCs on the PU surfaces. Therefore, the nanocomposite foams dipped in a mixed suspension of CNCs (0.50 and 0.75 wt%) and 1 g of GNPs showed combined wettability of hydrophilicity and hydrophobicity. Both oil and water were simultaneously and sequentially absorbed by these materials, as presented in Figure 5b and 5c. Additionally, sound absorption could be controlled by the foam structures such as pore size [101]. It should be noted that porous materials with a uniform structure could provide less sound absorption performance in comparison with foams with hierarchical pore structure owing to the greater tortuous propagation pathways and more reaction area. This allows foams with the hierarchical pore structure to have better sound absorption performance with the broader sound absorption frequency range. For example,

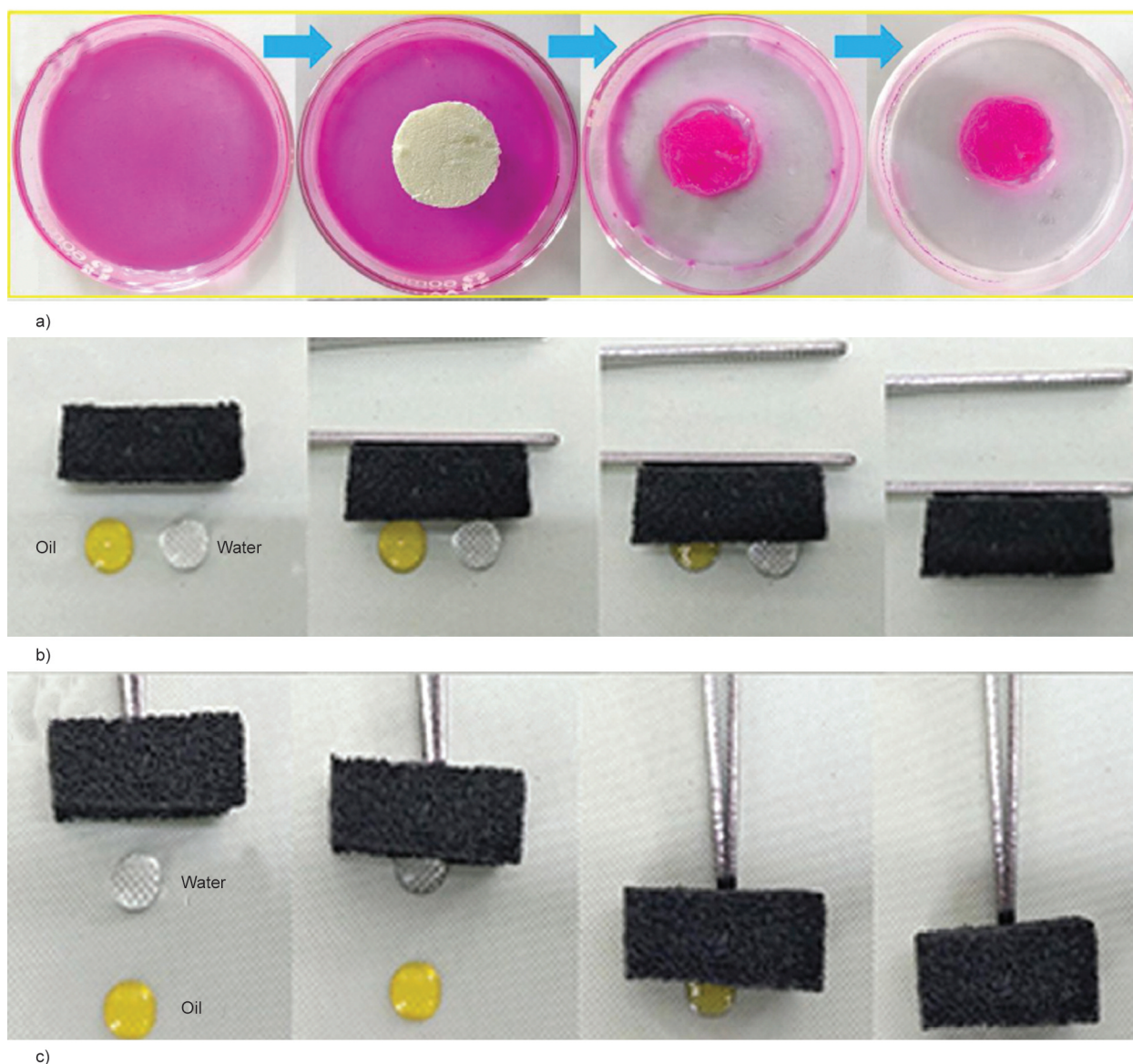


Figure 5. (a) Adsorption ability of the fluorescent dye (rhodamine B) on the ZIF-8 functionalized foam. Reprinted from Ma *et al.* [118] with the permission of Elsevier. (b) Simultaneous and (c) sequential absorption of water and oil on the surface of the polyurethane (PU) foams coated with CNCs (0.75 wt%) and graphene nanoplatelets (GNPs). Reprinted and adapted from Zhang *et al.* [100] with permission of John Wiley and Sons.

CNFs were distributed inside the melamine foams (MFs), and the formation of the CNF layers was observed around the MF skeletons. This approach fabricated a hierarchical-structured foam with macropores and mesopores. Macropores were observed in the MF structure, while mesopores were found from the CNF films generated inside the MF foam. These combined effects expanded the propagation path of sound waves and increased the multiple reflection and scattering, resulting in efficiently broadening the sound absorption performance range. In comparison with traditional materials like sheep wool, natural fibers and natural rubber and PU foams at the same thickness, the CNF/MF nanocomposite foams with the

hierarchical pore structure exhibited better sound-absorbing properties.

4.3. Microwave absorption

Microwave absorption would be another promising performance of porous materials which could transform electromagnetic radiation into thermal energy. It has shown promise of carbon nanotubes (CNTs) as electromagnetic interference shielding owing to high electric conductivity. The addition of CNTs in porous materials to offer ultrabroad-band microwave absorption performance has attracted more interest [105, 108]. He *et al.* [108] have recently developed foam-based microwave absorbers using the Pickering

emulsion method. CNFs and PLA were used to form a 3D structure, and the addition of Fe₃O₄ in this system would increase electromagnetic loss and obstruct polarization. An aqueous suspension of CNFs and CNTs was mixed with an oil phase of PLA with ferrous oxide (Fe₃O₄), and then an oil-in-water Pickering emulsion was freeze-dried to form a lightweight nanocomposite foam with magnetic properties (Figure 6a and 6b). This ultralight nanocomposite foam possessed not only excellent electromagnetic wave absorption but also presented great thermal insulation and photo-thermal conversion. With increasing CNT contents, the temperature measured from the nanocomposite foams (64.4–70.4 °C) placed on the heating state with a temperature of 220 °C for 30 min was significantly lower than that of the commercial PVA (82.7 °C) and PU (74.6 °C) foams, as presented in Figure 6c–6f. Also, the higher photo-thermal conversion could be achieved with the addition of CNTs and Fe₃O₄ because both CNTs and Fe₃O₄ absorbed light and transformed it to thermal energy. Moreover, the ultralow-density foam (9.2 mg·cm⁻³) with a well-interconnected porous structure and strong hydrogen bonding between CNFs/CNFs and CNTs/CNFs was prepared using a freeze-drying approach [105]. The CNT/CNF foam showed the reach of the effective absorption bandwidth of 29.7 GHz (2.3–18 and 26–40 GHz), which could cover 99% of the measured bandwidth, and its specific microwave absorption performance was more than 80 000 dB·cm⁻²·g⁻¹. This good ultrabroad-band microwave absorption performance of the CNT/CNF foam was attributed to the ultrahigh porosity as high as 99% and a large amount of the interpenetrating network of microwave transmitting CNFs and microwave-attenuating CNTs in the foam cell wall. This nanoscale architecture of CNFs and CNTs reduced the impedance gap, and lessened microwave energy reflection. When the microwave radiation propagated into the foam, the electromagnetic resonance loss occurred due to the porous microstructure, which controlled the microwave absorption in the low frequency range (Figure 6g). The enhanced microwave absorption in the high- and ultrahigh-frequency ranges was dominated by the conductive CNT networks. In addition, the rapid conversion of incident microwave energy to thermal energy was attributable to the long-range induced currents on the foam structure. A recent finding of Zeng *et al.* [119] has reported ultralight CNF foams assisted with metal carbides and nitrides (MXenes) exhibited

the high-performance electromagnetic interference shielding effectiveness of 189 400 dB·cm⁻²·g⁻¹, which was much greater than that of the microwave absorbing materials such as carbon, metal and MXene-based materials. This was due to the ultralight density (1.5 mg·cm⁻³) and the unique oriented micro honeycomb-like 3D cell wall architecture constructed by well-dispersed CNFs interacted with 2D MXene nanosheets. Also, the electromagnetic interference shielding performance was dependent on the material thickness and angle between the direction of the incident electromagnetic wave propagation and the direction of cell wall orientation.

4.4. Conductivity

Conductivity is an important feature for electronic applications. Although carbon and metal nanofillers have been widely studied to develop conductive nanocomposite foams, the dispersion and rigidity of these carbon and metal nanofillers limit the applications of the materials. Therefore, attempts have been made to use nanocellulose to prepare conductive nanocomposite foams with conductive nanofillers for electronic applications. Wu *et al.* [102] have used CNFs to assist the dispersion of GNPs in developing nanocomposite foams for light/electro-to-thermal energy storage. A melamine sponge was dipped in a suspension of CNFs and GNPs, and this step was repeated for 1, 3, and 5 cycles. Finally, the CNF/GNP-coated melamine sponge was immersed in a PEG solution to form a conductive nanocomposite foam. The homogenous dispersion of GNPs in water was observed with aids of CNFs, while the precipitation of GNPs occurred for the GNP suspension without CNFs. The nanocomposite foams with a higher number of dip-coating cycles provided higher thermal conductivity owing to the formation of GNPs along with the foam skeleton, which provided a continuous pathway of thermal conductivity. CNFs were also applied to disperse silver nanowires and to link between the conductive nanowires and PU [99].

4.5. Biocompatibility

Biodegradable bimodal nanocomposite foams have been considered as a high potential material for the application of osteogenic differentiation in bone therapies [88, 89]. However, the formation of scaffolds with high mechanical properties and high porosity is still challenging. To solve this problem, the improvement in mechanical properties of the scaffold

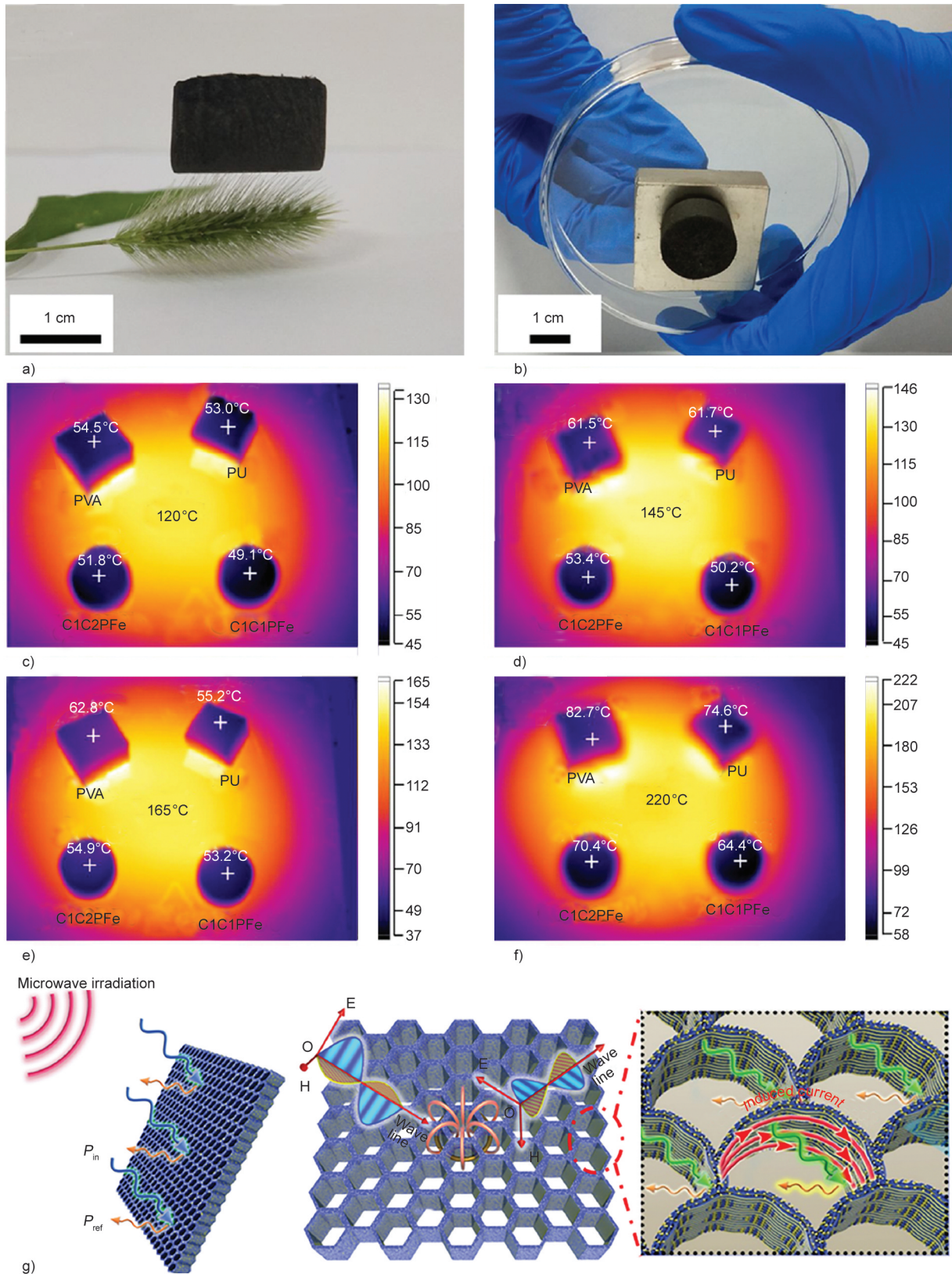


Figure 6. Photographs of the lightweight poly(lactic acid) (PLA) composite foams with cellulose nanofibers (CNFs), carbon nanotube (CNTs) and ferroferric oxide (Fe_3O_4): (a) on top of grass hairs and (b) interaction with a magnet and thermal infrared images of poly(vinyl alcohol) (PVA), polyurethane (PU), CNF-1/CNT-1/PLA/ Fe_3O_4 foam (C1C1PFe) and CNF-1/CNT-2/PLA/ Fe_3O_4 foam (C1C2PFe) placed on the state with the temperature of (c) 120 °C, (d) 145 °C, (e) 165 °C and (f) 220 °C after 30 min. Reprinted and modified from He *et al.* [108] with permission of Elsevier. (g) Mechanism of the microwave absorption of the CNT/CNF nanocomposite foam. Reprinted from Xu *et al.* [105] with permission of the American Chemical Society.

with the dispersion of nanocellulose in the matrix would be a solution [88, 89]. Also, an inflammatory response caused by nanocellulose was less observed owing to the high biocompatibility of nanocellulose [114]. The addition of CNCs in the PU matrix improved strength and Young's modulus of the scaffolds owing to strong hydrogen bonding formed between hydroxyl groups of CNCs and urethane groups of the polymer matrix. Results of MTT assay (cell metabolic activity measurement) and cytotoxicity showed that all CNC/PU nanocomposite foams with excellent biocompatibility could support cell proliferation and osteogenic differentiation in bone tissue engineering. Furthermore, the study of poly(ϵ -caprolactone) (PCL) bimodal foams reinforced with phosphor-calcified CNCs by Jafari *et al.* [89] showed similar results. With the increase of CNC contents, the higher improvement in mechanical properties and osteoconductivity of the scaffolds was observed. Figure 7a and 7b present the PCL nanocomposite foams with 1% of phospho-calcified cellulose nanowiskers (PCCNWs) before and after cell culture. Recently, nanocomposite foams fabricated by deposition of hydroxyapatite (HAP) on CNCs have been reported, and results showed that the coating of HAP on CNCs could develop the nanocomposite foams with high porosity and mechanical properties, which could be used for bone tissue engineering [114]. The use of CNCs to improve mechanical properties of the highly porous bioactive glass-based scaffolds has also been reported [115]. The bioactive glass-based scaffolds were coated with CNCs using the dip-coating method. The compressive strength of the CNC-coated scaffolds was found to be 0.06 ± 0.01 MPa, which was higher than that of uncoated scaffolds (0.02 ± 0.01 MPa), and the addition of CNCs improved the work of fracture of the scaffolds from 3.1 ± 0.3 to 13.5 ± 1.8 N. This notable improvement of the coated scaffolds by CNCs was attributed to the formation of the strong network and mechanical interlocking between CNCs. Greater mechanical properties of the CNC-coated scaffolds were noticed in comparison with those of the uncoated scaffolds when the materials were tested with an intimated *in vivo* condition. Biocompatibility of the uncoated and CNC-coated scaffolds was studied by the cell behavior of osteoblast-like cells. Figure 7c presents confocal laser scanning microscopy (CLSM) images of the uncoated and CNC-coated scaffolds after incubation. After 2 weeks of cultivation, more cells grew

and spread on the uncoated sample while a small amount of the round-shaped cells was mostly observed on the CNC-coated scaffold struts. After 3 weeks of cultivation, the number of cells on surfaces of the uncoated and coated scaffolds was comparable. This could suggest the CNC-coated scaffolds had similar cell compatibility to bioactive glass-based scaffolds. Therefore, these biocompatible composite scaffolds could possibly be used for bone tissue engineering.

5. Conclusions and challenges

On 1st June 2018, ASICS, a Japanese athletic equipment company, launched the first commercial shoe featuring CNFs in the name of GEL-KAYANO™ 25. CNFs are introduced to the low-density foam used for midsoles to create better durability and stability for more comfortable and longer running experiences. Although there are still limited products of the nanocomposite foams with nanocellulose in the market, and examples of the nanocomposite foams with nanocellulose discussed in this review have been only prepared on a lab-scale, there are novelty and promising results which could shed light on the possible processing ways to develop nanocomposite foams with nanocellulose in a mass production. Researchers have found that the addition of a low concentration of nanocellulose in polyols during a mixing step could prepare the PU nanocomposite foams with higher mechanical properties. The preparation step is facile, and could be possibly adapted for industrialization. This would enlarge applications, and increase price of the PU nanocomposite foams. Moreover, this foam products could be used as a core structure for lightweight laminate materials with high specific mechanical properties which would be suitable for construction and transportation applications. In addition, surface modification of nanocellulose is very useful for fabricating composite foams with hydrophobic polymers using melt processing. It should be noted that the future trend of the nanocomposite foams with nanocellulose would focus on specific applications as many works have shown the promising features of the nanocomposite foams with nanocellulose, and this is more distinct when nanomaterials such as silver nanowires, graphene nanoplatelets and carbon nanotubes are combined with nanocellulose. Although nanocellulose could not provide any conductive performances, it could be used to assist the homogeneous dispersion of these

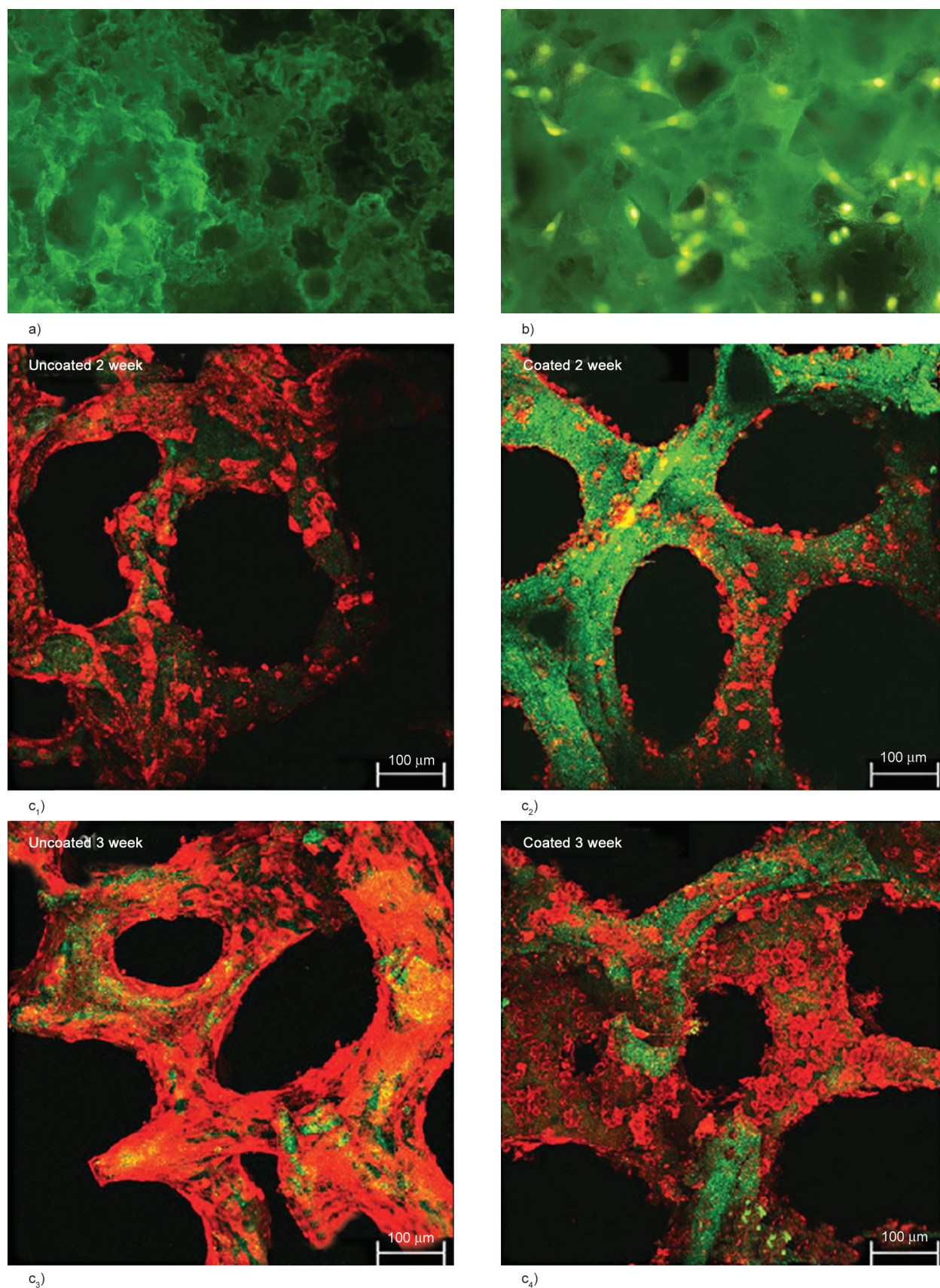


Figure 7. Foams with 1% of phospho-calcified cellulose nanowhiskers (PCCNWs) (a) before and (b) after cell culture. Reprinted with adapted from Jafari *et al.* [89] with permission of American Chemical Society. (c₁–c₄) Confocal laser scanning microscopy (CLSM) images of the uncoated and CNC-coated scaffolds after incubation for 2 and 3 weeks. Reprinted from Li *et al.* [115] with permission of Royal Society of Chemistry.

nanoparticles or as a framework, and the low thermal expansion of nanocellulose is a benefit for expanding usage of the nanocomposite foams in a wide range of temperatures.

This review addresses the recent development of cellulose nanocomposite foams and presents a remarkable performance of the nanocellulose reinforced foams with other nanoparticles, which can be possibly utilized in a wide range of applications such as self-extinguishment, oil/water separators, electronic devices, and tissue engineering. Promising approaches to conquer or weaken the limitation between hydrophilic nanocellulose and hydrophobic polymer matrices are highlighted which could be adapted to fabricate other porous materials. Lastly, this review would attract more researchers to work in the field of the nanocomposite foams with plant-based nanocellulose, and the interesting performances associated with enhanced mechanical properties of the polymeric nanocomposite foams with nanocellulose and other nanoparticles could shed more light on commercialization in the near future.

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