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Review Article

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Naturally or artificially constructed nanocellulose architectures for epoxy composites: A review

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Abstract: Applications of carbon fiber reinforced epoxy-based composites have been highly restricted due to their high cost in the manufacturing process. Cellulose, a cheap and abundant material from nature, shows excellent mechanical property and structural stability. It shows huge potentials in substituting carbon fiber/epoxy with cellulose/epoxy composites to fulfill the great demands for composites with good performance and a reasonable price. This paper first reviews works about the preparation and regulation of cellulose materials based on the very basic concepts of top-down and bottom-up. Then research about the interfacial regulation between cellulose and epoxy has been discussed in two broad classes of covalent and non-covalent modification. Finally, the enhancement effect of cellulose reinforcement has been discussed in two broad classes of dispersive reinforcement and continuous phase reinforcement. The latter can be further divided into three classes according to the dimension feature (1D, 2D, and 3D). The results show that the nanolization of cellulose is necessary for guaranteeing the strength of composites, while the formation of macroscopic and continuous structures can ensure Young's modulus of composites.

Keywords: cellulose, epoxy resin, composites, interfacial structure regulation, mechanical properties

1 Introduction

Composites play an important role in modern society in meeting the increasing demand for structural materials nowadays. Served as the typical composite materials with excellent performance, carbon fiber reinforced polymer (CFRP) has been widely applied in various fields. However, the cost of the critical carbon fibers could be a big issue if applications of CFRP want to be achieved. And the development of the substitution for carbon fibers can be of common interest in the field of composites.

Cellulose is believed to be the feasible substitution due to its outstanding features of low cost, high strength, high modulus, etc. For example, the tensile strength of a natural sisal fiber (micrometer-scale) is about 511–635 MPa [1]; the theoretical tensile strength and Young's modulus of cellulose crystal (cellulose I) is up to 7 GPa [2] and 80–200 GPa, respectively [3,4]. Cellulose also exhibits a better thermal-mechanical property (a very low thermal expansion coefficient ($<5 \times 10^{-6}\,\mathrm{K}^{-1}$) and a breaking strength of up to $67\,\mathrm{kJ\,m}^{-2}$) than most polymer, metal, and ceramic materials [5]. Cellulose shows good structural stability, as well as a high activity of chemical modification on its surface (abundant –OH groups) [6]. Similar to carbon fibers, cellulose materials can meet the rigorous requests of serving as the reinforcing component of the composite.

This paper aims to focus on the topic of epoxy composites reinforced with cellulosic architectures either naturally or artificially constructed. First, works about preparing cellulosic materials based on the two very basic concepts of top-down and bottom-up have been reviewed; the discussions about the interfacial modification between cellulose and epoxy are subsequently introduced; finally, the reinforcement effect of cellulosic architectures with the difference in spatial dimension to the composites has been

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discussed and summarized. We believe that cellulose/epoxy composites can be of viable substitution to CFRP in fulfilling the large demand in various applications of the low to mid-range, which exhibit lower requirements for composites. For example, natural fiber composites can be applied in the fields of building materials (e.g., highly transparent composites in substitution of glass), automotive (advantages in the specific strength and cost) [7], and so on.

2 Preparation of cellulosic architectures

Cellulose materials show a high degree of flexibility and designability in regulating their structure and morphology. Based on the two very basic concepts of top-down and bottom-up, a series of cellulosic architectures, with scales of nano to macro, with spatial dimensions of zero to three, can be prepared. For top-down methods, usually, cellulosic materials of the micron-size to the nanoscale can be received through dissociation of natural cellulose materials; for bottom-up methods, they prefer to produce macroscopic architectures (e.g., cellulose fibers/fabrics, cellulose films/papers, or cellulose aerogels) instead, through the generalized regeneration of cellulose.

2.1 Preparation of cellulose materials based on top-down concept

Natural cellulose has a hierarchical structure [8], as shown in Figure 1. Micron-sized cellulosic fibers are usually composed of hundreds of nanoscale Cellulose Microfibrils (CMFs) [9]. CMFs can be constructed by dozens of cellulose molecular chains [10–12]. Therefore, the concept of top-down can be of the subtractive manufacturing process to the raw cellulose. By dissociating natural cellulose to different degrees, a series of products of micro to the nanoscale can be received, as shown in Figure 2 [13].

2.1.1 Preparation of nanocellulose

The starting materials of preparing nanocellulose are usually the micron-sized natural cellulose fibers, named Microfibrillated Cellulose (MFC, as shown in Figure 3a). These cellulose fibers can be received from the pulp and paper industry [14].

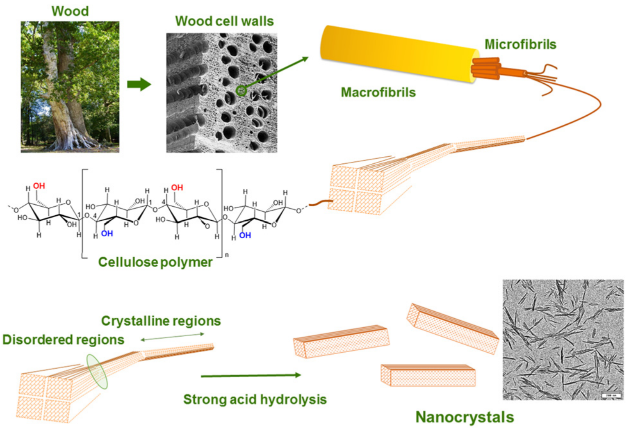

Figure 1: Schematic diagram of the multiscale structure of natural cellulose [8].

Spindle-shaped cellulose nanocrystals [Cellulose Nanocrystals (CNCs)] or Cellulose Whiskers (CWs) can be prepared by acid hydrolysis [15,16], as shown in Figure 3c. Since the hydrolysis only occurs in the accessible region, including the low crystalline and the amorphous region [17], the resulting crystalline region is almost free of structural defects [9]. Acid hydrolysis of cellulose is a heterogeneous reaction process. On the one hand, protons break β-glycosidic bonds of cellulose to make CNCs shorter [18,19]; on the other hand, CNCs get narrower after peeling off the derivatized chains on the crystal (e.g., in the sulfuric acid environment [20]). As the hydrolysis time increases, the product gradually transforms from spindle shape into spheres with decreasing the aspect ratio [21], as shown in Figure 3d. The size of CNCs is also related to the source of cellulose [9]. For example, CNCs prepared from bacterial cellulose show a length and width of 100–1,000 and 5–10 nm, respectively [22],

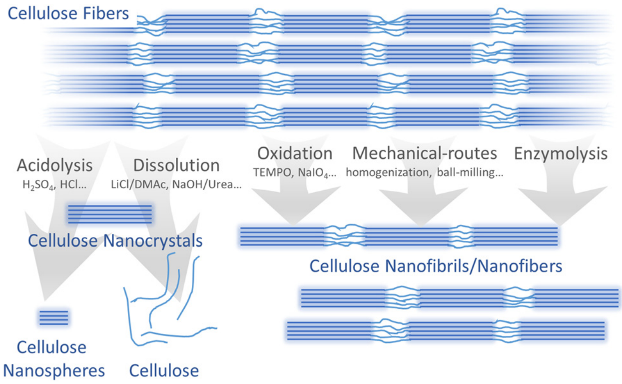

Figure 2: Schematic diagram of preparing nano-sized cellulose products by top-down methods.

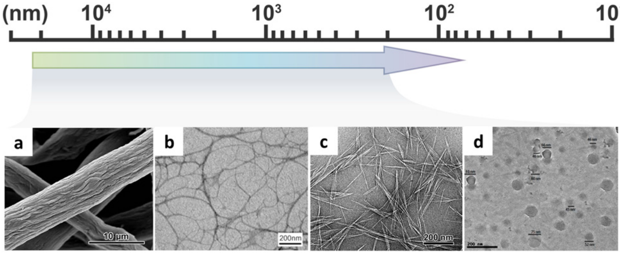

Figure 3: Morphology of cellulose products in different kinds of scale: (a) microfibrillated cellulose (MFC) [24]; (b) cellulose microfibrils (CMFs) [25]; (c) cellulose nanocrystals (CNCs) [24]; (d) cellulose nanospheres [21].

while CNCs prepared from hardwood pulp exhibits a length and width of 140–150 and 4–5 nm, respectively [23].

Oksman *et al.* [26] and Hassan *et al.* [27] reported that rod-shaped CNCs can be prepared through the selective dissolution of cellulose in LiCl/DMAc solvent. The size of CNCs is similar to that prepared by the acidolysis method (about 20 nm in diameter and hundreds of nanometers in length). FT-IR characterization indicates that this process is a non-derivatization process, so the products are easy to aggregate. Zhang [28], Qiu *et al.* [29], and Wei *et al.* [30] reported that rod-shaped CNCs with a diameter and length of about 10–30 nm and hundreds of nanometers, respectively, can be prepared by aqueous solvents of NaOH/Urea [28,29] or TBAH [30] (tetra butylammonium hydroxide). It is also possible to prepare the rod-shaped CNCs with the ionic liquids family, such as TBAA/DMAc [31], 1-butyl-3-methylimidazole chloride [32], and 1-ethyl-3-methylimidazole acetate [33]. The obtained CNCs show a diameter of 1–50 nm and a length of 40–600 nm.

Another kind of nanoscale cellulose product, named cellulose nanofibrils (CNFs), can be prepared by several methods, such as high-pressure homogenization [34], ultrasonication [35], ball milling [36], steam explosion [37], aqueous counter collision [38], twin-screw extrusion [39], etc. Usually, CNFs exhibit a width of 20–50 nm and a length of 500–2,000 nm, as shown in Figure 3b. The principle of this method is based on the mechanical shearing force or impact force provided by the high-pressure and high-shearing environment that is acting on the cellulose fiber, thereby causing it to dissociate and fibrillate. The difference between CNFs and CNCs can be attributed to the retainment of the amorphous regions that connect the crystals in the direction parallel to cellulose molecular chains after treatments, as shown in Figure 2. The retained amorphous region in the crystal intervals makes CNFs highly flexible (similar to a nunchaku). However, these methods of mechanical treatment are usually applied accompanied by other methods, such as oxidation, enzymatic, hydrolysis, etc., in order to increase efficiency and reduce energy consumption.

The oxidation methods can make exposing hydroxyls groups of accessible cellulose molecules derivatized. The introduced groups will disturb the formation of intermolecular hydrogen bonds among cellulose molecules in the accessible amorphous regions; meanwhile, this process usually does not cause the depolymerization of cellulose molecules. Therefore, CNFs with a longer length and larger aspect ratio can be received. Piperidine reagents, water-soluble nitroxyl radicals [40], are reported to catalyze the oxidation of the alcoholic hydroxyl group at the C6 position of the cellulose crystal surface to the carboxyl group efficiently and selectively in an aqueous environment [41–43]. The treated CNFs have a width of 3–4 nm, a length of micrometers (>1 μm), and a large aspect ratio. Their aqueous solution exhibits good dispersibility, transparency, water retention, and high viscosity [41,43–46]. Since the surface of CNFs is negatively charged ($-COO^-$), simple stirring in water can make CNFs redispersed if they are agglomerated [44,45], but the thermal stability is reduced to a certain extent [47]. Besides, CNFs can be prepared through sodium periodate oxidation at the C2 and C3 of cellulose [48]. But, the β-glycosidic bond of cellulose molecular chain breaks significantly at the same time [49], so the morphology of the product can be adjusted from spindle to round particles by adjusting the reaction time and temperature [50].

Some specific enzymes, such as endo 1,4-*b*-glucanase, exo-glucanase or cellobiohydrolase, or *b*-glucosidase, etc., can be used to degrade the cellulose in regions of amorphous and low crystallization [51] so that CNFs can be prepared. The enzyme-treated CNFs show similar morphology to that prepared by the TEMPO oxidation method, but the surface charge density is relatively low [52]. The features of simple process, mild reaction conditions, and environmentally friendly make enzymolysis a promising method for preparing CNFs. But there are issues of long operation periods and high costs that need to be solved.

2.1.2 Preparation of macroscopic cellulose products

Cellulose is known as the "skeleton of plants" that make plants strong and self-supporting. The arrangement of cellulose chains in biomass has been optimized to well-organized after years of evolution. Therefore, cellulose does not need to be excessively processed to the nanoscale and turns into architectures for utilization. Based on the concept of top-down with minimal structural damage, we only need to simply remove the noncellulosic component in the biomass (e.g., wood, bamboo, etc.); meanwhile, the macroscopic shape of biomass can be retained.

The lignin component in biomass can be removed through cooking/bleaching in NaOH/Na_2SO_3 [53], $NaClO_2$/glacial acetic acid [54], or H_2O_2/(acetic acid) steam [55]. Generally, the degree of delignification can be controlled by the processing time and temperature [56]. Hu *et al.* found a well-oriented cellulosic structure after the lignin and hemicellulose components of wood have been removed [57,58]. The delignified wood has a loose structure with multiscale pores. Through hot-pressing treatment, the densified wood exhibits significant improvement in mechanical properties [59,60], as shown in Figure 4. By introducing resin with matching refractive index into pores of the delignified wood, a transparent wood with advantages of lightweight, transparency, and environmental friendliness can be prepared [57,61,62] and widely applied as building materials [53] (served as windows [63], walls [64], etc.). It can also be used for optical devices [65], optoelectronic devices [66], oil/water separation [67], functional hydrogels [68], etc.

2.2 Preparation of cellulose materials based on bottom-up concept

The concept of bottom-up can be of the additive manufacturing process, by which cellulose architectures (e.g., cellulose fibers/fabrics, cellulose films/papers, or cellulose aerogels) can be regenerated by stacking of cellulose chains. It is worth noting that the crystal structure [69], as well as the intermolecular interactions (hydrogen bonding and van der Waals interactions) [70], of regenerated cellulose materials has changed during the regeneration process.

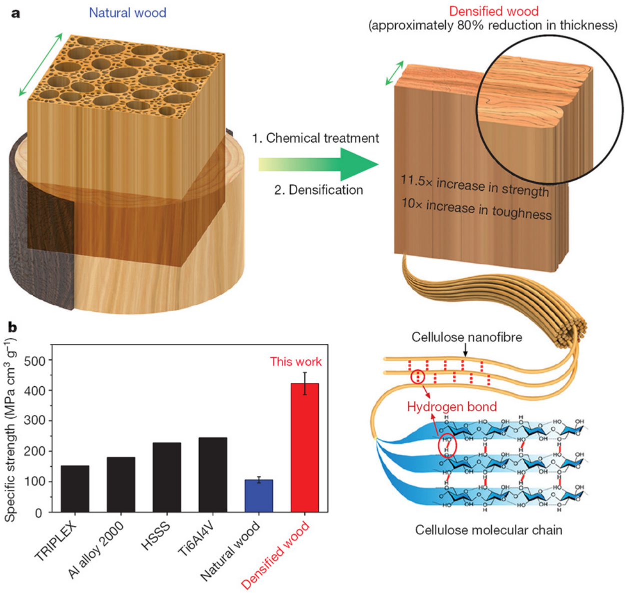

Figure 4: Schematic diagram of transforming natural wood into densified wood and its specific strength [60].

We can prepare regenerated cellulose fibers (1D materials) by dissolving cellulose in solvents such as NMMO [71], ionic liquid [72], TBAH/urea [73], NaOH/urea [74], NaOH/ZnO [75], etc., followed by the regeneration process, as shown in Figure 5a and b. The diameter of the fibers is about dozens of micron. The best mechanical performance of commercially available cellulose fibers (Lyocell) reaches approx. 65 cN/tex (~1 GPa) [76], but there is still a gap with carbon fibers.

2D cellulosic materials, such as cellulose films or papers, can be prepared through the general regeneration process [77,78], as shown in Figure 5c and d. The mechanical properties of cellulose films can be improved by physical and/or chemical cross-linking strategies [79,80]. For cellulose papers, the difference from films is that papers are formed by stacking of micron-sized cellulose fibers [81] or the nanoscale CNFs [82], rather than cellulose molecules. Through the filtration method, cellulose (nano)paper can be prepared [81–83]. The mechanical properties of cellulose papers can be improved by reducing the size of the stacking unit. For example, the strength and toughness can be significantly improved from 6.7 to 275.2 MPa and 0.13 to 16.9 MJ/m^3, respectively, if the fiber diameter is reduced from micron (27 μm) to nanoscale (11 nm) [82]. In a particular case, bacterial cellulose (synthesized by Acetobacter xylinum and so on [84,85]) is usually collected as a film, but composed of CNFs-like and highly crystalline cellulose nanofibers [86]. A special case is the electrospinning technology that could produce nanoscale cellulose filaments, but is usually collected as a film-like product [87].

3D cellulosic materials, such as cellulose aerogels, can be prepared through the general regeneration process, as shown in Figure 5e and f. Usually, the construction of hydrogels is the prerequisite for preparing aerogels. In addition to conventional molding methods, 3D printing provides technological approaches to construct cellulose hydrogels with complicated model structure [88,89]. After that, we need to remove the solvent phase through technologies of freeze-drying [90], supercritical drying [91], or even room temperature drying [92], while maintaining the cellulose skeleton structure as much as possible. A step of solvent exchange is necessary for facilitating the drying [93]. Usually, a porous structure with a three-dimensional network can be obtained. CNFs are good

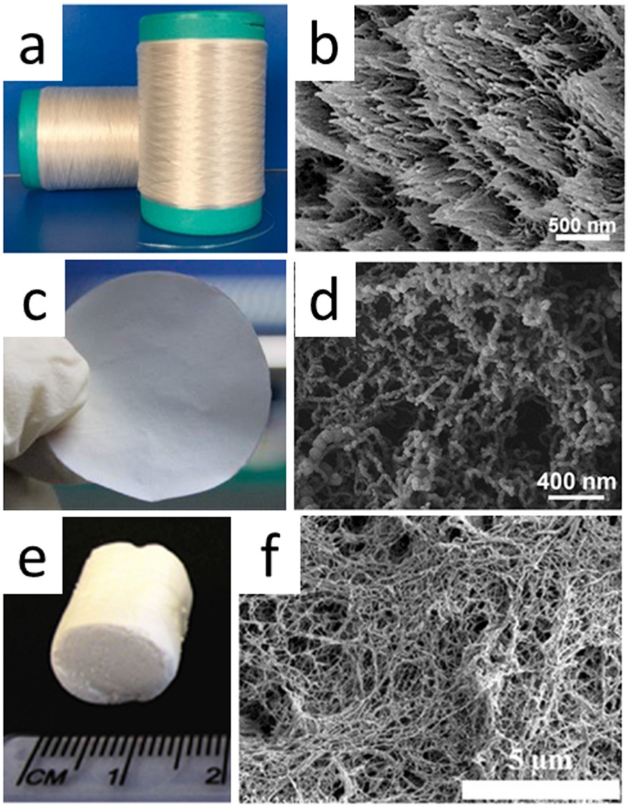

Figure 5: Photos and morphology of cellulose products with different dimensionality: cellulose materials of (a and b) 1D fibers [98]; (c and d) 2D films [99]; (e and f) 3D aerogels [100].

starting materials for building macroscopic aerogel materials [94], even with a low concentration of down to 0.6 wt% [95]. For freeze-drying, the size and shape of pores are highly related to the freezing process. Chen *et al.* [96] and Chu *et al.* [97] have introduced the technology of directional freeze-drying for preparing cellulose aerogels with ordered and anisotropic structures.

3 Interfacial issue between cellulose and epoxy

Cellulose is hydrophilic due to its abundant hydroxyl groups. Epoxy is a series of thermosetting polymer with various structures. Epoxy groups are the feature of epoxy resin that can cross-link through heating with curing agents. Polar groups (e.g., hydroxyl groups, ether bonds, and ester bonds) or nonpolar groups (e.g., aromatic rings and alkanes) can be introduced to epoxy according to demand. The application of waterborne epoxy ensures a good dispersibility and interface compatibility of cellulose materials in the epoxy matrix. However, the high water content of epoxy will make resin shrink and limit its application [101]. For hydrophobic epoxy resins, the interfacial issue between cellulose and epoxy will be the challenge [102]. However, the abundant hydroxyl groups on the surface of cellulose provide the possibility of solving this issue through surface modification strategy, by which the interfacial interactions and stress-transfer will be improved. Based on the review of researches in this field, the surface modification strategy can be generally divided into two categories: non-covalent modification and covalent modification.

3.1 Non-covalent modification of cellulose

Surfactants (e.g., amphiphilic block copolymer [103], Res.-CBD protein [104]), polymers [e.g., polyaniline [105], or nanoparticles (e.g., boehmite [106])] can be introduced to adjust the amphiphilicity of cellulose surface [107], thereby enhancing the interaction between cellulose and epoxy matrix, as well as improving the dispersibility. Adsorption of triethanolamine (TEA) on CNFs would lead to the in situ polymerization of epichlorohydrin and bisphenol A around CNFs [108]. The dispersibility of CNFs in the epoxy matrix can be guaranteed by the formation of hyperbranched CNFs. Interestingly, the hyperbranched structure also promotes the cross-linking of epoxy.

Compared with adding exogenous additives, controlling the amount of lignin in cellulose can also adjust the hydrophobicity of cellulosic materials, thereby improving the interface compatibility between cellulose and epoxy [109,110]. By using CNFs nanopaper containing a mass of lignin to strengthen epoxy resin, the modulus of the composite was increased from 2.9 to 5.65 GPa, and the tensile strength was increased from 65 to 134 MPa [111].

3.2 Covalent modification of cellulose

Covalent modification refers to the formation of covalent bonding through chemical reactions during the modification process, by which functional groups or polymers can be grafted to the surface of cellulose. A typical example can be the case of CNTs/epoxy composites in that modification of CNTs is crucial to the dispersity and interfacial interactions [112]. Common modification reactions include esterification, etherification, silanization, etc. The challenge of covalent modification is to realize the modification while keeping the crystal structure of cellulose.

3.2.1 Esterification of cellulose

Esterification refers to the formation of ester bonds through reactions of cellulose hydroxyl groups with acids. Pyridine or imidazole is usually served as catalyst. The degree of esterification is closely related to the reaction conditions, such as temperature, cellulose/acid ratio, and hydrolysis time. Abraham *et al.* [113] reported the acetylation of CNFs by using acetic anhydride (Ac) as a derivatization reagent and iodine as the catalyst. The hydrophobic Ac-CNCs can be uniformly dispersed in epoxy resin through acetone and ultrasound. With the addition of 0.5 wt% Ac-CNCs, the strength and modulus of the epoxy resin can be increased by 73% and 98%, respectively. Wang *et al.* [114] reported that modification of CNCs with dodecane succinic anhydride could enhance the interfacial interactions between cellulose and epoxy. A two-step method has been used to modify CNFs [115]. First, it was reacted with tannic acid (TA) and then reacted with hexadecyl amine (HDA). The modified CNFs–TA–HDA exhibits good dispersibility and interfacial interactions. The obtained CNFs–TA–HDA/epoxy composite shows a higher Young's modulus, tensile strength, and work of fracture. Trinh and Mekonnen [116] used lauroyl chloride to modify CNCs and found that the introduced aliphatic chain can increase the hydrophobicity and dispersibility of CNCs. Composite containing 0.2 wt% modified CNCs exhibits enhancements of tensile strength (77%) and modulus (44%). Peng *et al.* [117] studied the influence of alkane chain length on the dispersibility of modified CNCs in epoxy. CNCs modified by acetyl and hexanoyl show good dispersibility, thereby improving the mechanical properties of nanocomposites. However, CNCs modified by dodecanoyl show a negative impact.

3.2.2 Silanization of cellulose

Silanization is considered to be an effective method to improve the dispersibility of nanofillers in a hydrophobic matrix [118]. Two typical classes of reagents, named chlorosilane [119] and alkoxysilane [120], are usually used to silanize cellulose. The silanized bacterial cellulose can be well-dispersed in epoxy resin only by mechanical stirring and ultrasonic treatment [121], and the tensile strength of composites can be promoted by 37% with the only addition of 0.3 wt% silanized bacterial cellulose. When functional groups that can react with epoxy resin have been introduced by the silanization process, the covalent connection between cellulose and epoxy resin can be constructed through the coupling effect of the silanization agent to significantly improve the mechanical properties of composites. For example, by using KH540 [122] or KH550 [123] to modify CNCs, the amino groups can continue to react with the bio-based epoxy resin containing groups of diphenolic acid. Besides, cellulose modified with silane compounds containing epoxy groups (such as KH560 [124]) also shows the ability to further react with epoxy resin.

3.2.3 Polymer graft modification on cellulose surface

The above-mentioned surface modification methods are about introducing groups (such as alkane chains, silanes, etc.) onto the surface of cellulose. Long-chain polymers or two-dimensional nanomaterials (e.g., graphene oxide [125]) can also be grafted onto the surface of cellulose to further improve the interface compatibility with the matrix. Polymer graft modification on the surface of cellulose can be achieved through three types of polymerization mechanisms: radical polymerization, ionic polymerization, and ring-opening polymerization. From the perspective of grafting strategies, it can be divided into three main categories [126]: (1) graft a prepolymerized polymer chain to cellulose – this method requires reactive functional groups on both prepolymerized polymer and cellulose; (2) initial *in situ* chain propagation reactions on the surface of cellulose – the grafting density is high, but the structure and DP of grafts show a polydispersity distribution; (3) copolymerization strategy usually needs to introduce olefin (such as vinyl) into cellulose forming macromonomers, and then copolymerizes with other monomers. Polyethyleneimine (PEI) was grafted onto the surface of CNFs by using the strategy (1) [127].

4 Cellulose/epoxy composites reinforcement strategies

The reinforcement phase of composites needs to be of high strength and high modulus for improving the mechanical properties of composites. CFRP is one of the successful cases in the family of composite and so we can find CFRP products all around us. The form and forming process of CFRP is of guiding significance to the cellulose/epoxy composites. Carbon fibers are 1D materials with ultra-high modulus and strength. The mechanical properties of carbon fibers and CFRP are highly related to the type of carbon fiber used. Besides, the form of carbon fibers (e.g., short/long fibers, fabric), as well as the dispersion in the composites, dominates the properties, as shown in Figure 6. Carbon fibers can be cut into short fibers and evenly dispersed as a reinforcement phase in the matrix. However, the enhancement is limited due to the discontinuousness of the reinforcement phase in the matrix. Making the long carbon fibers parallelly orientated along a direction in the matrix can receive anisotropic composite material. The performance in the direction of perpendicular to the fibers is poor which makes the composites not practical. In contrast, carbon fiber fabrics are widely used as the reinforcement phase in CFRP due to their macroscopic and continuous structure in two dimensions. Moreover, carbon fibers can be further woven with 3D braiding technology to form a 3D structure for composites.

Based on the discussion above, the reinforcement strategies of cellulose/epoxy composites can be preliminarily divided into two categories: dispersion strengthening and continuous phase enhancement, as shown in Figure 7. The former can be further divided into the reinforcement of particles and short fibers according to the difference in size and aspect ratio of the reinforcement phase. The latter can be further divided into reinforcements of 1D long fibers, 2D layered structure, and 3D network structure according to the difference in the dimension of the reinforcement phase.

4.1 Dispersion strengthening strategy

Short fibers (e.g., MFCs) can be used for strengthening composites. The good thing is that there is no serious dispersion issue even without surface modification of cellulose [128], though the modification still helps to improve mechanical performance. As shown in Table 1, the content of MFCs in the composite is usually above 10%. But the effect of reinforcement is limited to an improvement of 30% in tensile strength and 60% in modulus with a fiber content of less than 15% [129].

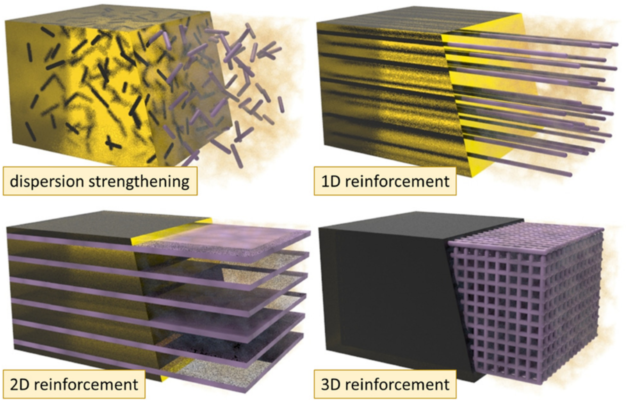

Figure 6: Spatial distribution of different forms of reinforcement in the composites.

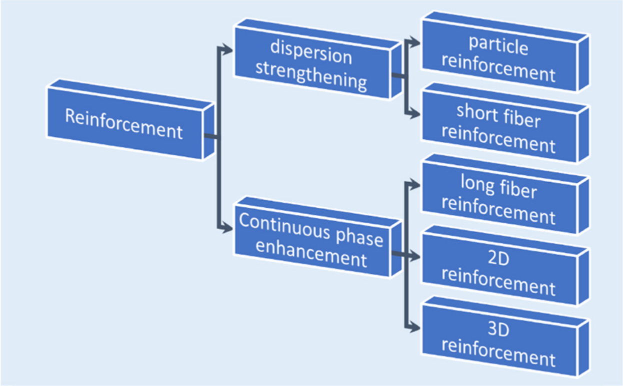

Figure 7: Strengthening methods of cellulose reinforced epoxy composites.

In contrast, nanoscale cellulose materials, such as CNFs, can provide a more effective reinforcement at a low content, as shown in Table 1. Saba *et al.* [130] reported that the addition of 0.5–1.0% CNFs could enhance the strength, modulus, elongation at the break, and impact strength of epoxy by 30, 100, 50, and 120%, respectively. Yue *et al.* [131] found that the storage modulus of epoxy resin can be significantly enhanced by 100 times (from 0.024 to 2.47 GPa) above T_g by CNFs-like bacterial cellulose. But, natural nanocellulose (e.g., CNCs, CNFs) prepared by the top-down concept shows a strong trend of agglomeration in the matrix due to their small particle size and high specific surface area. For example, Omrani *et al.* [132] reported that direct dispersion of CNFs in epoxy resin could cause agglomeration of CNFs when the content reached 0.5 phr. It is generally believed that the content of cellulose is the key factor to affect the dispersion, and the high content of nanocellulose is difficult to disperse in epoxy with high viscosity [133]. Emami *et al.* [103] found that the optimal content of CNCs reinforcing epoxy resin is about 2%. Therefore, the method of directly adding cellulose into epoxy is simple, but the dispersion is usually poor that affect the properties of the composites. The content of nanocellulose is usually below 5–10% to avoid negative effects [134].

The addition of an organic solvent to the epoxy matrix can solve the problems of dispersing nanoscale cellulose in the high viscosity epoxy resin by reducing the viscosity. Organic solvents of acetone [141], ethanol [135], dimethylacetamide [142], and dimethylformamide [143] are conventional choices. The combination of DMF solvent exchange and freeze-drying technology can

Table 1: Plots of mechanical properties (Young's modulus and tensile strength) of cellulose/epoxy composites versus content of cellulose reinforcement particles (categorized as micron-size MFCs [128,129], nanoscale CNFs [121,134,135], and nanoscale CNCs/CNWs [113,114,136–140])

<table>
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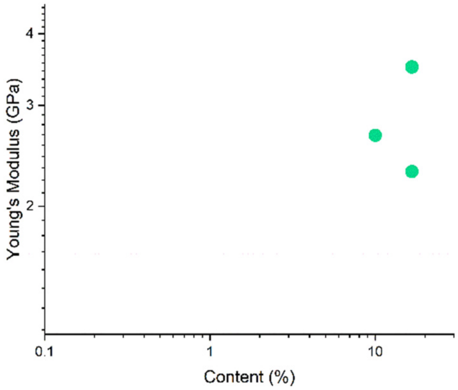
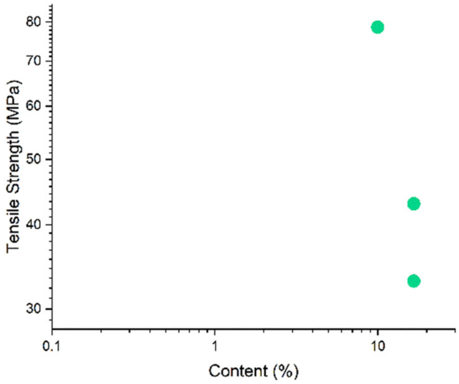
High aspect ratio</td><td>
</td><td>
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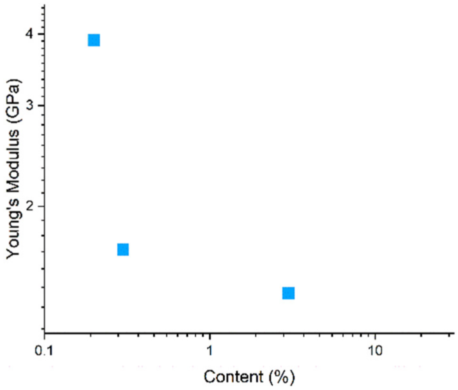
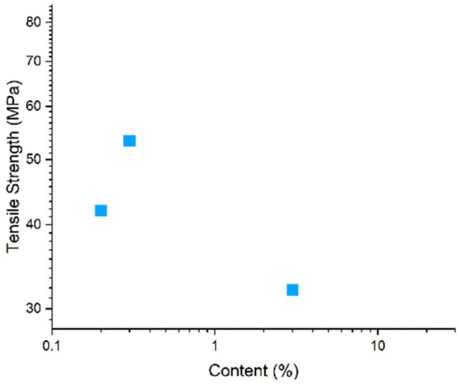
Nanoscale
High aspect ratio</td><td>
</td><td>
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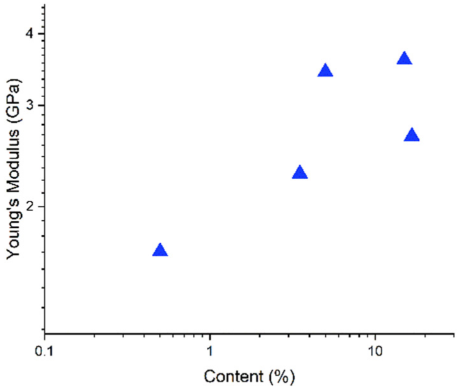
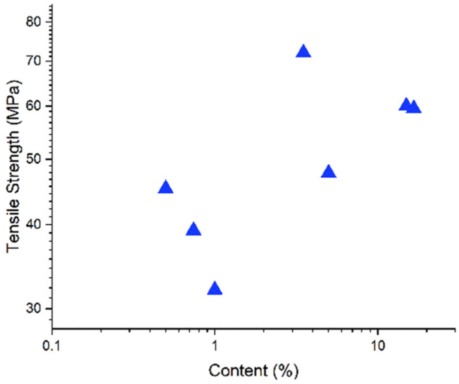
Low aspect ratio</td><td>
</td><td>
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</table>

guarantee a good dispersion of up to 20 vol% CNCs in epoxy [143].

Figure 8 shows the plot of tensile strength vs Young's modulus of dispersion strengthening composites, reinforced with micron MFCs or nanocellulose (e.g., CNFs, CNCs, CNWs). No obvious breakthrough in both tensile strength and Young's modulus can be found, neither reinforced with micron MFCs nor with nanocellulose. This is actually ascribed to the fact that the spatial distribution of these reinforcement particles is discrete. We believe that the mechanical properties of cellulose/epoxy composites can be further improved if these cellulose particles can be made into a continuous structure. Therefore, research on continuous phase enhancement strategy can be of great importance to improve and optimize the mechanical properties of cellulose/epoxy composites.

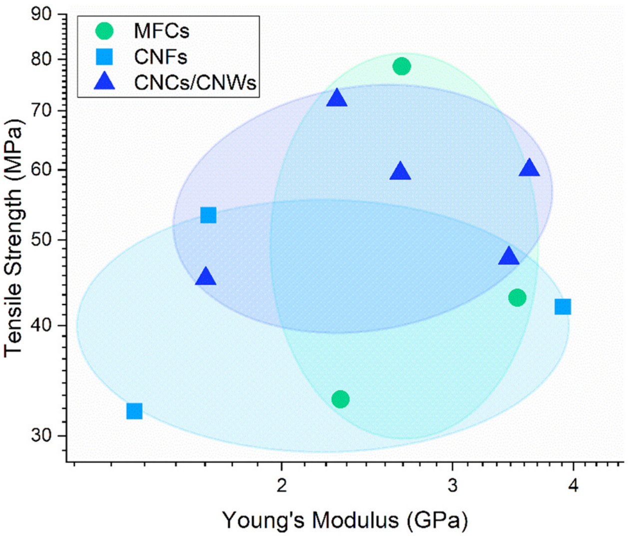

Figure 8: Ashby plots comparing tensile strength vs Young's modulus for epoxy composites reinforced with micron MFCs [128,129] and nanoscale CNFs [121,134,135], nanoscale CNCs/CNWs [113,114,136–140].

4.2 Continuous phase enhancement strategy

Usually, 1D long fibers without structures of braided or 3D woven are not the best option for reinforcing the composites due to the possible formation of structural defects of anisotropy and occurrence of nonlinear deformation of fracture [144].

For the prefabricated cellulose materials with a 2D layered structure (e.g., films, papers, or fabrics), it is a good choice to reinforce epoxy. For cellulose (nano) papers, it can be prepared by vacuum filtration of nanocellulose suspension or hot-pressing BC gel (refer to Section 2.2). The forming process of 2D cellulose/epoxy composites is similar to CFRP [145,146], as classified into two methods: (1) vacuum-assisted resin infusion (VARI) technology [147,148], as shown in Figure 9a; (2) hand lay-up molding technology [102,149], as shown in Figure 9b. Besides, the high-pressure pressing process to the uncured composite can be of possibly great improvement to the mechanical properties of composites (e.g., bacterial cellulose nanopaper/epoxy) [150]. The dispersing issue is no longer a problem since cellulose has been prefabricated into a structure of macroscopic and continuous in two dimensions. Therefore, composites with a high amount of cellulose reinforcement phase can be easily prepared without worrying about its dispersibility. For example, the volume fraction of cellulose in the cellulose nanopaper/epoxy composites was as high as 80 vol% [103].

Lee *et al.* [148] compared the enhancement effect of 11 sheets of stacked CNFs nanopapers and bacterial cellulose nanopapers to epoxy and found that the former is still slightly inferior to the latter. That indicates the amazing reinforcement effect of the high-strength BC nanopaper on epoxy resin [151]. The difference is ascribed to two reasons: (1) bacterial cellulose exhibits a higher crystallinity; (2) the interstratified gap among layers is hard to be impregnated by epoxy resin. Infiltrating performance can be improved by increasing the porosity of cellulose nanopaper. By using organic solvents (e.g., ethanol [152]) instead of water, the porosity can be well-adjusted, and the mechanical property (especially Young's modulus) of composites can be improved.

We can use prefabricated cellulose materials with a 3D network structure (e.g., cellulose aerogels, refer to Section 2.2; delignified wood, refer to Section 2.1.2) to enhance epoxy. Cellulose aerogels are usually quite porous with pore size ranging from tens of nanometers to hundreds of microns [153–155]. The open-pore structure of aerogels can ensure the formation of a bicontinuous phase structure of cellulose and epoxy. The forming process of 3D cellulose/epoxy composites can also be classified into two methods: (1) VARI technology [156]; (2) direct dipping

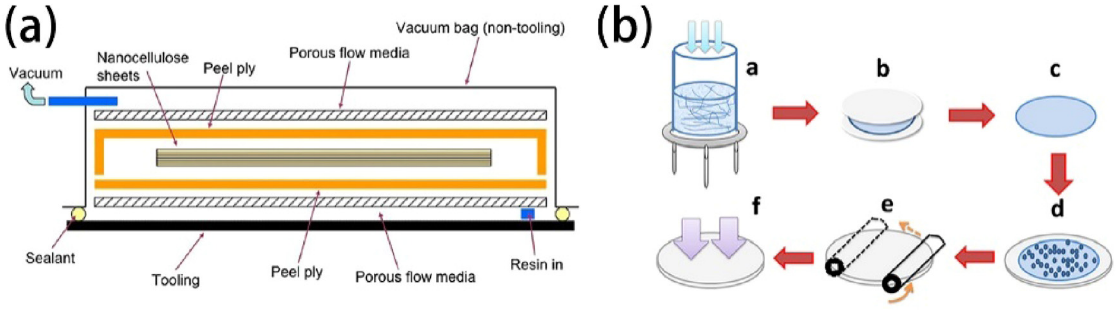

Figure 9: Schematic diagram of preparing cellulose nanopaper/epoxy composites. (a) Impregnating nanopaper by vacuum-assisted resin infusion molding [147,148]. (b) Manually immersing nanopaper in epoxy resin or coating epoxy resin on the surface of nanopaper [102,149].

method [157]. Nair *et al.* [158] reinforced epoxy resin with prefabricated CNFs aerogel (18–23 wt%). The tensile strength and elongation at break of the composites have increased from 62.5 to 108.25 MPa and from 2.92 to 4.81%, respectively. Similar results were also reported by Ansari *et al.* [159] and Nissilä *et al.* [156,160].

In addition to the artificially constructed cellulose materials with a 3D network structure, the "skeleton" of natural plants (such as bamboo, wood, etc.) can be used to compound with epoxy resin. The "plant skeleton" can be received by removing the lignin from the biomass through chemical treatments, as mentioned in Section 1.1.2. Generally, VARI technology is preferentially used for forming the composites. Several times of resin injection may be needed to fulfill the 3D network structure with viscous epoxy [53]. The mechanical properties of the composites show significant anisotropy due to the oriented arrangement of cellulose fibers in natural wood, but this can be overcome by the multilayer structure with cross-arrangement [161]. Frey *et al.* [162] found that hot-pressing and densification of the delignified wood show a more excellent reinforcing effect that a modulus of up to 70 GPa and tensile strength of 600 MPa can be achieved by final composites. The mechanism of enhancement is attributed to the formation of mechanical interlock between the epoxy resin and the delignified wood in which wrinkles are formed after the compression. Kalali *et al.* [163] used delignified bamboo to strengthen the epoxy resin. Compared with natural bamboo, the tensile strength shows an increment from 69 to 162 MPa, and the toughness is also improved. Wu *et al.* [164] found that the difference between the inner and outer walls of bamboo, as well as the heat treatment, shows a great influence on the performance of the delignified bamboo/epoxy composite. By cross-linking delignified bamboo with boric acid treatment, the obtained composites exhibit ~2 times increments of tensile strength, modulus, and impact strength [165].

4.3 Comparison of different enhancement strategies

The Ashby plot of modulus versus tensile strength of epoxy composites reinforced with different strategies is shown in Figure 10. The introduction of micron-sized cellulose does not contribute much to improving the strength of composites, though the modulus can be significantly improved. In contrast, nanocellulose can effectively increase the strength of the composite materials, while the increment of modulus is not obvious. From the viewpoint of microscopic, the improvement of strength depends on the interfacial interaction between reinforcement and matrix. Nanocellulose can form more interfaces with the matrix due to its higher specific surface area. The strength of composite materials can be further improved if the technology of interface modifications can be adopted. However, reinforcement of nanocellulose does not help to improve the modulus of composites obviously since it is reinforced with a noncontinuous phase. Therefore, it is important that the beneficial structural features of both nanocellulose and micron-sized cellulose can be retained and integrated.

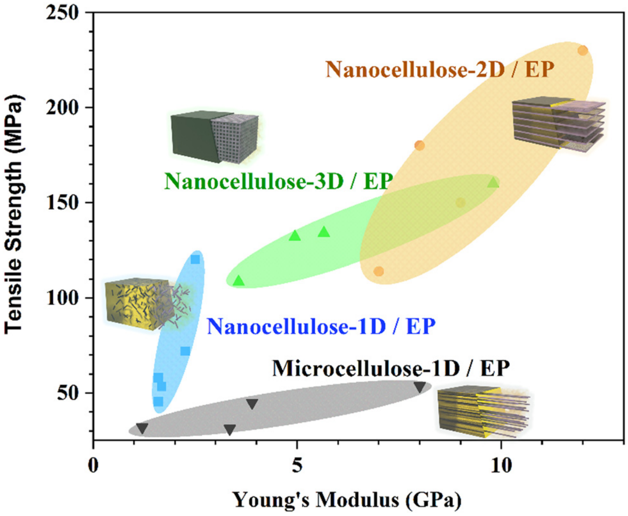

Figure 10: Ashby plots comparing tensile strength vs Young's modulus for epoxy composites reinforced with 1D reinforcement of microcellulose [166–169] and nanocellulose [103,113,114,121,170], as well as 2D [149,171,172] and 3D [111,158,159,173] nanocellulose architectures.

If nanocellulose can be prefabricated into a reinforcement material with a macroscopic and continuous structure in two (e.g., films, papers, or fabrics) or three (e.g., cellulose aerogels, delignified wood) dimensions, the disadvantages of both nanocellulose and micron-sized cellulose fibers as dispersion strengthening agents can be overcome. That is the reason that the utilization of nanocellulose reinforcement with 2D or 3D structures exhibits significant improvement in both Young's modulus and tensile strength, as shown in Figure 10.

Compared to the 2D cellulose reinforcement, 3D cellulose reinforcement can provide a porous structure with open pores so that structures of the bicontinuous phase and mechanical interlocking can form. In theory, 3D cellulose/epoxy is a better choice for composites. However, we found that the strength and modulus of 3D cellulose/epoxy composites are inferior to those reinforced with 2D cellulose. This may be ascribed to the fact that the strength and modulus of cellulose aerogel materials prepared based on current technology are relatively low. They cannot provide good structural support and stress transmission, and the enhancement effect is not so obvious. The formation of a cross-linked network may be quite important for receiving a tough 3D cellulosic architecture [174]. What needs illustration is that works related to super wood (delignified wood) are not included in the 3D cellulose/epoxy in Figure 10. This is attributed to the fact that these works exhibit large data deviation and less regularity.

5 Outlook and perspectives

Cellulosic materials possess good mechanical properties, structural stability and morphological diversity and are suitable for compounding with epoxy resin to prepare high-performance composite materials. This article first discusses the preparation of various cellulosic materials based on the two very basic concepts of top-down and bottom-up. For the top-down concept, various cellulose products with scales of the nanometer (e.g., CNCs, CNFs) to micrometer (e.g., MFC) can be produced through technical means of acid hydrolysis, controlled dissolution, mechanical treatment, oxidation, enzymatic hydrolysis, and so on. By removing lignin from biomass (e.g., wood, bamboo), the plant skeleton known as super wood or delignified wood can be prepared. On the other hand, based on the concept of bottom-up, there are formations of various cellulose architectures through the artificial construction of cellulose units, such as cellulose molecular chains, CNCs, CNFs, or MFC. The shape characteristics of the cellulose architectures can be of 1D (e.g., CNFs, regenerated cellulose fibers), 2D (e.g., films, papers, or fabrics), or 3D (e.g., cellulose aerogels, delignified wood).

The above-mentioned cellulose materials can be used to reinforce the epoxy resin. From the view of dimension, the enhancement strategies can be divided into categories of 1D, 2D, and 3D; from the perspective of structural continuity, enhancement strategies can be divided into dispersion strengthening strategy and continuous phase enhancement strategy. In terms of size differences, the cellulose reinforcement can be divided into micron-size or nanoscale. Improvement of strength depends on the interfacial interaction between reinforcement and matrix. But modulus is very related to whether the composite is reinforced with a continuous phase. Therefore, prefabricated 2D/3D nanocellulose reinforcement with a macroscopic and continuous structure can guarantee a significant improvement in both Young's modulus and tensile strength.

In addition to the morphological and dispersing factors of cellulose reinforcement, the interface compatibility between cellulose and epoxy matrix still dominates the mechanical properties of the composite. The solution can be roughly divided into two categories: non-covalent modification or covalent modification. The former is related to adding exogenous additives (e.g., surfactants, nanoparticles) or retaining the lignin content in cellulose to adjust the hydrophobicity of cellulosic materials. The latter involves chemical reactions of esterification, etherification, silanization, graft, etc.

The field of cellulose/epoxy composite is still worthy of more attention, though some progress has been made. It is believed that the future of this field lies in the development and optimization of 3D cellulose/epoxy composites. One example is the epoxy reinforced with super wood that can achieve a modulus of up to 70 GPa and tensile strength of 600 MPa [162]. The current problems are: (1) the mechanism for the high performance of 3D cellulose reinforcement is still unclear; (2) construction of high-performance 3D cellulose reinforcement; (3) surface modification of cellulose in the limited space of the 3D porous structure; (4) the reliability and consistency of 3D cellulose reinforcement prepared from raw cellulose of different regions and different batches [175].

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