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Abstract

Cellulose and protein are the two most abundant naturally occurring polymers. Both polymers are renewable and biodegradable. The exploration of various applications of these two polymers is vital to sustaining development of our society as far as the environment and resource are concerned. Due to the strong mechanical strength and modulus and high aspect ratio, nanocellulose in the form of a nanowhisker and nanofiber has been extensively studied as reinforcing fibers. The nanocellulose/protein composite has been attracted much research

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attention to make fully biodegradable materials. The good chemical structure compatibility of the cellulose fiber and the protein matrix imparts strong interfacial interaction and hence resulting in great improvement of mechanical properties. Another unique property of the protein composite films reinforced with nanocellulose of <500 nm in diameter is the high optical transparency even though the fiber content is as much as 30 wt%. Because of the superhigh length-to-diameter ratio of nanocellulose, cellulose nanofibers or whiskers and protein matrix readily form an interpenetrating network (IPN) alike composite material. Such a structure enhances the thermal stability and barrier properties and reduces the moisture absorption and water swelling ratio of the nanocellulose/protein composite materials.

Keywords

Cellulose • Nanostructure • Protein • Composite

1 Introduction

Fiber-reinforced composite materials display excellent mechanical properties and low density giving them high specific strength and stiffness, so they have been applied in many areas such as aircraft and automotive parts, constructing materials, medical applications, sporting goods, etc. The two components, i.e., fiber and matrix, of most commercialized composite materials are from petroleum chemicals. With concerns of diminishing fossil fuels, and of the pollutions (e.g., poor degradability, emission of toxic gases) upon dumping in landfills or incineration for energy recycling, these composites are not environmentally benign materials. Consequently, there are growing research interest and practical demands in developing bio-composites or “green” composites using fully sustainable, biodegradable, and yearly renewable fibers and resins [1–4]. In terms of the cost and abundance, cellulose fibers and plant proteins are the most promising fiber and matrix candidates for the fully green composite materials, among the many biodegradable fibers and resins [5–7].

Due to the abundance, renewability, easy availability, low cost, biodegradability, biocompatibility, and high mechanical strength, cellulose fibers have long been applied as reinforcing fibers for the manufacturing of composites [8, 9]. Particularly, cellulose nanofibers with one nanoscale dimension have aroused many research interests as reinforcing fillers because their mechanical properties are superior to microfibers [10], for instance, the elastic modulus and mechanical strength of cellulose nanowhiskers are in the order of 100–150 and 10 GPa [11–13], respectively; additionally, nanocelluloses have larger surface area and consequently more surface atoms than their microscale counterparts because of their nanosize, leading to better contact with matrix at the interfaces. Moreover, a well dispersion of nanocellulose in the matrix would effectively induce a percolating nanocellulose network in the composite and therefore efficiently improving the properties of a nanocomposite, such as their superior thermal, mechanical, and barrier properties

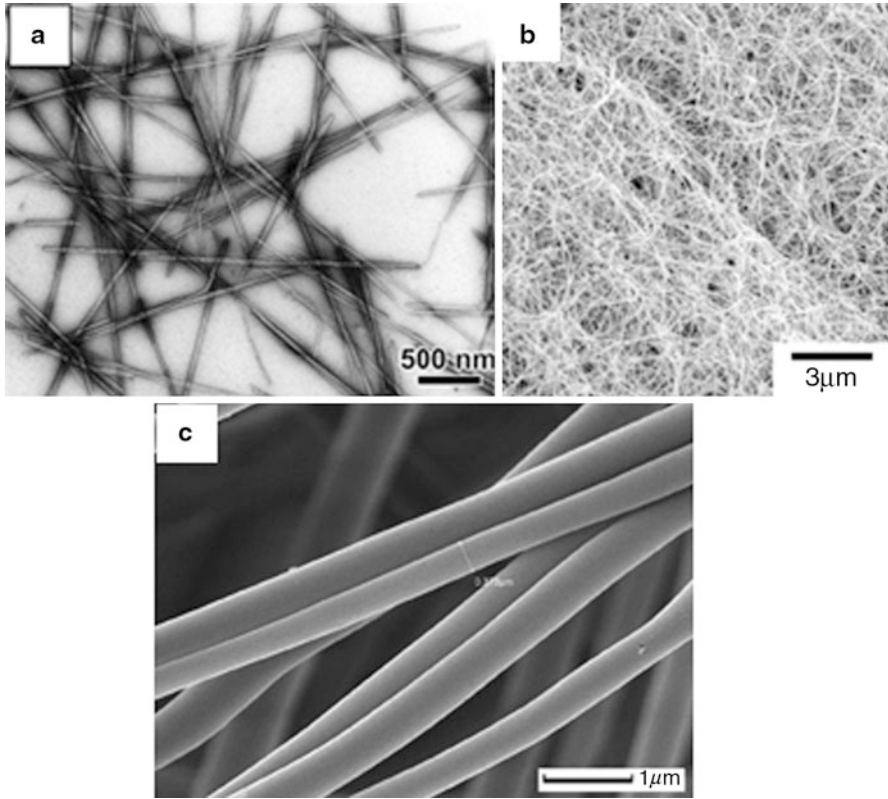


Fig. 23.1 Nanocelluloses in the form of (a) cellulose nanowhisker, (b) bacterial cellulose, (c) electrospun cellulose nanofiber (Reproduced from Ref. [18, 27, 34])

even at a very low reinforcement content (<5 wt%), added to a better recyclability and low weight [14, 15].

Nanocelluloses in forms of cellulose nanowhisker (CNW) and cellulose nanofibers including bacterial cellulose nanofibers (BCNF) and electrospun cellulose nanofibers (eCNFs) have been frequently studied as reinforcing fibers in composites [12, 16, 17]. Figure 23.1 shows the morphology of these nanostructured celluloses. The CNWs are prepared by acid hydrolysis of raw celluloses [18]. The length and width are around respective 100–2,000 nm and 3–60 nm for most CNWs: thus, their aspect ratios (L/d , L : length and d : diameter) are in the range of 1–100 [18]. BCNF is produced by bacteria, like *Acetobacter xylinum*. The length of BCNF is up to several tens micrometers, which is much longer than CNWs, and their diameter and crystallinity are 20–50 nm and 60–75 % [16], respectively. Young's modulus (E) of BCNF is 116 GPa [19]. The newly developed eCNFs from electrospinning are tens to hundreds nanometers in diameter and about several centimeters in length [20]. Thus, their L/d values are >10,000, orders of magnitude more than that of CNWs. The top-down electrospinning method can easily fabricate

plenty of nanofibers to meet the needs for practical applications [21]. Due to the characteristic ultrafine fiber diameter, ultrahigh specific surface areas, and aspect ratios, eCNFs have also found application in the composite materials [17, 22, 23].

Soy protein is an agricultural coproduct with relatively low cost, abundant availability, and renewability [24]. It contains 18 different amino acids. Among them, glutamic acid and aspartic acid contain carboxyl groups; lysine and arginine contain amino groups; and serine, threonine, and tyrosine contain polar hydroxyl groups. The amino acids are connected through peptide (amide) bonds to form polypeptide chains [1]. These functional groups on the chains cannot only be utilized to chemically modify soy proteins but interact with other polymers through hydrogen bonding and therefore providing convenient ways to improve their properties. Soy protein is easily processed both in solution and in melt state. Away from its isoelectric point pH 4.5–5, in either direction, the soy protein molecules are water soluble [1]. In the presence of plasticizers like water and glycerol, it can be hot pressed into plastic sheets [24, 25]. As a result, soy protein has been extensively studied as a fully sustainable and biodegradable resin. However, broad applications of the neat soy protein film are restricted due to disadvantages such as brittleness, poor gas and moisture barrier, and bad water resistance. The addition of plasticizers is able to make flexible soy protein film, while an impregnation of nanofillers such as chitin whisker and nanocellulose can effectively reinforce and toughen soy protein plastics. Additionally, the water resistance of soy protein is improved as well [26].

From the viewpoints of strong mechanical properties of fibers, the processability of matrix, and the structural compatibility between fiber and matrix, nanocellulose/protein is a good pair for the fabrication of green composites. Such composites may display not only improved mechanical properties (strength, stiffness, and toughness), but also enhanced thermal stability, water resistivity, and moisture barrier ability [15, 24]. Specifically, the nanocellulose/soy protein composites can maintain the optical transparency of soy protein film even though the nanocellulose content is as high as 50 wt% [27]. This property is the most significant difference from the microfiber/soy protein composite.

In this chapter the preparation methods including solution casting, hot pressing, and electrospinning of nanocellulose/protein composites are briefly described. Their mechanical, thermal, optical, and water absorption properties are discussed in relation to the fiber morphology and size, dispersion in the matrix, and fiber/matrix interfacial structure. Due to the excellent properties of the nanocellulose/protein composites, they can be promisingly utilized in areas of packaging materials, structural materials, and biomaterials.

2 Preparation Method of Nanocellulose/Soy Protein Composites

2.1 Solvent-Casting Processing

Protein shows good solubility in weak basic aq. solutions ($\text{pH} \geq 8$). Nanocelluloses were dispersed into film-forming protein solutions, followed by casting and drying.

Homogeneous dispersion of nanofibers in solutions should be reached in order to efficiently improve the properties of the resulting nanocomposite. Pereda et al. [15] fabricated CNW/sodium caseinate (SC) composite films by the solvent-casting method. The CNWs were dispersed in water by ultrasonication then mixed with the SC aq. solution. They were poured into Teflon Petri dishes and dried at 35 °C in a convection oven to evaporate excess water; the composite films were then obtained. In the case of nanofibrous mats used as reinforcing fibers, the mats were placed flatly in a quadrate poly(tetrafluoroethylene) (PTFE) trough, into which soy protein isolate (SPI)/H₂O solutions were then added. The mixture was air-dried at ambient conditions to remove most of the water and then dried at 50 °C for 36 h [27]. For the solvent-casting method, about 95 wt% of the mixture solution is water. Therefore, a large amount of energy is consumed in the drying process. Additionally, the sedimentation of nanocellulose in the film-forming solution in the period of drying may occur, resulting in a nonuniform distribution of nanocellulose in the films.

2.2 Hot-Pressing Method

Soy protein displays thermoplasticity, so it can be conveniently processed by the hot-pressing method, through which Wang et al. [24] fabricated CNW/soy protein isolate (SPI) composite films. The CNWs (size: 1.2 mm × 90 nm, aspect ratio l/d : 13.3) and SPI ($M_w = 2.05 \times 10^5$) were dispersed separately in distilled water and stirred for 30 min at room temperature. They were then mixed and stirred for 2 h to obtain a homogeneous dispersion. The resulting dispersion was freeze-dried, and 30 wt% of glycerol was added. The mixture was then placed in a mold, covered with two polished stainless steel plates, as shown in the setup (Fig. 23.2). The temperature of the mold was controlled to 140 °C, and the pressure was quickly increased to 20 MPa. The sample was kept at 140 °C for 10 min and then

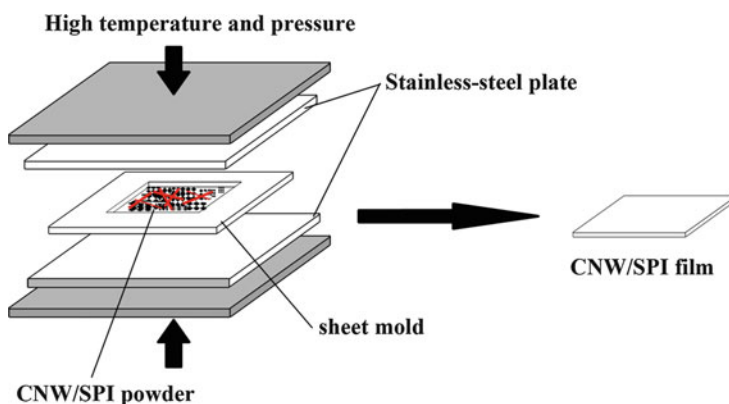


Fig. 23.2 Nanocellulose/soy protein composite film prepared through hot pressing

wind-cooled to room temperature. In a similar procedure, soy protein concentrate (SPC) films reinforced with micro-/nano-fibrillated celluloses (MFC) were reported by Huang and coauthors [28, 29]. They prepared SPC/H₂O and MFC/H₂O suspensions separately, then mixed them under strong stirring to reach even dispersion. The mixture solution was adjusted to pH 8.0 and stirred in air at 75 °C for precuring. The precured resin was then poured in a PTFE-coated mold and dried in an airflowing oven at 35 °C to get specimens in a sheet form, followed by hot pressing at 120 °C and 8 MPa to obtain MFC/SPC composite film. Compared to the time-consuming solvent-casting method, the hot-pressing method is quick.

2.3 Electrospinning Method

In the method of electrospinning, the charged fluid at the tip of the nozzle forms a Taylor cone under electrostatic force and surface tension. A polymer jet is ejected from the cone when the surface tension is overcome by the electrostatic force. The jet is solidified with solvent evaporation and thinned under whipping instability. Fibers with diameter down to tens of nanometers are fabricated. Moreover, the top-down electrospinning method can easily fabricate massive nanofibers to meet the needs for practical applications. *Bombyx mori* silk fibroin (SF) nanofiber mats reinforced with CNWs were fabricated through electrospinning [30] (Fig. 23.3). The electrospinning solution was prepared by dissolving SF in 98 % formic acid, followed by adding the concentrated CNW aq. suspension. Under the stretching of electrostatic force, CNWs in the composite nanofibers predominantly align in the longitudinal fiber axis.

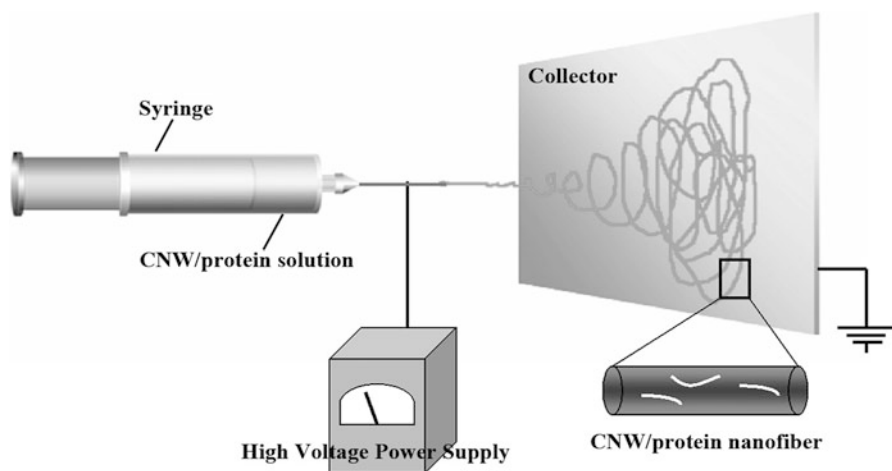


Fig. 23.3 Electrospinning setup for the preparation of CNW/silk fibroin composite nanofiber

3 Properties of Nanocellulose/Protein Nanocomposite Film

3.1 Mechanical Properties

The primary objective of embedding of nanocellulose in protein films or fibers is to improve their mechanical properties. The high specific surface area, aspect ratio, high tensile strength, and Young's modulus of nanocellulose are dedicated to provide effective reinforcing abilities [12, 18]. In the case of CNW/SC composite films, an addition of only 3 wt% CNWs gave more than a twofold increase in the tensile modulus of the composites, due to an even dispersion of CNW in the SC matrix and the strong interfacial interaction between CNW and caseinate. Nevertheless, the strain at break (ϵ_b) decreased with increasing CNW content in the composites [15]. For CNW/SPI composite films prepared from hot pressing, the tensile strength at break (σ_b) and E increased respectively from 5.8 to 8.2 MPa and from 44.7 to 90.6 MPa at 43 % relative humidity (RH) when the CNW content increased from 0 to 20 wt%, indicating that the incorporation of CNWs into the SPI matrix improved the mechanical properties of the SPI, as a result of high mechanical strength and modulus of the CNWs and the strong interfacial interactions caused by hydrogen bonds between the CNWs and the SPI [24]. As for the MFC-reinforced SPC specimens [29], the E of the composite film increased significantly from 589 MPa for SPC containing 15 parts of glycerol to 2,346 MPa for SPC containing 15 parts of glycerol and 40 parts of MFC. This is almost a fourfold increase. A same trend was observed for their fracture stress, which increased from 21.7 to 71.2 MPa, which is about 3.3 times higher than the control SPC film. Additionally, their toughness increased from 2.7 to 5.3 MPa, an increase of about 100 %. Such an effective reinforcement is related to the good interfacial adhesion between MFC and SPC. The rich hydroxyl groups on the MFC provide the condition for a good interfacial adhesion between MFC and soy protein molecules through hydrogen bonding. Though the interfacial strength of nanocellulose/soy protein has not been known yet, Jansson et al. [31] reported that the interfacial shear strength between soy protein and ramie cellulose fiber (microfiber) was as high as 29.8 MPa. In addition, the fine diameter and rough surface of the MFC fibrils provided significantly large areas for interfacial interaction with the SPC resin. Therefore, the MFC fibrils can effectively increase the load transfer efficiency in the composites, resulting in good mechanical properties of the MFC/SPC composite films [29].

The reinforcing efficiency of CNW on the mechanical strength and modulus of the electrospun silk protein nanofiber was obvious as well [30]. Though the mechanical property of an individual CNW/SF nanofiber was not measured to directly show the enhancement, the σ_b and E of the CNW/SF composite nanofibers increased with the CNW content. The σ_b and E of the neat SF nanofibrous mat were 12.5 and 309 MPa, respectively. The σ_b and E of the CNW/SF composite nanofibrous mats with 4 wt% CNWs were 38.5 and 1,237 MPa, which were about three and four times higher than that of the neat SF nanofibrous mat, respectively, while its ϵ_b significantly dropped to 4.8 % (Fig. 23.4a–b).

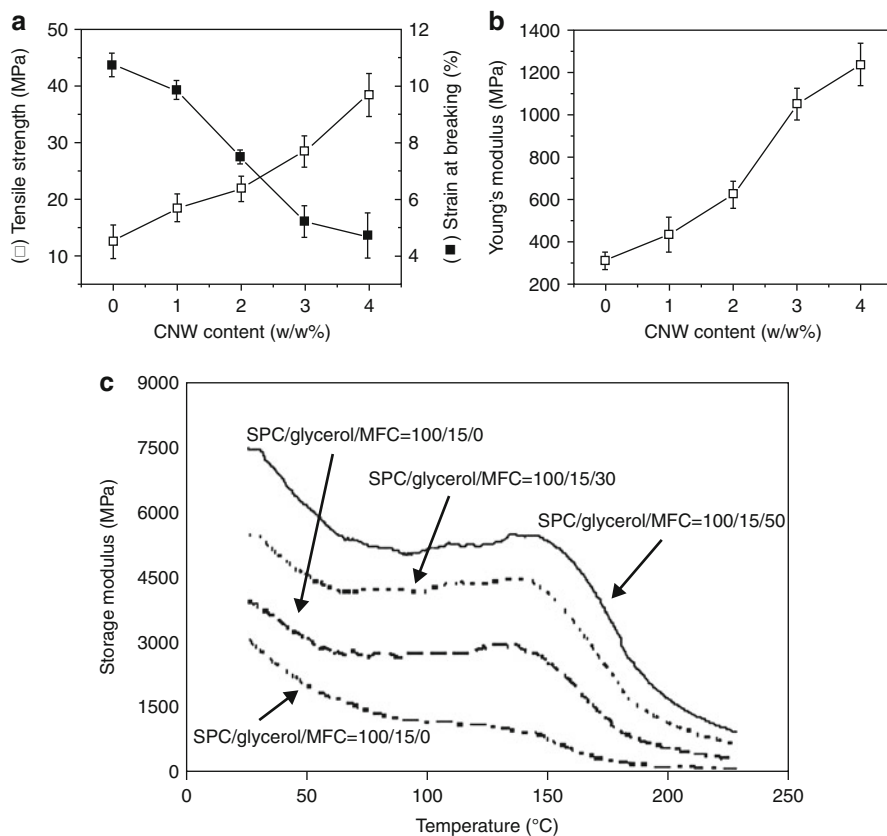


Fig. 23.4 (a) Tensile strength and strain at breaking and (b) Young's modulus of electrospun CNW/silk fibroin nanofiber mats as a function of CNW content; (c) storage moduli of SPC resins reinforced with MFC, glycerol as plasticizer (Reproduced from Ref. [29, 30])

The cellulose have abundant hydroxyl groups on its molecular chains, while the SF molecules are rich in amine, amide, carboxyl, and hydroxyl groups, so CNWs and SF matrix can form hydrogen bonds at the interfaces in the composite nanofibers. Therefore, the authors thought that the even distribution of CNWs in the SF matrix and interfacial adhesion between CNWs and SF play important roles in improving the mechanical properties of CNW/SF composite nanofibers.

For the SPI composites reinforced with eCNF mats, the σ_b and E increased substantially with eCNF content in the composite films [27]. It was 13 times the σ_b of the neat SPI film for the composite film with eCNF content of 22%. And the E of eCNF/SPI with 22 wt% eCNF was 200 MPa, a substantial increment from 30 MPa of the neat SPI film. During stretching, the loading on the SPI matrix transfers to the reinforced fiber. Moreover, composite films cannot rupture easily because the reinforcement cellulose nanofibers act as bridges inhibiting the propagation of crack. Thus, eCNF can reinforce the mechanical strength of composite materials.

With more reinforcing nanofibers impregnated in the SPI resin, higher volume of nanofibers per unit cross-section area of the composite contributes to the enhancement of stress and modulus. The increasing of modulus follows the rule of mixtures as in a composite. In a uniform strain situation, the fiber and matrix combine to give the overall modulus according to $E(\text{comp}) = E(\text{fiber}) * V + E(\text{matrix}) * (1 - V)$. As V goes up, the stiffer phase (the fiber) dominates the mechanical properties. With the embedding of as small as 7.5 % eCNF in the SPI matrix plasticized with glycerol, the failure strain of composite film decreased significantly from 275 % to 25 %. In the eCNF/SPI composite films, the rigid reinforcing cellulose nanofibers restrain the elongation of composite film. As a result, the strain of eCNF/SPI composite film is relatively low.

3.2 Thermal Properties

The thermal stability of nanocellulose/protein composites is generally improved as compared to the neat proteins, partly because of (i) the more thermally stable nature of cellulose than that of proteins, (ii) percolating nanocellulose network in the protein matrix, and (iii) strong interfacial interaction. As demonstrated by Huang and coauthors [29], the MFC/SPC composites showed an improved thermal property compared with the neat SPC resin. SPC with 15 parts of glycerol has a decomposition onset temperature at about 236 °C, which increased to about 257 °C after the addition of 40 parts of MFC.

However, the effect of nanocellulose on the glass transition temperature (T_g) of protein matrix is controversial for various composite systems. In the case of CNW/SC composites [15], a T_g increase was found as compared to the neat SC. Due to the hydrogen-bonding interaction at the interfaces, the CNWs could restrict the mobility of SC chains in the vicinity of the interfacial areas, resulting in a red shift of T_g . However, the authors pointed out that not only the moisture content of the films is decreasing in the testing process but also that cross-linkage in SC films can be induced simply by heating. These two conditions would also contribute to the increase of the T_g . The T_g of MFC/SPC composites increased as well [29]. As measured by the dynamical mechanical analysis (DMA), the T_g increased from about 165 °C for SPC containing 1.5 parts of glycerol to 180 °C for SPC containing 1.5 parts of glycerol and 40 parts of MFC. These findings are similar to the T_g increasing effect of nanocellulose on the CNW/poly(L-lactic acid) nanocomposite [32].

However, in other studies the effect of nanocellulose reinforcement on T_g was the opposite. For the CNW/SPI composites, the T_g of SPI decreased from -44.3 °C to -51.5 °C as the CNW content increased from 0 to 15 wt% [24]. Due to the ultrahigh specific surface areas and nanometer size of CNW, a strong hydrogen-bonding interaction between the CNW and SPI at the interfaces is generated, leading to an improvement of the SPI molecular chain segments mobility in the matrix. As a result, T_g decreased with the addition of CNW in the SPI. Some other polymer matrices such as CNW/starch composites showed this similar phenomenon [33]. The incorporation of nanocellulose in protein matrices has been found to significantly increase the

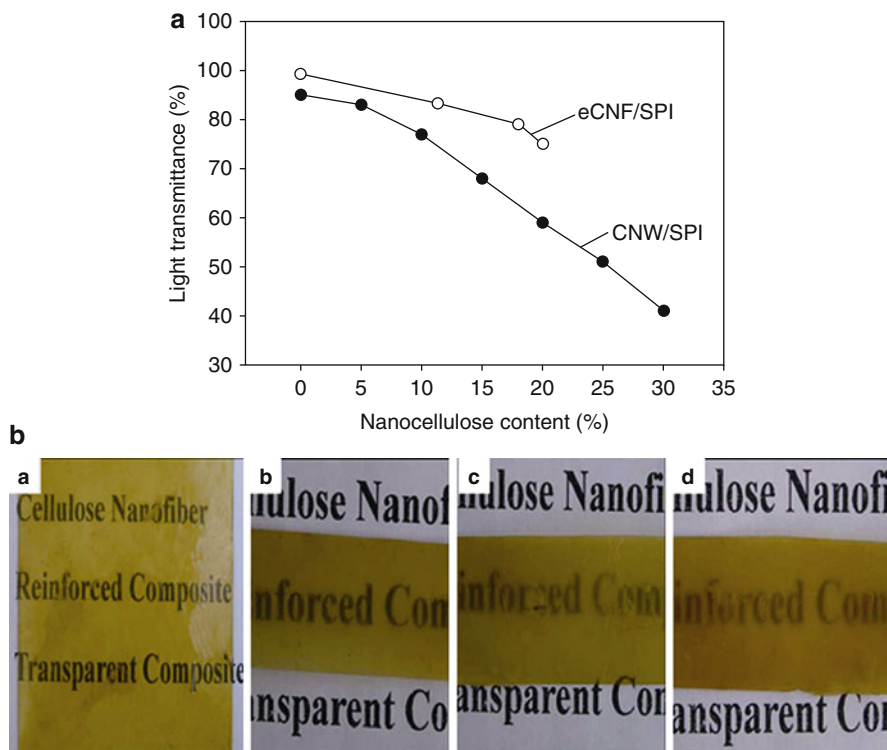


Fig. 23.5 (A) Light transmittance of CNW/SPI composite films at 800 nm and eCNF/SPI composite films at 700 nm. (B) Appearance of eCNF/SPI composite films with eCNF content of (a) 0 %, (b) 7.7 %, (c) 12.6 %, (d) 30.5 % (Reproduced from Ref. [24, 27, 35])

storage modulus (E') of proteins, especially when the working temperature is over T_g , as demonstrated by the MFC/SPC composites [29] (Fig. 23.4c).

3.3 Light Transmittance of Nanocellulose/Soy Protein Composite Films

The incorporation of nanocellulose in protein matrices has been reported to cause transmitted light loss mainly due to the light refraction/reflection at the nanocellulose/protein interfaces. The CNW/SC composite films became less transparent as the nanocellulose content increased [15]. With an increase of the CNW content from 0 to 20 wt%, the light transmittance at 800 nm for the CNW/SPI composite films decreased from 85.1 % to 58.8 % and further dropped to 40.7 % when the CNW content increased to 30 wt% (Fig. 23.5A). The obvious reduction in the light transmittance was regarded as a resultant of phase separation causing severe light scattering at the interfaces [24].

Chen et al. reported an optically transparent SPI composite film reinforced with high content of eCNF [27]. The light transmittance of pure SPI film at 700 nm was 89 %. The eCNF film is white in color with light transmittance of ca 7.5 % at 700 nm. The impregnation of 20 wt% eCNF in the composite film reduced the transmitted light to 75 % at 700 nm, indicating that the embedding of as high as 20 wt% eCNF in the composite film did not result in significant loss of transmitted light (Fig. 23.5A). In view of the possible more light scattering on the much larger eCNF (200–940 nm) than that on the CNW (90 nm), the surprisingly more transmitted light of eCNF/SPI than that of CNW/SPI with 20 wt% nanocellulose suggests a more even distribution of eCNF in the SPI matrix. A digital photo of SPI and eCNF/SPI composite films placed on letters was shown in Fig. 23.5B. The neat SPI film is highly transparent. With impregnation of eCNF in SPI resin matrix, letters under the composite films can still be seen clearly, though the clarity decreases with the increasing of eCNF content. Because of the refractive index (RI) difference between the reinforcing eCNF and the SPI matrix, severe light refraction and reflection at the large amount of fiber/SPI interfaces are supposed to occur. Thus the composite films with 20 wt% fiber content are expected to show poor light transmittance. However, the eCNF/SPI composite films showed good light transmittance. This should be attributable to (i) the ultrafine diameter of the fibers. The light scattering is small when it strikes fibers with a diameter smaller than the visible light wavelength [16, 34–37]; (ii) the good eCNF/SPI interfacial structure reduces the light loss caused by the light scattering and reflectance at the interfaces. It should be pointed out that the eCNF/SPI composite film with 20 wt% eCNF is not optically transparent. In order to improve the light transmittance of eCNF-reinforced composite materials, the diameter of nanofiber should be much smaller than 400 nm. In a similar work, it is very impressive that the poly(vinyl alcohol) (PVA) film reinforced with 40 wt% eCNF fibers of 250 nm in diameter was still optically transparent with 85–88 % light transmittance. Additionally, the light transmittance of eCNF/PVA was insensitive to temperature [34]. More astonishingly, it was reported that BCNF-reinforced epoxy composite film is optically transparent even fiber content is as high as 70 % in the composite [16], when the diameter of BCNF is less than 50 nm.

3.4 Water Resistivity of Nanocellulose/Protein Composite Films

SPI is a hygroscopic polymer due to the presence of amine, amide, carboxyl, and hydroxyl groups. Thus, it is readily to adsorb moisture and swell in aq. solution. Obviously, this characteristic would certainly hinder its application in a wet state. The neat SPI sheet with 30 wt% glycerol absorbed nearly 40 wt% water. However, the water uptake of the CNW/SPI composites with 30 wt% CNW content decreased to 25 wt%, indicating an improvement in the water resistivity. Huang et al. [24] regarded that the strong interaction between the CNW and SPI leads to an enhancement of water resistance of the composite.

For the MFC/SPC composite films, the moisture content of the SPC resin (15 parts of glycerol and 40 parts of MFC) decreased to 13.1 % from 15.2 %

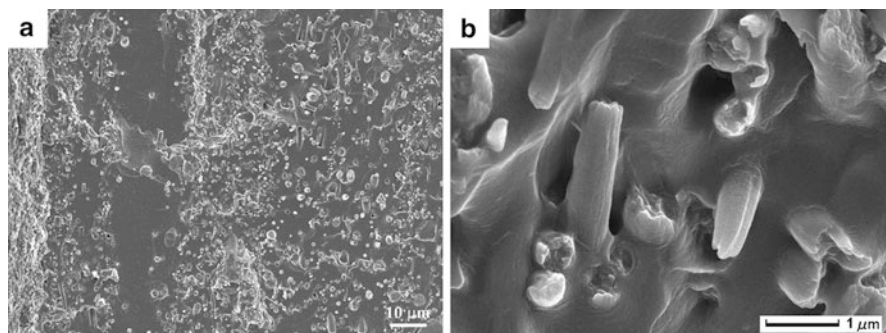


Fig. 23.6 SEM images of fractured eCNF/SPI composite films at different magnifications (Reproduced from Ref. [27])

moisture content of the neat SPC resin (15 parts of glycerol) [29]. The highly crystalline nature of the MFC cannot absorb significant amount of moisture in spite of its highly hydrophilic nature. Nevertheless, the decreased moisture content in the protein composite would contribute to the increased stiffness and decreased elongation at break since water is an effective plasticizer for soy protein.

The embedding of nanocellulose in polymer matrices is able to improve the moisture barrier of protein films. The presence of nanocellulose is thought to increase the tortuosity in the materials leading to slower diffusion processes and, hence, to lower permeability [15]. The poor permeability, high aspect ratio of nanocellulose, and its even dispersion in the matrix would enhance the barrier properties of the composite films. It was found that the addition of CNW to the neat SC films produced an initial increase in the barrier properties to water vapor, and then, the permeability decreased as CNW content increased.

By impregnation of eCNF in the SPI matrix, the swelling ability of SPI decreased steadily with eCNF content [27]. The swelling ratio of composite film reduced substantially from 106 % to 12.7 % as eCNF content increased from 0 % to 21.3 %. Besides the widely accepted conception of strong eCNF/SPI interfacial interaction, the IPN structure also contributes to the reduction of water swelling. As shown in the cross-section SEM images of CNM/SPI composite (Fig. 23.6a), a large number of eCNFs interpenetrate through the SPI matrix to form an IPN alike network. The swelling of SPI filling in the pores within the eCNF mat is restricted by the dimensionally stable eCNF network, resulting in low swelling ratio of CNM/SPI composite film.

3.5 Interfacial Structure and Its Effect on the Properties of Composite Films

The dispersion of nanocellulose in the soy protein matrix plays a critical role in the macro-properties like mechanical, thermal, and optical properties of the composites.

Due to the hydrophilic nature of cellulose and soy protein, a relatively even distribution of nanocellulose in soy protein matrix can be normally achieved without dependence on the preparation methods. For instance, Wang et al. [24] reported a homogeneous dispersion of CNW in the SPI composite prepared from hot pressing. For the protein composite nanofiber from electrospinning, the FE-SEM and TEM of fractured SF nanofiber mat reinforced with 4 wt% CNW showed that the CNW was evenly dispersed in the SF matrix and aligned along the fiber axis [30].

The SEM image of the cross-sectional surface of eCNF/SPI composite films displayed random distribution of eCNF in the SPI matrix. Some broken fiber ends protruded out the fractured surface, while a few fibers flatly layered on the surface. There were also some very shallow cylindrical cavities (Fig. 23.6b), which were generated from the pullout of eCNFs whose end is very near the fractured surface. No obvious delamination was observed at the interfaces of eCNF/SPI; adherence of SPI on the broken fibers was obvious. These results indicated that the reinforcing eCNF and SPI resin matrix has excellent interfacial interaction [38]. The energy consumed by fibril pulling-out and breaking contributes to the increased toughness of nanocellulose/protein nanocomposites.

Nanocellulose is rich of hydroxyl groups on the surface, while soy protein has plenty of amine, amide, carboxyl, and hydroxyl groups on the molecular chains. Therefore, the nanocellulose filler should have structure miscibility with soy protein matrix through hydrogen-bonding interaction. The strong interfacial adhesion was demonstrated by the soy protein remnant on the micro-ramie cellulose fiber [39]. This interaction force should become much stronger because of the very large specific surface areas of cellulose nanofibers making more hydroxyl groups available to form more hydrogen bonds.

4 Perspectives of Nanocellulose/Soy Protein Nanocomposite

The excellent mechanical properties and low density of nanocellulose/protein composites impart them high specific strength and stiffness. Such weight savings are highly desirable for applications in aerospace and transportation to reduce weight and associated fuel consumption [1]. The environmental benign SPC-based “advanced green composites” should find applications from sports gear to auto parts and from electronics to primary structural parts for housing. The biocompatibility of CNW/SPC membranes was confirmed by cell culture and in vivo implantation experiments. The results revealed that human umbilical vein endothelial cells (ECV304) grew well on this biomaterial. In comparison with the pure cellulose membrane, because of the incorporation of SPI and the resultant alteration of microstructure, the SPI-modified membranes showed an improved in vivo biocompatibility and biodegradability in the implantation experiments. These cellulose/SPI membranes warrant further explorations in biomedical fields [40].

However, much research work should be done before they are capable of replacing some of the traditional microfiber-reinforced composite materials. Due to the ultrashort length of CNW and BCNF, they are difficult to be assembled or aligned in one direction, leading to a random distribution in the protein matrix. Thus, they can hardly be engineered to obtain required properties in different directions by appropriate fiber placing in different layers of the laminated structure like using microfibers [1]. Additionally, though individual nanocellulose shows high mechanical properties, its reinforcing efficiency is far below expectation mainly due to the weak percolating nanocellulose networks which is formed by the physical contact among the short nanocelluloses. As a result, their applications are restricted to only noncritical and non-load-bearing parts, such as packaging, casings, etc. They are inapplicable for the load-bearing structural applications where high strength and stiffness are required [1, 9]. In order to substantially improve the mechanical strength and to reduce the water uptake of protein composites, the soy protein matrix should be chemically and/or physically modified, and a novel plasticizer instead of glycerol for the soy protein composite has to be developed.

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