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Natural cuticle-inspired chitin/silk fibroin/cellulose nanocrystal biocomposite films: fabrication and characterization

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Abstract

This study aims at developing a green sustainable bio-inspired composite film by combining the flexible chitin/silk fibroin matrix (CT/SF) and the rigid cellulose nanocrystals (CNC) with the multilayer chiral nematic structure. The effects of CNC concentration on the chemical bonding, optical- and micro-morphology, thermal stability and mechanical properties of chitin/silk fibroin/cellulose nanocrystal (CT/SF/CNC) were comprehensively investigated. The results indicate that a critical concentration for CNC at 2 wt% can display the obvious iridescent color domains of biocomposite films with potential optical functional property. There is a color shift from blue to yellow-red corresponding to the higher concentrations at 3.5 and 5.0 wt%, respectively. The concentration of CNC also affects the transition of conformation of SF from the random to the β-turn as well as the bonding ability between SF and CT. The CT/SF/CNC-3.5 wt% with the excellent optical and mechanical properties as well as the improved thermal stability breaks the conventional conflict between increased strength and compromised ductility. Its tensile strength and elongation at break effectively elevate by 282% and 42%, respectively.

1. Introduction

Nature has rendered continuous inspirations from biomolecular components and nanoscale structures to design and fabricate novel biomimetic materials with diverse functional properties including high strength and roughness as well as excellent biocompatibility and energy absorption [1]. This phenomenon mainly attributes to the hierarchical and periodic arrangement of the hard and soft phases. Natural biological architectures, typically such as arthropod cuticles and crustacean exoskeletons, smartly combine rigid polysaccharide nanofibers with flexible protein together to construct unique ordered hierarchically self-assembled structures, which presents outstanding mechanical performance coupled with light weight and additional functionalities [2–5]. This kind of interesting laminated helical structure is a result of extremely long-term evolution and selection [6]. Many bio-inspired composites have been considered as the next generation green innovation materials. Hence the selection of renewable raw materials with abundant amounts, easy isolation and low costs as well as the fabrication of multi-layer helical nanostructures have become the significant factors to obtain the high-performance bio-inspired composites.

Plant-derived cellulose, animal-derived chitin and silk fibroin are several most abundant renewable biopolymers in the world [7, 8]. Recently, cellulose nanocrystals (CNC) have been paid considerable attention...
on the development of advanced sustainable biomimetic materials owing to its intrinsic birefringence [9], remarkable strength and modulus [10, 11], as well as excellent chemical and thermal stability [12, 13]. The short rod-like CNC prepared from acid-catalyzed hydrolyzing native cellulose can be uniformly dispersed in water with strong electrostatic repulsion derived from sulfate ester groups on CNC surface, which facilitates the formation of chiral nematic phase of liquid crystals, even retaining the helical structure in solid-state films under the appropriate drying condition [14–16]. CNCs with the high degree of crystallinity exhibit extraordinary mechanical strengths that can rival common Kevlar and stainless steel [17]. However, efforts to emulate helicoidal bio-nanomaterials with CNCs have been done with limited success due to its excessively brittle nature [4, 12, 18]. The addition of polymer or plasticizer can effectively improve their ductility. Currently, evaporation-induced self-assembling becomes a facile way to prepare and control the structure and properties of CNC. Several researchers reported that Bouligand biocomposite films were fabricated by a single casting mixing CNC with polyethylene glycol and poly(vinyl alcohol), which exhibited outstanding flexibility with ordered CNC arrangement at the expense of elastic modulus and tensile strength [19–21]. Natarajan et al. [17] improved the stiffness and ductility of biomimetic CNC films by adding tunicate-based CNCs with high aspect ratios into the wood-based CNCs with low aspect ratios, which contributed to the transfer of shear stress on CNC-CNC own interfaces due to the increase of overlap length in CNC films. Tardy et al. [2] prepared the three-dimensional chiral-nematically ordered CNCs by soft substrate with tessellated architecture and rigid support. The microtemplated CNC films compared to the conventional flat CNC films effectively strengthened the toughness of films through a high tortuous fracture propagation in three-dimensional directions.

Chitin, as the second most abundant natural polysaccharide after cellulose, exists in organisms in the manner of ordered nanofibers [22]. However, biomimetic composites derived from chitin nanofibers are uneasy to prepare because of their weak solubility in most solvents [23]. Silk protein is a type of special renewable biopolymers, which can offer various properties of structure and biology with versatile formats [24]. Chitin/silk biocomposites have been explored for various potential applications including substitutes of non-degradable plastics in food packaging as well as medical and clinical bioproducts. Nevertheless, the mechanical strength of the biocomposites was much lower than that from the individual component. The major reason was that the components failed to reproduce the ordered arrangement as chitin and protein found in natural cuticle [25–27]. Chitin and silk were successfully co-assembled as chitin/silk biocomposite films that chitin nanofibers embedded in the silk fibroin matrix with the entangled structure in hexafluorosopropanol solvent [28], which was confirmed to have a superior strength and toughness. Chitosan, the deacylated chitin, mixed with silk fibroin was casted over a microstructured polydimethylsiloxane mound to produce the laminated-structural chitosan/silk fibroin biocomposite film with unexpected strength and toughness [29].

In our previous study, CNCs with strong electrostatic repulsion were easily affected by other component and chitin was also easily crystallized under the inappropriate drying condition. Herein, to investigate the combination and potential properties of the three crucial biopolymers (cellulose nanocrystal, chitin and silk fibroin), we report a green and facile approach to fabricate the flexible bioinspired chiral nematic chitin/silk fibroin/cellulose nanocrystal biocomposite films with multi-layer structures. Chitin and silk fibroin as the flexible matrix, and cellulose nanocrystals as the reinforcement nanofiber was introduced into the compound system to tune the film relative properties with helical structure. The target properties of biocomposite films were evaluated and characterized by ultraviolet-visible spectrophotometer (UV–vis), scanning electron microscope (SEM), polarized microscope (POM), Fourier transfer infrared spectroscopy (FTIR), X-ray diffraction (XRD), thermogravimetric analyzer (TGA) and electro-mechanical instrument.

2. Experimental

2.1. Materials

Alamo switchgrass ( Panicum virgatum L.) was obtained from Center for Renewable Carbon, The University of Tennessee, Knoxville, USA. Chitin powders were bought from Sigma-Aldrich Co., Ltd. Bombyx mori silk cocoons were supplied by Northwest Silkworm Base of China. Regenerated cellulose dialysis membranes (MWCO of 8000–14 000) were purchased from Shanghai Yuanye Biological Technology Co. Ltd, China. The other reagents with analytical grade were bought from Shanghai Taitan Technology Co., Ltd, China.

2.2. Pretreatment of raw materials

Cellulose nanocrystals were prepared by sulfuric acid hydrolysis according to our previous reported method [30]. The obtained CNC suspensions were concentrated to 0.5, 1.0, 2.0, 3.5 and 5.0 wt% by evaporation at room temperature. Silk fibroin was extracted from bombyx mori cocoons by 0.5% w/v sodium carbonate (Na2CO₃) solution for 30 min to remove sericin protein. Residual Na2CO₃ was rinsed by deionized water for several times then dried at 60 °C to keep constant weight. Subsequently, silk fibroin was dissolved in a ternary solvent system
(calcium chloride/ethanol/water) at 75 °C for 2 h. The silk fibroin solution was centrifuged at 6000 rpm for 10 min after dialysis with regenerated cellulose dialysis membranes in deionized water for 3 days to remove low molecular weight substances. Finally, the concentration of SF solution was adjusted to 3.5 w/v%. The weighted chitin, sodium hydroxide and urea with the weight ratio of 2.5:11:4 were dispersed in deionized water under constant stirring at –12 °C for 48 h to obtain a transparent chitin solution. The concentration of the chitin solution was set at 2.5 w/v%.

2.3. Fabrication of CT/SF/CNC biocomposite films

The prepared CT solution and the SF solution were sufficiently mixed to obtain the CT/SF solution at the mass ratio of 4:1, and then the mixing solution was cast in a petri dish with the diameter of 35 mm and dried in a vacuum-drying oven for 2 h at the –0.05 MPa. Subsequently, 1 mL of CNC solution with various concentrations (0.5, 1.0, 2.0, 3.5 and 5.0 wt%) mixed with 10 wt% aqueous solution of polyethylene glycol (PEG) and was sonicated at 40% output for 30 s. Then the mixing suspension was cast onto CT/SF composite matrix and dried for 12 h at 35 °C and relative humidity (RH) of 30% in an incubator. Afterward, the step was replicated to cover the CT/SF composite matrix again to form the sandwich structure with three layers in figure 1.

2.4. Characterization

2.4.1. Macro- and micro- morphology analysis

The surface macro-morphology and the cross-section micro-morphology of CT/SF/CNC biocomposite films were observed by a digital camera and scanning electron microscopy (SEM, Sigma 300, Zeiss, German) at an accelerating voltage of 2 kV, respectively. The fractured specimens in liquid nitrogen for micro analysis were clamped in a mount holder using double-sided tape and coated with gold for 40 s in a SPI sputter coating system (West Chester, PA, USA) before observation. The polarized optical micrographs (POM) were obtained through a German Zeiss polarized optical microscope at the transmission mode with a 10× objective.

2.4.2. Ultraviolet-visible spectrophotometry (UV–vis) analysis

UV–vis spectra of the biocomposite films were collected using a UV–visible spectrophotometer (Perkin Elmer, Lambda750). The reflected wavelength varied from 200 to 800 nm for each sample.

2.4.3. Fourier transfer infrared spectroscopy (FTIR) analysis

FTIR spectra of biocomposite films were recorded using a Tensor 27 instrument (Bruker, German) equipped with an attenuated total reflection (ATR) accessory. All the data were recorded in the wavenumber range of 4000 to 600 cm⁻¹ at a resolution of 4 cm⁻¹ over 32 scans.
2.4.4. X-ray diffraction (XRD) analysis
X-ray diffraction measurements of biocomposite films were carried out on a Rigaku diffractometer (Ultima IV, Japan) with a step increment of $2\theta = 0.02^\circ$. The Cu Kα radiation with a wavelength of 0.1542 nm and a Ni filter of 20 $\mu$m was generated at 40 kV and 40 mA. The diffraction data were collected in a range of $2\theta = 5^\circ$–50°.

2.4.5. Thermogravimetry (TG) analysis
Thermal stability of the biocomposite films was examined on a TG209-F1 thermogravimetric analyzer (Netzsch, German) under a nitrogen atmosphere. About 10 mg samples were heated from 40 to 800 °C at a rate of 5 °C min$^{-1}$.

2.4.6. Mechanical testing
Mechanical properties of the biocomposite films were tested by a universal mechanical testing machine (Instron 1185, UK) loaded with a tensile force of 50 N at room temperature. Prior to the measurements, the samples with the dimension of 20 mm $\times$ 10 mm $\times$ 0.1 mm (length $\times$ width $\times$ thickness) were conditioned at the RH of 50% for 48 h. At least five replicates were tested for each sample to obtain the standard deviations.

3. Results and discussion
3.1. Macro- and micro-morphology and optical properties
The photographs of CT/SF/CNC biocomposite films with various CNC concentrations from 0.5 to 5.0 wt% are displayed under white light illumination perpendicular to the film surface in figure S1 (Supporting information available online at stacks.iop.org/MRX/8/036402/mmedia). There was a slight deformation for all the biocomposite films because of uneven shrinkage or delamination from the Petri dish during the process of evaporation-induced self-assembling. The CT/SF/CNC-0.5 wt% film shows a high transparency due to effectively tuning for the CF/SF composite matrix without any crystallinity prior to CNC being introduced. With the increase of CNC concentration from 0.5 to 1.0 wt%, the transparency of CT/SF/CNC-1.0 wt% film tends to slightly decrease but remains colorless. The biocomposite film begins to exhibit obvious iridescent color domains when the concentration of CNC achieves to 2.0 wt%. With the further increase of CNC concentration to 3.5 and 5.0 wt%, the corresponding reflected colors of CT/SF/CNC-3.5 wt% and CT/SF/CNC-5.0 wt% shift from blue to yellow-red.

UV–vis spectra in figure 2 show a continuous rise in peak reflectance wavelength from 450 to 650 nm with CNC concentration increasing, which is in qualitative agreement with the structural colors observed in the photographs. Additionally, a little yellow-green color is noticed around the center of the circle for the CT/SF/CNC-5 wt% film, corresponding to a broad UV–vis reflectance peak, which can be explained as the diverse helix orientation of multidomain chiral nematic structure at the high CNC concentration [31, 32].

The micro-structures of the CT/SF/CNC biocomposite films with and without iridescent structural colors were further comparatively analyzed using polarized optical microscopy, as seen in figure 3. The CT/SF/CNC-
3.5 wt% biocomposite films with helical structure displays a prominent orange-red shifting of structural color, which proves the formation of chiral nematic structure. Meanwhile, the helicoidal architecture of the composite films by CNC self-assembling are also confirmed by the Bouligand curves, as observation of SEM images on the film cross-sections in figure 4 [17]. The CT/SF/CNC biocomposite film with 0.5 wt% CNC concentration displays the ordinary layered arrangement of CNCs without any twisting angle during the evaporation, as seen in figure 4(a). The CT/SF/CNC biocomposite films gradually shift to a higher pitch as the increase of CNC concentration from 2.0 to 3.5 and 5.0 wt% in figures 4(b)–(d), corresponding to the average value of pitch rising from 450 to 575 and 650 nm. Interestingly, the pitch value \(P\) is found to correlate well with \(\lambda\) according to the formula \(\lambda = (nP/2)\) [33], where \(n\) is defined as the refractive index, approximately equaling to 2 [34]. The relatively low concentration is uneasy to influence the interactions of CNC. The elevation of the CNC concentration increases electrostatic repulsion owing to the increase of surface charge density, resulting in a larger pitch of the chiral nematic structure of biocomposite films, which leads to a red shift of the reflected color [35, 36]. This result is consistent well with the color transition mentioned in macro-morphology analysis as well as the previous report [17, 37].

3.2. FTIR analysis

The FTIR curves of the CT/SF/CNC biocomposite films with various CNC concentrations are illustrated in figure 5. The broad band at 3020–3600 cm\(^{-1}\) is associated with stretching vibrations of O–H overlapped with stretching vibrations of N–H in CNC, CT and SF [38, 39]. The band at 1042 cm\(^{-1}\) with relatively strong peak is mainly assigned to the stretching vibrations of the C–O–C and the C–OH side groups in SF and CT molecular chains [8]. The absorption band at 1663 cm\(^{-1}\) corresponds to the carbonyl stretching of amide I in CT and SF as well as the C=O in CNC [40, 41]. The bending vibrations of amide II (N–H) and amide V (N–H out-of-plane bending vibration) in SF are also observed in the bands of 1553 cm\(^{-1}\) and 684 cm\(^{-1}\), respectively [42]. These characteristic bands demonstrate that the CT/SF/CNC biocomposite films were well combined together by our facile method.

Figure 3. POM of CT/SF/CNC biocomposite films: a. 1.0 wt% CNC; b. 3.5 wt% CNC.

Figure 4. SEM of CT/SF/CNC biocomposite films with various concentrations of CNC: a. 1.0 wt% CNC; b. 2.0 wt% CNC; c. 3.5 wt% CNC; d. 3.0 wt% CNC.
Additionally, it is noticed that there is a decreasing intensity for the peak at 1663 cm$^{-1}$ as the CNC concentration increases from 0.5 to 5.0 wt%, which may be due to the reduction of hydrogen bonding between the C=O of chitin and the N–H group of SF. The amide II (NH) bending vibration at 1553 cm$^{-1}$, and the absorption band at 664 cm$^{-1}$ shift to the higher wavenumber probably due to the fact that the increase of CNC concentration affects the transition of conformation of SF from the random to the β-turn as well as the bonding ability between SF and CT$^{[43]}$.

### 3.3. XRD analysis

The X-ray diffraction graphs of CT/SF/CNC biocomposite films with varying concentrations of CNC are present in figure 6.

There are two weak diffraction peaks observed at 2θ = 9.5 and 20.2° with the addition of CNC at the low concentrations (0.5 and 1.0 wt%), which assigns to the characteristic peaks of silk fibroin and β-chitin$^{[28, 44, 45]}$. This implies that the biocomposite films of CT/SF/CNC-0.5 wt% and CT/SF/CNC-1.0 wt% mainly are in the amorphous phase, which is consistent with the transparent property during macro-morphology observation mentioned above. The diffraction peaks located at 2θ = 16.9 and 22.6°, corresponding to (110) and (200) crystal plane, are seen when the CNC concentration reaches to 2.0 wt%.

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**Figure 5.** FTIR curves of CT/SF/CNC biocomposite films with various concentrations of CNC.

**Figure 6.** XRD patterns of CT/SF/CNC biocomposite films with various concentrations of CNC.
Furthermore, it is noticed that CT/SF/CNC-3.5 wt% and CT/SF/CNC-5.0 wt% display additional diffraction peaks at 11.9 and 22.6°, the initial diffraction peaks at 16.9° slightly shifts to the lower values. According to classical Prague’s law $2d\sin \theta = \lambda$, it can be speculated that the spacing of the parallel atomic plane of CNC becomes larger probably due to the increase of helical pitch of CNC at the higher concentration.

3.4. TG analysis
Thermal stability is a critical index for bio-inspired materials with the iridescent colors since thermal degradation will disable the structural colors. The thermogravimetric (TG) curves of the CT/SF/CNC biocomposite films are illustrated in figure 7.

The weight loss observed in the temperature range of 40 to 140 °C can be explained as the residue moisture of the samples as well as small molecular substances like sodium hydroxide or urea from solvent system in the biocomposite films. The main thermal degradation of the biocomposite films occurs in the temperature range of 240 to 450 °C. In this stage, the mass for silk fibroin, chitin and cellulose nanocrystal sharply losses as the temperature increasing, which is related to the oxidation, deacetylation, cleavage of glycosidic linkage of cellulose and chitin, pyranose ring opening as well as the breakage of amino acid residue side chain groups and peptide chain groups in silk fibroin [8, 46–48]. The TG curves of biocomposite films move toward to the higher temperatures as the increase of CNC concentration. As seen in figure 7, there are significantly elevating temperatures for CT/SF/CNC-1.0 wt%, CT/SF/CNC-2.0 wt%, CT/SF/CNC-3.5 wt% and CT/SF/CNC-5.0 wt% at 30% mass loss ($T_{30\%}$) from 185.4 to 190.9, 213.7, 213.3 and 210.9 °C compared to CT/SF/CNC-0.5 wt%, respectively, as well as at 50% mass loss ($T_{50\%}$) from 220.4 to 225.9, 349.7, 359.1 and 394.0 °C, respectively. It can be concluded that the addition of CNC with helical structure effectively makes the biocomposite films more stable atthe heating process. The similar thermal decomposition behavior of cellulose nanocrystals added in chitosan was reported by our previous study [8].

3.5. Analysis of mechanical properties
The tests of mechanical properties were carried out to evaluate the bio-inspired enhancing effect by combining flexible CT/SF matrix and rigid CNC fillers with the unique hierarchically ordered structures. The results for tensile strength and elongation at break of the CT/SF/CNC biocomposite films with various CNC concentrations are present in figure 8. The CT/SF/CNC-0.5 wt% exhibits the lowest tensile strength (2.39 MPa) and elongation at break (162%) compared to the other groups. There is an obvious ascending trend on tensile strength of biocomposite films with the concentration of CNC increasing from 0.5 to 5.0 wt%, corresponding to the strength value rising from 2.39 to 11.1 MPa. It is remarkable that the tensile strength of biocomposite films is significantly improved when the CNC concentration achieves to 3.5 wt% with the maximum increasing rate of 116%. The tensile strength further elevates by 21% with the CNC concentration up to 5 wt%.

On the other hand, the CT/SF/CNC-2.0 wt% exhibits the highest elongation at break (248%) as compared to the other specimens possibly due to the synergistic enhancement from strong flexible CT/SF matrix, helical layered structure of CNCs as well as the effective stress transfer through a good interfacial adhesion of three components. However, the elongation at break of biocomposite films tends to decline after the CNC...
concentration exceeding 2 wt%. Interestingly, the CT/SF/CNC-3.5 wt% breaks the conventional conflicting goal between increased strength and compromised ductility, resulting in the simultaneous enhancements of tensile strength and elongation at break.

There was a similar reinforcing effect on stiffness of chitosan films and tensile strength of silk fibroin hydrogel with the rate of increase of 87% and 200%–266% after addition of CNC reported by Khan et al [49] and Dorishetty et al [50]. Similar results were observed by et al Kassab for CNC as reinforcement in k-carrageenan biopolymer. They observed that the modulus and strength were increased by 21, 36, 65 and 74% as the increase of CNC content from 0 to 1, 3, 5 and 8 wt% [51]. Enescu et al [52] also indicated that CNC had a positive effect on elevating the Young’s modulus of neat chitosan films but no significant modification for their tensile strength and elongation at break. Khadivi et al [53] reported that CNC/polyethylene glycol/polyurethane composites with 0.5 wt% CNC loading had a remarkable improvement on modulus, tensile strength, and elongation at break of composite matrix compared to the control, whereas the higher addition amount of CNC resulted in a reverse result. Additionally, CNC was modified using octadecyl isocyanate by Pinheiro et al [54]. There was no effect on the tensile strength but a best performance on elongation at break for CNC/poly(butylene adipate-co-terephthalate) composites at the loading of 3 wt% CNC. A marked increase but a sharp drop was found for the loading of 5 and 7 wt% CNC, respectively, compared to the neat one.

Although the mechanical properties of CNC/polymer composites were studied by many researchers, the effect of the CNC on polymer matrices has not been fully understood with the variations in the results of mechanical reinforcement. Therefore, it is necessary for further study to investigate the mechanism of action of the CNC on the various types of biopolymer matrices.

4. Conclusion

The natural cuticle-inspired biocomposite films were successfully fabricated by cellulose nanocrystal, chitin and silk fibroin through a facile strategy, which can remarkably improve the thermal stability and the mechanical performance of biocomposite films through tailoring the multi-layer chiral nematic structure combining the flexible chitin/silk fibroin matrix with the rigid cellulose nanocrystals. It is a critical concentration for CNC at 2 wt% that can display the obvious iridescent color domains with potential development of optical functional property. There is a color shift from blue to yellow-red corresponding to the higher concentrations at 3.5 and 5.0 wt%, respectively. The concentration of CNC also affects the transition of conformation of SF from the random to the β-turn as well as the bonding ability between SF and CT. The CT/SF/CNC-3.5 wt% with the excellent optical and mechanical properties as well as the improved thermal stability breaks the conventional conflict between increased strength and compromised ductility. Its tensile strength and elongation at break effectively elevate by 282% and 42%, respectively.

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