High Strength Chitin Nanocrystals/Alginate Filament Prepared by Wet-Spinning in “Green” Coagulating Bath

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Abstract

Chitin nanocrystals (ChNCs) are an alternative biomaterial of remarkable mechanical stiffness, biocompatibility and sustainability. Wet-spinning is a convenient pathway to control alignment direction and give full play to the advantages of high strength of ChNCs. Herein, sodium alginate (SA) was added as thickener and cross-linking molecules to improve the gelation rate and orientation degree of 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO)-oxidized carboxylated ChNCs in CaCl_2 coagulating bath. The effects of additive amount of SA on the morphology and microstructure of wet-spun filaments were systematic studied. The optimized concentration of SA was 0.8%, and tensile strength and orientation degree of the corresponding filament were 261 MPa and 29.8%, respectively. The changes of optical properties and surface morphology during drying process were monitored via polarizing microscope. The addition of glycerinum and glucose had negative influence on the formation of hydrogen bonds between ChNCs, leading to the decrease of mechanical strength and suppressing the formation of wrinkles on the surface of filament. The stretching process could improve the mechanical strength but cause reduction of strain ratio. This bio-based composite filament with good biocompatibility had potential application in the field of biomedical.

Introduction

With the increasing awareness of environment protection consciousness, biopolymers, especially polysaccharides, have gained considerable attentions worldwide as alternative biodegradable materials to traditional synthetic polymers due to their biocompatibility, high strength and biodegradability.(Ates et al. 2020; W. Zhang et al. 2020)

Chitin is one of the most abundant biopolymers, composed of β -(1,4)-linked 2-acetamido-2-deoxy-D-glucose, and biosynthesized by crustaceans, mollusks, algae, fungi, and insects.(Shamshina et al. 2019) Recently, chitin was typically utilized in the form of nanocrystals for advanced applications in sensor, lithium-ion battery separator, tissue engineering scaffolds and wound dressing.(Narayanan et al. 2020; Shabunin et al. 2019; Suginta et al. 2013; T.-W. Zhang et al. 2019) There are two typical processes to prepare chitin nanofibrils. “Bottom-up” process constructs chitin nanofibrils via dissolution and regeneration, and “top-down” process refers to the destruction of chitin particles into nano-sized fibrils. Due to the huge energy consumption of simple mechanical shearing treatment, chemical pretreatment prior to mechanical shearing is developed as one of the most common process in “top-down” strategy. Acid hydrolysis is a frequently used pretreatment method, which degrades most of amorphous regions and makes crystalline regions easily separated in the following mechanical treatment.(Barkhordari & Fathi, 2018) By applying pretreatment of TEMPO-mediated oxidation or partial deacetylation, numerous charged groups (carboxyl or amino groups) are introduced into the surface of crystalline regions and significantly improve the dispersibility and stability of chitin nanofibrils.(Yimin Fan et al. 2008, 2010; Jiang et al. 2018) The charged nanofibrils have huge application potential in various forms, such as film, gel and sponge.(Fang et al. 2020; Liu et al. 2021; Ye et al. 2020) However, the high mechanical strength of

chitin nanofibrils (1.6-3 GPa) has not fully exploited in these materials due to the random arrangement (Bamba et al. 2017).

Wet-spinning is a promising alternative for assembling nanostructure in high orientation degree for a long time. The general rule of chitin wet-spinning is using a harsh and non-green solvent, such as ionic liquid, N,N-dimethylacetamide/LiCl, CaCl_2 /methanol or alkali/urea, to dissolve chitin molecules and then regenerating recrystallized chitin filament in a coagulating bath.(Duan et al. 2018) Actually, exploiting water-dispersed nanofibrils of high crystallinity to develop high-order filaments can avoid the use of environmentally harmful solvent. As the most abundant biopolymer, cellulose nanofibrils have been used to form super strong filaments via wet-spinning in adjusted conditions.(Abe & Utsumi, 2020; Geng et al. 2017) However, preparing highly oriented wet-spun chitin nanofibril filaments is a topic that has been studied only to a limited extent till now. And the coagulation bath solvents used in the few reports are all organic or harsh solvents (Das et al. 2012; Torres-Rendon et al. 2014; L. Wang et al. 2020).

SA is a kind of water-soluble polysaccharide, which is mainly extracted from natural marine plants and consists of β -D-mannuronate units and α -L-guluronate units.(Hecht & Srebnik, 2016) Due to the high content of carboxylate groups, SA can form gel in the presence of multivalent metal ions. The fast gelation of SA in Ca^{2+} solution has been utilized to prepare SA fibrous gel by wet-spinning, and the gel was widely used as drug release material for advanced biomedical application.(He et al. 2012; Q. Wang et al. 2010; Zhou et al. 2020) Cellulose nanofibrils and chitin nanofibrils added as reinforcement additives remarkably enhanced the mechanical strength of wet-spun SA filaments.(Urena-Benavides et al. 2010; Watthanaphanit et al. 2008)

In this work, SA was added into TEMPO-mediated oxidized ChNC dispersion as gelation enhancement agent. Carboxylated ChNCs were homogeneously mixed with SA and quickly formed gel filament when injected into CaCl_2 solution. The effects of SA concentration and needle diameter on the morphology and strength of wet gel filaments were systematically studied. The arrangement patterns of ChNCs during forming process on the surface and inside were both measured. The orientation degree of dried filament were discussed corresponding to the mechanical properties. The influences of wet-stretching procedure and addition of glycerinum and glucose were also analysed from the aspects of hydrogen bond formation and ChNCs orientation.

Experimental Section

Materials

Chitin powder from shrimp shell was purchased from Aladdin. TEMPO was acquired from Sigma-Aldrich. SA and other chemical reagents were purchased in analytical or higher grade and used without further purification.

Preparation of ChNCs

The TEMPO/NaBr/NaClO oxidation of chitin was applied to oxidize chitin and performed according to the reported process.(T. Saito et al. 2007) Chitin (1 g) was added in distilled water (50 mL) containing TEMPO (0.1 mmol) and NaBr (0.1 g), then NaClO (6 mmol) was added dropwise to the mixture for selective oxidation of C6-hydroxy groups to carboxyl groups. During the oxidation, the pH was maintained at 10 by adding 0.5 M NaOH solution. After NaOH solution was no longer consumed for 20 min, a small amount of ethanol was added to quench the oxidation. The water-insoluble fraction of oxidized chitin was washed with distilled water by repeated centrifugation. Then sonication was applied to a 0.2 wt % oxidized chitin suspension at 1000 W for 20 min using an ultrasonic homogenizer with a tip of Φ 2.4 cm. The ChNCs were obtained in supernatant by centrifugation.

Preparation of ChNC/SA mixture

The ChNC dispersion was concentrated to 3.0 wt% and mixed with desired amount of SA. The mixtures containing 0.3%-1.2% SA were presented as ChNC/0.3SA to ChNC/1.2SA. To modify the mechanical properties of the wet-spun filaments, glycerine and glucose were added in desired concentration of 0.75%-6% and 1%-3%, respectively.

Preparation of ChNC/SA composite filaments

The ChNC/SA mixtures were spun in coagulating bath (0.1 M CaCl_2 solution) from an injection syringe (20 mL) with a needle of Φ 0.6 mm at a rate of 4 mL/min or Φ 0.9 mm at 9 mL/min. After complete coagulation, the ChNC/SA gel filaments were taken out from CaCl_2 solution and washed with distilled water. Some ChNC/SA gel filaments were stretched with the rates of 0%, 30% and 50%. Then all gel filaments were dried in oven at 25 °C.

Analyses

The carboxylate content of TEMPO-mediated oxidized chitin sample was measured according to a previously reported method.(Tsuguyuki Saito & Isogai, 2004) The oxidized chitin (0.1 g) was added in distilled water (60 mL) and the pH of dispersion was adjusted to 2.5-3.0 by adding 0.5 M HCl solution. Then, 0.05 M NaOH solution was added in the dispersion at a rate of 0.1 mL/min by using an automatic titration system. The pH values and conductivity values were recorded every 15 seconds till pH increased to 11. The carboxylate content was calculated from the curves of pH and conductivity values. The chitin samples were freeze-dried and subjected to X-ray diffraction (XRD) analysis using an Ultima IV diffractometer (Rigaku, Japan) with Cu K α radiation (λ = 0.1548 nm) at 40 kV and 30 mA, and the diffraction angle 2θ was 5°-35°. The chitin samples were soaked in 0.01 M HCl solution to protonate carboxyl groups, and then the freeze-dried samples were measured using a Fourier transform infrared (FTIR) spectrometer (Bruker, USA) in reflection mode from 400 cm^{-1} to 4000 cm^{-1} . The morphologies of ChNCs were measured by a Dimension Edge atomic force microscope (AFM) (Bruker, USA) in tapping mode using a standard silicon cantilever. The rheological properties of ChNC dispersion and ChNC/SA mixtures were characterized by a RS6000 rheometer (HAAKE, Germany) at 25°C. The morphologies of ChNC/SA filaments were observed by a polarizing microscopy (Zeiss, Germany). The microstructure of surface and cross section of ChNC/SA filaments were measured by a scanning electron microscope

(SEM). The orientation degrees of ChNC/0.8SA film and filament were measured by a wide-angle X-ray scattering (WAXS) instrument (Xenocs, France). The mechanical properties of ChNC/SA film and filaments were measured using a universal tester instrument (Instron, USA) equipped with pneumatic fixture and a 500 N load cell.

Results And Discussion

Characterization of ChNCs

TEMPO/NaBr/NaClO oxidation system is commonly used in the preparation of ChNCs, which introduces large amount of carboxylate groups into the surface of chitin crystalline regions and improves the electrostatic repulsion force between ChNCs. Figure 1a showed the curves of pH and conductivity values during the titration of TEMPO-mediated oxidized chitin (T-chitin) with 8 mmol/g NaClO, and the carboxylate content calculated was 1.232 mmol/g. After immersed in 0.1 M HCl solution, the carboxylate groups were protonated and exhibited obvious adsorption peak at 1740 cm^{-1} in FTIR spectrum (Fig. 1b). Although degradation was inevitable during TEMPO-mediated oxidation, the well-ordered crystalline regions were mostly remained Indestructible, and the XRD spectrum of T-chitin presented typical diffraction peaks of α -chitin structure at 9.6° , 19.6° , 21.1° and 23.7° (Fig. 1c). As significant degradation of amorphous regions occurred during oxidation, the crystallinity index of T-chitin had an obvious improvement from 87.9–91.6%. When suffering ultrasonic treatment, the strong electrostatic repulsion force between carboxylate groups in the surface of chitin crystalline regions significantly enhanced the separation efficiency of ChNCs. Due to the well dispersed ChNCs in water, the birefringence of ChNC dispersion was clearly recognized with cross polarizers (Fig. 1d). The morphologies of ChNCs were identified by AFM after diluting ChNC dispersion to the concentration of 0.001 wt%, the average length and diameter of ChNCs were 357 nm and 7.2 nm, respectively, which were similar to the ChNC prepared in previous reports (Yimin Fan et al. 2008; Liu et al. 2021). Because of the high content of introduced carboxylate groups, the rod-like ChNCs separated from each other individually and exhibited high stability with ζ -potential value of -42.6 mV.

Wet-spinning of ChNC/SA gel filaments

The preparation process of ChNC/SA composite gel filaments were shown in Fig. 2a. Because of the electrostatic repulsion effect between carboxylate groups, ChNCs and SA molecule chains were separated individually and the mixtures were stable and homogeneous. When extruded from the injection needle, ChNCs and SA molecule chains were forced to form a structured orientation arrangement paralleling to the shear direction. The carboxylated ChNCs and SA had a synergistic effect in gelation process, and as a result, the highly aligned ChNCs and SA were immediately immobilized via ionic bands.

The pure ChNC dispersion was transparent in visible light range and showed light white color. The addition of SA made the mixture become light proof. Figure 2b depicted the viscosities of ChNC/SA mixtures under different shear frequencies. The mixtures were typical pseudoplastic fluids and exhibited

the property of shear thinning. With the increasing concentration of SA, the viscosities of mixtures were gradually improved.

The content of SA had significant influence on the viscosity of ChNC/SA mixture and the following gelation process of filament. All the mixtures were extruded from an inject needle of Φ 0.6 mm at injection speed of 4 mL/min. According to the previous work about TEMPO-oxidized cellulose nanofibrils with metal counterions, when divalent or trivalent metal ions were added into cellulose nanofibril dispersion, micro hydrogel particles were formed via ionic band between nanofibrils.(Kubo et al. 2019) But the mechanical strength of metal ion cross-linked cellulose nanofibril hydrogel was too weak.(Dong et al. 2013) The pure ChNC dispersion with concentration of 3.0% could not form a continuous linear gel filament because of the weak ionic bonds between ChNC and the slow gelation rate, which was unable to suppress Plateau-Rayleigh instabilities of the ejected stream. The addition of SA effectively improved the stability of formed gel filament in CaCl_2 solution. As shown in Fig. 3a, when the concentration of added SA was 0.3%, although the ChNC/SA filament was successfully and continuously prepared, the sheath of filament was rugged and the cross section did not exhibit a clear interface. As the concentration of SA increased to 0.5%-1.2%, the rapid in-situ crosslinking significantly suppressed the diffusion of ChNCs, the filaments formed tight structure with smaller diameters (Fig. 3b-d).

Oriented ChNCs caused the light interference and exhibited uniform color under POM. ChNCs were forced along shearing direction and immediately anchored to form an axial alignment at the interface when ChNC/SA mixture was ejected into coagulation bath. As Ca^{2+} ions permeated from surface to the core of filaments, and the gelation direction led to a typical Maltese cross pattern. Due to the property of pseudoplastic fluid, ChNCs and SA in the interior of filament would convert back to a disordered state after the shearing force of syringe needle disappeared. As the concentration of SA increased, the higher viscosity and more rapid gelation rate made the Maltese cross pattern clearer with larger part of uniform color from interface to center axis.

The addition of SA had a significant effect on the porosity of filaments, the pores inside the filaments became smaller with high concentration of SA. At the same time, more compact arrangement of ChNCs and SA were formed at the interface of filaments, and as the gelation was faster with more SA, the orientation of ChNCs along the axial direction was clearly improved (Fig. 3e-h).

Analysis of dried ChNC/SA filaments

After washed with distilled water, the filaments were hung on a support with both ends fixed and dried in oven at 25 °C. The drying process contained the radial shrinkage and axial shrinkage of the filaments (Fig. 4a). In the primary stage, the radial shrinkage ratio was large and the diameter of filament decreased obviously along with the evaporation of surface moisture. The axial shrinkage straightened the hanging filament and further improved the orientation of ChNCs along the axial direction. The color observed under POM changed dramatically from cyan to green, yellow, orange, carmine, blue and emerald till complete dry (Fig. 4b). The order of the color change matched the Michel-Lévy interference color chart for decreasing birefringence.

Due to the inhomogeneity of cross-linking inside the filament, the unbalance of interfacial tension and internal stress during drying caused the wrinkles of filament surface after drying (Fig. 5a). meanwhile, a denser surface with stronger shrinkage resistance formed during gelation led to the collapse of the surface into the interior, especially for filaments wet-spun from Φ 0.9 mm needle.

Table 1

Mechanical properties of dried ChNC/SA filaments with different concentration of SA injected from needles of Φ 0.9 mm and Φ 0.6 mm.

Dried filaments	Tensile strength (MPa)	Strain at break (%)	Young`s Modulus (MPa)
ChNC/0.8SA-film	91.2 $\pm$ 5.49	2.28 $\pm$ 0.215	261 $\pm$ 12.3
ChNC/0.5SA- Φ 0.6 mm	205 $\pm$ 10.3	1.73 $\pm$ 0.267	514 $\pm$ 15.7
ChNC/0.8SA- Φ 0.6 mm	261 $\pm$ 12.6	2.42 $\pm$ 0.381	485 $\pm$ 12.8
ChNC/1.2SA- Φ 0.6 mm	217 $\pm$ 10.7	2.99 $\pm$ 0.422	390 $\pm$ 16.2
ChNC/0.5SA- Φ 0.9 mm	94.5 $\pm$ 8.56	2.19 $\pm$ 0.325	128 $\pm$ 8.51
ChNC/0.8SA- Φ 0.9 mm	119 $\pm$ 9.72	3.05 $\pm$ 0.539	143 $\pm$ 8.64
ChNC/1.2SA- Φ 0.9 mm	104 $\pm$ 10.9	3.14 $\pm$ 0.626	154 $\pm$ 11.8

The orientation degree of ChNCs and cross-linking have significant influences on the mechanical properties of composite filaments. Figure 5b indicated the stress-strain curves of ChNC/0.8SA film prepared from homogeneous dispersion with disorderly arranged ChNCs and ChNC/SA filaments injected from needles of Φ 0.9 mm and Φ 0.6 mm. The self-assembly ChNC/0.8SA film had strong stiffness with tensile strength of 91.2 MPa and Young`s modulus of 261 MPa based on the formation of a large number of hydrogen bonds between either ChNCs or SA molecule chains (Table 1). In theory, wet-spinning could improve the orientation degree of ChNCs and the mechanical strength of filaments. However, the tensile strength of ChNC/SA filaments injected from Φ 0.9 mm needle just had slight increases in the range of 3.3–27.7 MPa, and the Yangsmods modulus, which were 204.8-260.9 MPa and 389.6-514.4 MPa, respectively. The addition of SA improved the orientation of ChNCs, but excess SA would lead to unnecessary cross-linking of SA molecule chains with ChNCs, reducing the formed hydrogen bonds between ChNCs. As a result, the optimal addition concentration of SA was 0.8%, the tensile strength of the corresponding filament was 260.9 MPa, which was higher than those in previous reports. (Das et al. 2012; Torres-Rendon et al. 2014; L. Wang et al. 2020) The ChNC/0.8SA film and ChNC/0.8SA filament from Φ 0.6 mm were measured by WAXS. In the 2D diffraction pattern image of ChNC/0.8SA filament, the intensity was clearly recognized on the equator, which did not appear in the image of ChNC/0.8SA film. The difference in intensity between film and filament was obvious in azimuthal intensity profiles, and the orientation degree calculated was improved from 0.32–29.76% after wet-spinning (Fig. 5c).

Similar to pure ChNC film, the dried ChNC/SA filaments were very brittle and easy to break when suffering shear force perpendicular to the axis.(Y. Fan et al. 2012) Glycerinum was added to modify the flexibility of

ChNC/SA filaments. As shown in Fig. 6a, the values of tensile strength and Yang's modulus decreased with more addition of glycerinum, and the maximum strain ratio had a slight increase in the meantime.

ChNCs and SA were both polyhydroxy polysaccharides and had strong hydrophilic property, so the relative humidity of testing environment had a significant effect on the mechanical properties of ChNC/SA filaments. The water molecules were in competition with ChNCs and SA for forming hydrogen bonds with them. As expected, when the relative humidity increased from 45–70%, the tensile strength and Yang's modulus of ChNC/0.8SA filaments had a sharp decrease to 176.5 MPa and 194.5 MPa, respectively. The influences of glucose and stretching ratio were measured under 70% relative humidity. Glucose is the basic unit of cellulose, and was reported to have the ability to thicken the mixture and suppress the formation of wrinkles.(Kose et al. 2019) The glucose molecules formed hydrogen bonds with ChNCs and SA molecule chains, reducing the tensile strength defect in filament partly and improving the elongation ratio (Fig. 6b). However, too much glucose would cover the surface of ChNCs and SA molecule chains, and interface the hydrogen bonding between them, causing the decrease of both strain ratio and tensile strength.

As the gel filaments were elongated to exact length, the cross-linked ChNCs and SA chains would slip in a limited space, forcing the axial of ChNCs rotated along the stretch direction and SA molecule chains straight. As a result, the orientation degree of dried ChNC/SA filament was improved. As shown in Fig. 6c, when the elongation ratio was 50%, the tensile strength and Yang's modulus were improved to 210.4 MPa and 217.9 MPa, respectively. However, due to the decrease of elastic stretching, the elongation strain ratios had an obvious decrease.

Conclusion

Pure ChNCs with carboxylate content of 1.232 mmol/g were unable to suppress Plateau-Rayleigh instabilities effectively when injected into CaCl_2 solution. The addition of SA improved the viscosity of mixture and stability of wet-spun gel filament via cross-linking. When the concentration of SA increased, the inside structure of gel filaments became denser and the ChNCs on the surface exhibited higher orientation degree. The optimal concentration of added SA was 0.8%, and the maximum tensile strength value and orientation degree of corresponding dried ChNC/SA filament was 261 MPa and 29.8%, respectively. Glycerinum and glucose molecules could interfere the formation of hydrogen bonds between ChNCs and SA molecule chains, and further improve the flexibility of dried filaments. The stretching ratio of wet-spun gel filament had a positive effect on the mechanical strength of dried sample. The well assembled ChNC/SA filament with high mechanical strength had huge application potential in composite nanomaterials.

Declarations

Conflicts of interest

There are no conflicts to declare.

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Figures

Figure 1

The titration curves of pH and conductivity of T-chitin dispersion (a), FTIR (b) and XRD (c) spectra of chitin raw material and T-chitin, AFM image of ChNCs and birefringence photograph of ChNC dispersion (d).

Figure 2

Schematic representation of wet-spinning ChNC/SA filaments in CaCl₂ solution and the corresponding orientation change and cross-linking reaction of ChNCs and SA molecule chains (a), the viscosity and photos of ChNC/SA mixtures with different concentration of SA (b).

Figure 3

POM images of cross section (top) and axial plane (middle and bottom) of ChNC/SA gel filaments with SA concentration of 0.3%, 0.5%, 0.8% and 1.2% (a-d), SEM images of cross section center (top) and surface (bottom) of freeze-dried ChNC/SA gel filaments with SA concentration of 0.3%, 0.5%, 0.8% and 1.2% (e-h), red arrow showed the axial direction.

Figure 4

Schematic representation of drying process of ChNC/SA gel filament (a) and OPM images of ChNC/0.8SA filament from wet to complete dry (b).

Figure 5

POM images of ChNC/0.5SA, ChNC/0.8SA and ChNC/1.2SA filaments (left to right) injected from needles of Φ 0.6 mm (top) and Φ 0.9 mm (bottom) (a), typical stress-strain curves of ChNC/0.8SA film and dried ChNC/SA filaments (b), azimuthal intensity profiles and 2D detector images of ChNC/0.8SA film and dried ChNC/0.8SA filament (c).

Figure 6

Mechanical properties of ChNC/SA/Gly filaments (a), ChNC/SA/Glu filaments (b), and ChNC/0.8SA filaments with different elongations (c).