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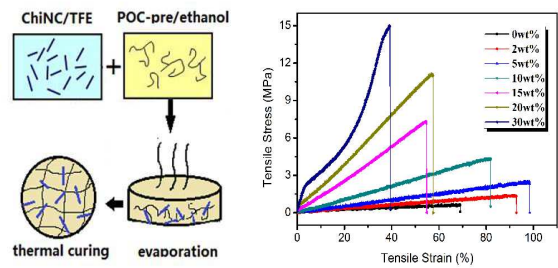
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Chitin nanocrystals successfully regulate the modulus and strength of poly(1,8-octanediol citrate) bioelastomer without the sacrifice of elongation.



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ARTICLE TYPE

Regulating the mechanical properties of poly(1,8-octanediol citrate) bioelastomer via loading of chitin nanocrystals

Yali Ji, *^a Xuemin Wang ^a, Kai Liang ^b

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Chitin nanocrystal (ChiNC), a biocompatible and biodegradable nanofiller, was used to regulate the mechanical properties of poly(1,8-octanediol citrate) (POC) elastomer. The facile casting/evaporation method was utilized to prepare ChiNC/POC nanocomposite and its structure and properties were characterized by Fourier transform infrared spectroscopy, wide angle X-ray diffraction, scanning electron microscopy, dynamic mechanical analysis, uniaxial tensile test and static water-contact-angle analysis, respectively. The results showed the ChiNCs were uniformly distributed in the POC matrix at any testing loading ratio and proved to be chemically bonded to the POC network, leading to a gradually increasing tensile modulus and strength with ChiNCs, concomitantly without causing damage to elongation at break. Thus to regulate the strength and modulus of POC by loading of ChiNCs can be realized. Furthermore, the incorporation of ChiNCs into POC networks provided more hydrophilicity. And the equilibrium swelling degree in PBS buffer was as low as 11%, which is in favour of *in vivo* usage.

1 Introduction

Biodegradable and biocompatible elastomer polymers have great potentials in the field of tissue engineering in that they have matchable mechanical properties especially to soft tissues and can sustain and recover from multiple deformations without causing irritation to the surrounding tissue once implanted in a mechanically demanding environment.¹ Numerous biodegradable elastomers, such as polyurethane thermoplastic elastomers,^{2,3} PCL-based thermoplastic elastomers,^{4,5} crosslinked poly(polyol sebacate) based elastomers (PPS),⁶⁻⁸ and crosslinked poly(diols citrate) based elastomers (PDC),⁹⁻¹¹ have been developed in the engineering of blood vessels, heart valves, nerves, cartilage, skin, bladder, and bone. Among them, citric acid derived biodegradable elastomers PDC have attracted much attention due to a broad range of controllable mechanical and degradation profiles along with surface affinities towards many cell types.¹²⁻¹⁷ This new class of biomaterials took non-toxic and FDA approved citric acid as monomer and was synthesized by a simple low-temperature melt polycondensation with available safe diol under additive-free condition. The mechanical properties of PDC could be tuned to meet the needs of tissue engineering by the diol type, the molar ratio of diol and citric acid, and the ultimate crosslinking density depending on the post-polymerization conditions. Generally, an increase in crosslinking density could enhance the mechanical strength or Young's modulus, however, the elongation at break inevitably decreased. Zhao *et al.* introduced acrylate or fumarate moieties to poly(1,8-octanediol citrate) (POC) network to provide a secondary crosslink network through free radical polymerization.¹⁸ This extra crosslink within the polyester network conferred an increase in the initial modulus,

stress at break, and elongation at break compared to POC control materials. Similarly, Yang *et al.* introduced a vinyl-containing monomer (maleic acid or maleic anhydride) into the pre-polymer network, named poly (alkylene maleate citrates) (PAMCs), which could be quickly crosslinked into a thermoset elastomer, either by photo-crosslinking, thermo-crosslinking, or both mechanisms.¹⁹ However, the crosslinks created during the radical polymerization were not readily degradable, hence unfavourable for *in vivo* tissue engineering usage. Dey *et al.* doped urethane bonds into the poly (diol citrate) polyester network to provide a new generation of crosslinked urethane-doped polyesters (CUPEs) by introducing hexamethylene diisocyanate (HDI) into pre-polymer solution and then post-polymerization.^{20,21} The additional urethane bonds within the polyester network acted as a chain extender and enhanced hydrogen bonding to endow elastomers with highly improved stress at break while still maintaining elongation at break. But, the HDI is a toxic reagent and unsafe *in vivo* use. From the materials science point of view, a single material type does not always provide the necessary mechanical and/or chemical properties desired for a particular application. The combination of nanofiller with various polymers to form polymer-based nanofiller-reinforced bio-nanocomposites is a promising route, especially for elastomers.¹ Commonly, the addition of inorganic fillers to elastomers can increase Young's modulus and elongation at rupture, simultaneously.^{22,23} The increase of these two antagonistic properties characterizes elastomeric composites.²⁴ Ameer *et al.* first produced a bio-ceramic-elastomer composite based upon PDC and hydroxyapatite (HA), which possessed mechanical properties comparable to native bone.^{25,26}

Chitin is the second most abundant biopolymer next to

cellulose and has many advantages such as non-toxicity, high crystallinity, biocompatibility and biodegradability.²⁷ Acid-treatment of chitin can dissolve away regions of low lateral order, resulting in elongated rod-like nanoparticles, termed "nanocrystals" (otherwise called nanofibrils, or nanowhiskers).²⁸ Chitin nanocrystal (ChiNC) is an emerging, novel nanofiller, and has been shown to bring about reinforcing effects on both synthetic and natural polymeric structures.²⁹⁻³² Herein, the ChiNC would be incorporated into POC matrix to form bioelastomer nanocomposites aiming to simultaneously increase tensile strength and elongation at rupture. Compared to the inorganic fillers, such as ceramics, glass microparticles, glass nanoparticles, glass nanofibers, and carbon nanotubes, which were non-degradable and might interfere with the body's natural remodeling mechanisms as the continuous presence of a foreign material might induce long-term inflammatory responses, the ChiNC is one of the most promising bio-nanofillers, possessing good biocompatibility and biodegradability. In addition, chitin is an alkaline polysaccharide, which will neutralize acidic physiological environment resulting from the degradation product of POC. In this system, the elongation at break of POC depended on the crosslinking density, while the strength and modulus could be tuned by loading ChiNCs. Thus, the effective regulation of mechanical properties of POC elastomer can be realized.

2 Experimental

2.1. Preparation of ChiNC

ChiNC aqueous suspension was prepared according to Dufresne's method²⁷ with minor modification. Briefly, chitin flakes (from shrimp shell, Sigma-Aldrich Co., USA) were hydrolyzed in 3 mol·L⁻¹ HCl under stirring and refluxing for 6 h. The ratio of the HCl solution to chitin was 30 cm³·g⁻¹. The residue was collected after centrifugation and the 6 h reflux in 3 mol·L⁻¹ HCl for the residue was repeated two more times. Then, the residue was washed with deionized water for three times by centrifugating and decanting the supernatant. The obtained suspension was further dialyzed in deionized water at room temperature for 3 days, followed by ultrasonic treatment for 20 min and subsequent filtration to remove residual aggregates. Finally, the clear suspension was lyophilized to obtain light brown powders. The yield was 55%. The density was 1.3388 g·cm⁻³, obtained from Ultrapycometer 1000 (Quantachrome Instrument Co., USA).

2.2. Preparation of Pre-polymer

POC pre-polymer was synthesized according to Yang's method.⁹ Briefly, equimolar amounts of citric acid (AR grade, Sinopharm Chemical Reagent Co., China) and 1,8-octanediol (AR grade, Sinopharm Chemical Reagent Co., China) were added to a 250 ml round bottom flask and exposed to a constant flow of nitrogen gas. The mixture was melted at 160 °C under vigorous stirring and then stirred for another hour at 140 °C to create a pre-polymer. Subsequently, the prepolymer was purified to remove unreacted monomers by dissolution in ethanol and precipitation in water. The purification process was repeated twice, and the prepolymer was collected, vacuum dried, and dissolved in ethanol to a concentration of 30% (w/v). The yield of purified prepolymer was about 78%.

2.3. Preparation of ChiNC/POC Nanocomposite

For the better dispersion of ChiNCs in POC prepolymer solution,

ChiNCs were redispersed in 2,2,2-trifluoroethanol (TFE) (99%, Alfa Aesar, China) solvent³³ rather than water, because water is a non-solvent for POC prepolymer. A desired amount of ChiNC suspension in TFE was mixed with POC prepolymer solution and further sonicated for an hour. Subsequently, the mixture was poured into a stainless steel flat dish and made the solvent fully evaporated in a fume hood, followed by post-polymerization at 80 °C in vacuum for 3 days. The mass ratios of ChiNCs filler to POC were controlled at 0:100 (0 wt%), 5:95 (5 wt%), 10:90 (10 wt%), 15:85 (15 wt%), 20:80 (20 wt%) and 30:70 (30 wt%). The true density of neat POC was 1.2006 g·cm⁻³, which was measured on Ultrapycometer 1000 (Quantachrome Instrument Co., USA).

2.4. Measurement and Characterization

Transmission electron microscopy (TEM) was used to evaluate the morphology and dispersibility of ChiNC. A drop of diluted ChiNC suspension in TFE was cast onto a carbon coated copper grid, slowly evaporated, and observed on a JEOL JEM-1230 transmission electron microscope. The ChiNCs were individually distributed and the estimated average length (*L*) and width (*d*) were around 300 nm and 20 nm, respectively, hence the aspect ratio *L/d* was around 15.^{33, 34}

The bioelastomer nanocomposites were cryo-fractured in liquid nitrogen and the cross-section morphologies were examined on SU8010 field emission scanning electron microscope (FESEM) (Hitachi, Japan).

Fourier transform infrared spectroscopy (FTIR) spectra were measured on a Nicolet 670 Nexus FTIR spectrometer at 4 cm⁻¹ resolution in the range of 400 to 4000 cm⁻¹.

Wide angle X-ray diffraction (WAXD) patterns were recorded on a D/Max-2550 PC diffractometer (Rigaku, Japan) at room temperature. The scan speed was 3° min⁻¹ in the range of 5 to 55°.

Dynamics mechanical analysis (DMA) were carried out on a DMA Q800 (TA Instrument, USA) performing at 1 Hz frequency and a heating rate of 5°C·min⁻¹ from -70 to 100 °C in a tension mode. The specimens with thickness about 0.2 mm-0.3mm were cut into 5 mm-wide strips using parallel blade cutter.

Uniaxial tensile tests were performed on a WDW 3020 material testing machine (Changchun Kexin Co., China) with a crosshead speed of 10 mm·min⁻¹ at room temperature. The samples were cut into rectangles 5 mm in width and 50 mm in length. The tensile modulus was calculated from the initial slope of the stress-strain curve (0-5% strain range). The results of tensile modulus, tensile strength and strain at break were the average of 5 specimens.

Static water-contact-angle (θ_w) was measured on a contact anglemeter (Dataphysics Co., Germany) at ambient temperature using the sessile drop method and image analysis of the drop profile. The reported values were an average of 10 individual readings each obtained within 5 seconds.

The swelling properties were measured in a phosphate buffer of pH 7.4 (PBS) and ethanol, respectively. Disk samples (10 mm in diameter, about 1 mm in thickness) of the known mass (*W*₀) were incubated in PBS or ethanol, removed at various time intervals, gently wiped with filter paper to remove excess liquid on the surface, and weighed (*W*₁). The percentage swelling of the discs was calculated using the expression [(*W*₁-*W*₀)/*W*₀] × 100%.

Three individual experiments were performed and data were

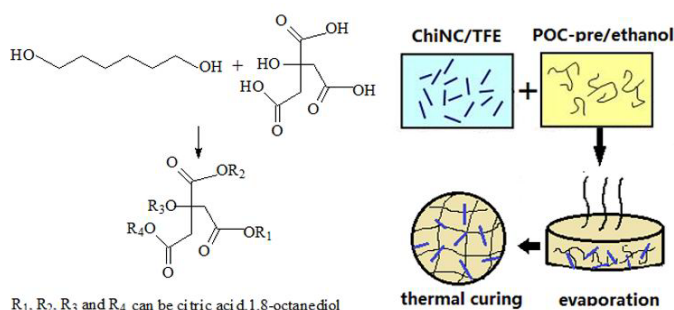


Fig. 1 Schematic fabrication of ChiNC/POC Nanocomposites.

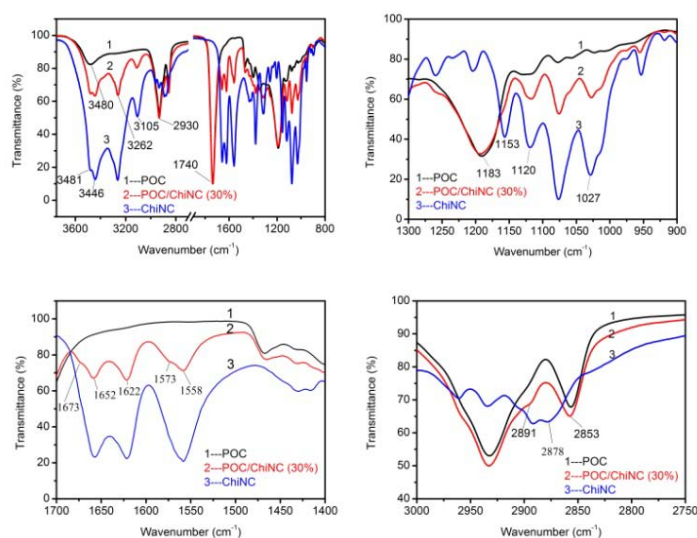


Fig. 2 FTIR spectra of POC and ChiNC/POC Nanocomposites.

averaged. After the swelling experiments, the discs were dried to constant weight (W_2) and sol content was calculated using the expression $[(M_0 - M_2)/M_2] \times 100\%$.

3 Results and Discussion

3.1. Structure and Morphology of the Nanocomposites

The nanocomposites were prepared by facile casting/evaporation method as shown in Fig.1. First, the POC pre-polymer was synthesized by a one-pot additive-free melt polycondensation of citric acid and 1,8-octanediol and then dissolved in ethanol. Subsequently, the well dispersed suspension of ChiNC in TFE was dropped into the POC pre-polymer solution. Through solvent evaporation followed by thermal curing of the mixture, the nanocomposites were obtained. It should be noted that the molar ratio of monomers and post-polymerization conditions control the crosslinking density and consequent mechanical properties of the neat POC. Ameer *et al.* had systematically investigated the relationships between them.^{9,35} Herein, we fixed the molar ratio of citric acid and 1,8-octanediol to 1: 1, and the post-polymerization conditions: 80 °C, 3d, in vacuum. Therefore, only the effects of ChiNCs on POC were considered.

To confirm the inclusion of ChiNCs into POC network, all the samples were subjected to analyze with FTIR spectroscopy. For clarity, only the results of POC, ChiNC/POC (30 wt%) and

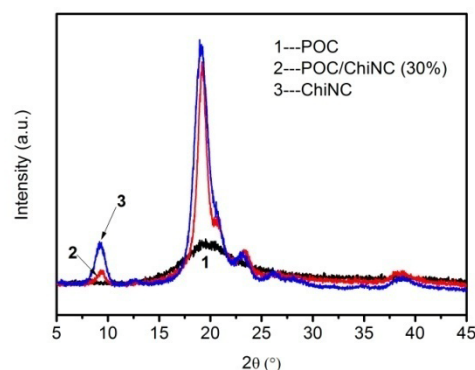


Fig. 3 WAXD patterns of POC, ChiNC and ChiNC/POC (30 wt%).

ChiNC were selected to be shown in Fig. 2. The typical peaks corresponding to POC and ChiNCs were both observed in ChiNC/POC nanocomposites, implying the formation of ChiNC/POC nanocomposites. The characteristic peaks for POC were assigned to the wavenumbers of ~ 1740 , ~ 2930 , ~ 2853 , ~ 3480 , and $\sim 1183 \text{ cm}^{-1}$ for the ester carbonyl ($\text{C}=\text{O}$) group, methylene (CH_2-C) group, methylene (CH_2-O) group, hydrogen-bond hydroxy ($\text{O}-\text{H}$) group, and $\text{C}-\text{O}-\text{C}$ group, respectively. The characteristic peaks for ChiNC were assigned to the signals of ~ 1652 , ~ 1622 , ~ 1558 , ~ 3481 , ~ 3446 , ~ 3262 , ~ 3105 , ~ 1153 , ~ 1120 , and $\sim 1027 \text{ cm}^{-1}$ for amide I bond ($\text{C}=\text{O}$, hydrogen-bond to $\text{H}-\text{N}$), amide I bond ($\text{C}=\text{O}$, hydrogen-bond to $\text{H}-\text{O}$), amide II band ($\text{C}-\text{N}-\text{H}$), hydrogen-bond hydroxy ($\text{C6}-\text{OH}$) group, hydrogen-bond hydroxy ($\text{C3}-\text{OH}$) group, $\text{N}-\text{H}$ group of the amide (intermolecular hydrogen bond), $\text{N}-\text{H}$ group of the amide (intramolecular hydrogen bond), $\text{C}=\text{O}-\text{C}$ group (ring), $\text{C3}-\text{OH}$ group, and $\text{C6}-\text{OH}$ group, respectively. Commonly, the peak height ratio of $\text{C6}-\text{OH}$ to $\text{C3}-\text{OH}$ was used to judge which hydroxyl group took derivation reaction. In the pure ChiNC, the peak height of $\text{C6}-\text{OH}$ was much larger than $\text{C3}-\text{OH}$, however, in the ChiNC/POC nanocomposites, the peak height of $\text{C6}-\text{OH}$ significantly decreased in comparison with $\text{C3}-\text{OH}$, implying $\text{C6}-\text{OH}$ may react with POC network during post-polymerization. In addition, the two new peaks appearing at 1673 cm^{-1} ($\text{C}=\text{O}$ vibration, due to the reaction of $\text{C6}-\text{OH}$ in ChiNC and carboxyl in POC prepolymer) and 1573 cm^{-1} (the amide $\text{N}-\text{H}$ band vibration, due to the reaction of $\text{C2}-\text{NH}_2$ in ChiNC and carboxyl in POC prepolymer) in ChiNC/POC nanocomposite could also confirm this point. Furthermore, the stretching vibration peak of 2878 cm^{-1} due to the methylene group ($\text{C6}-\text{H}_2$) in ChiNC did not clearly appear as that of 2891 cm^{-1} (CH_3) in the nanocomposite, further confirming the $\text{C6}-\text{OH}$ took part in the esterification with POC prepolymer. Thus, ChiNCs were not simply physically blended with POC, but chemically embedded into POC network.

The WAXD patterns of the POC, ChiNC/POC (30 wt%) and ChiNC are shown in Fig. 3. As seen, POC was amorphous. The incorporation of ChiNC into POC caused a series of diffraction peaks at $2\theta = \sim 9^\circ$, 19° , and 23° , which were attributed to the ChiNC for (020), (040) (110), and (130) crystal faces.

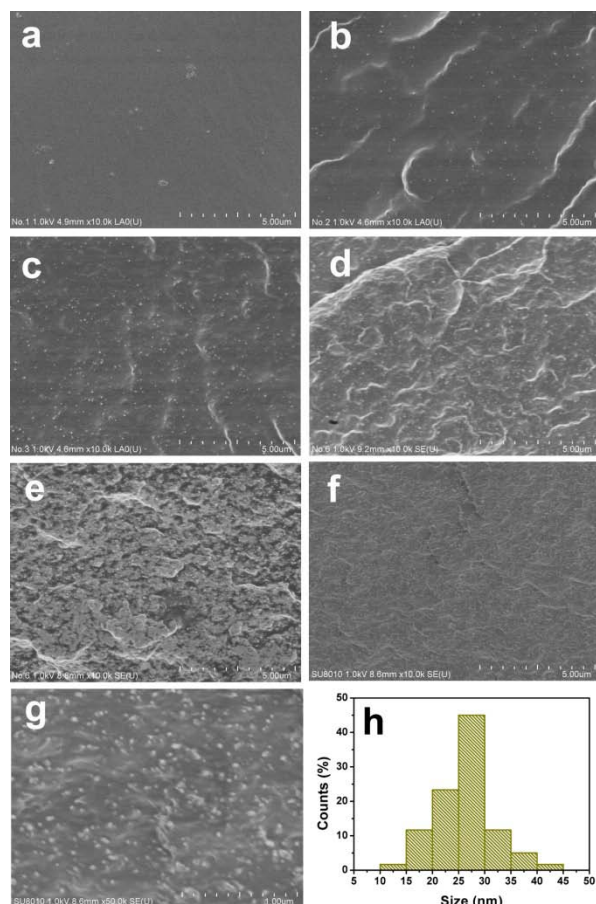


Fig. 4 Field emission scanning electron micrographs of the cross sections of POC and ChiNC/POC nanocomposites. (a) 0:100; (b) 5:95; (c) 10:90; (d) 15:85; (e) 20:80; (f) 30:70 (Scale bar = 5 μm); (g) the enlarged magnification of 30:70 nanocomposite (Scale bar = 1 μm); (h) the size distribution histogram of ChiNC in 30:70 nanocomposite.

FESEM was used to probe the dispersion of ChiNCs within the POC matrix (Fig. 4(a)(b)(c)(d)(e)). The white dots, of which size was mostly around 20~30 nm (Fig. 4h), nearly approaching the average diameter of ChiNCs (~20 nm), were representing ChiNC particles. Evidently, the ChiNCs were uniformly distributed in the POC matrix, even at 30 wt% loading ratio.

3.2. Mechanical Properties of the Nanocomposites

Dynamic mechanical analysis was performed for the samples. Fig. 5(a)(b)(c) show the plots of storage tensile modulus E' , loss modulus E'' and loss angle tangent $\tan\delta$ as a function of temperature for both unfilled and filled POC films. A single-step modulus drop was displayed for all the samples, which is an indication of a typical rubbery elastomer. At low temperature, the E' s of unfilled and filled POC remained at $10^3\sim 10^4$ MPa. It was evident that increasing the loading of ChiNC successively improved the values of E' , and the highest modulus was obtained from the nanocomposite with 30 wt% ChiNC loading, nearly a 2.5-fold increase in comparison to unfilled POC (at -60 °C). This sort of enhancement in modulus was a good evidence for the strong reinforcing tendency of ChiNCs to the POC matrix. From -30°C, a sharp modulus drop appeared. This modulus drop

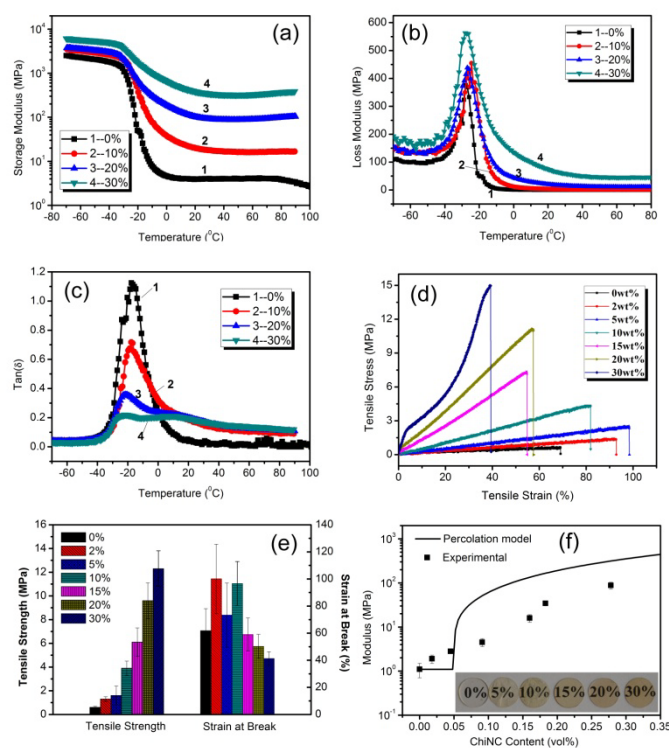


Fig. 5 (a) Storage tensile modulus E' , (b) loss modulus E'' , and (c) loss angle tangent $\tan\delta$ vs temperature at 1 Hz in DMA for POC and ChiNC/POC nanocomposites; (d) (e) (f) uniaxial tensile tests for POC and ChiNC/POC nanocomposites. Inset is the photos of the corresponding nanocomposite films.

corresponded to α -relaxation process relating to the glass transition. Over the glass transition, the modulus became roughly constant over a wide temperature region called the rubbery plateau region until thermal decomposition. With the increase of ChiNC loading, a significant increase in rubbery modulus was observed. For the 30wt% POC nanocomposite, its rubbery modulus at 37 °C was more than 83 times higher than that of the unfilled POC. The E'' peak generally reflects molecular processes that agrees with the temperature of the onset of segmental motion. In this case, the E'' peaks (Fig. 5b) occurred nearly at the same temperature region (-24~-27°C) for unfilled and filled POC, indicating the segmental environment for all the samples was similar. Hence the crosslinking degree for the filled and unfilled POC did not show much difference. $\tan\delta$ plot is usually a good measure of relaxation process. In Fig. 5(c), the $\tan\delta$ plots of neat POC and ChiNC/POC nanocomposites are very different. The neat POC had only one peak at -17°C, however, the nanocomposites had two peaks for 10% loading (-17°C and 10°C), 20% loading (-21°C and 10°C), and 30% loading (-21°C and 10°C). It was thought the first peak (lower temperature) represented the glass transition temperature T_g of POC, but the T_g 's for the samples with 20% and 30% loading were slightly lower than that of neat POC, implying a higher content of ChiNC would interfere with the crosslinking of POC in that the ChiNC with its -OH and -NH₂ groups took part in the post-polymerization and competed for consuming the -COOH groups of prepolymer, thus resulting in a reduced crosslinking degree

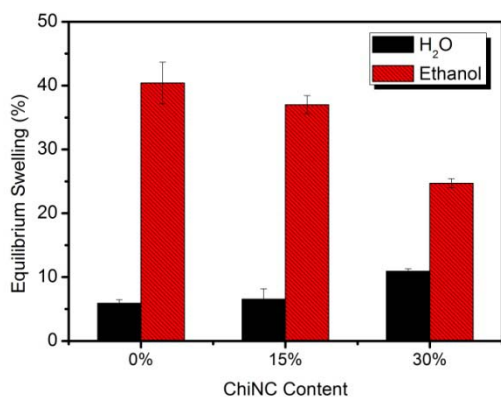


Fig. 6 Swelling properties of ChiNC/POC nanocomposite films in PBS (RT, 24 hours) and ethanol (RT, 24 hours).

Table 1 The measurement results of static water contact angle for ChiNC/POC films

Sample	0:100	5:95	10:90	15:85	20:80	30:70
Contact angle(°)	65.2	61.4	54.1	51.4	53.6	47.8
Image						

of POC. But such reduce was very limited, and in favor of increasing the elongation of POC. The second peak (higher temperature) for the nanocomposites was caused by ChiNCs, since ChiNCs exhibited the strong interfacial interaction with POC matrix through covalent and hydrogen bonds to limit the mobility of POC chains, thus resulting in a relaxation process at a higher temperature.

The uniaxial tensile results are depicted in Fig. 5(d) (e) (f). The incorporation of ChiNCs into POC network highly improved the tensile mechanical properties compared to that of unfilled POC. The tensile strength greatly increased from 0.6 MPa (0:100) to 12.3 MPa (30:70), and the initial tensile Young's modulus also significantly enhanced from 1.1 MPa (0:100) to 87.7 MPa (30:70), nearly an 87-fold increase. Furthermore, the strain at break, as we expected, increased from 61.9% (0:100) to 96.7% (10:90), then decreased to 41.3% (30:70). It should be noted that this drop of strain at break was possibly due to the limitation of the measurement setup, for the fracture locations in the stretched samples always occurred at the top edges of samples, i.e. along the frontier of the clamp, not in the central position of the samples, when more than 15% ChiNCs loading. Hence, we think the real strain at break should be larger than the data listed here. The percolation model was always used to predict the reinforcement of cellulose nanocrystal or chitin nanocrystal in polymer nanocomposites.^{36,37} Herein it was employed to quantitatively analyze the Young's modulus of the nanocomposites. The tensile modulus E_c of the nanocomposite is given by the following equations:

$$E_c = \frac{(1-2\psi+\psi V_f)E_m E_f + (1-V_f)\psi E_f^2}{(1-V_f)E_f + (V_f-\psi)E_m} \quad (1)$$

$$\psi = 0 \quad \text{for } V_f < V_c \quad (2)$$

$$\psi = V_f \left(\frac{V_f - V_c}{1 - V_c} \right)^b \quad \text{for } V_f \geq V_c \quad (3)$$

Here, E_f and E_m are Young's moduli of filler and matrix, respectively. V_f is the volume percentage of filler in the nanocomposite. The volume percentage of filler can be calculated according to the densities of the filler and the matrix. V_c is the critical volume fraction of the rigid phase at the percolation threshold, which depends on the aspect ratio L/d of filler as $V_c = 0.7/(L/d)$. Here, $L/d = 15$ from TEM analysis, therefore, V_c is 4.7 vol%. b is the corresponding critical exponent, where $b = 0.4$. The Young's modulus of the neat ChiNC films was measured as 2 GPa in this case and $E_m = 1.1$ MPa. The calculated curve based on the percolation model and the experimental data are shown in Fig.5(f). It clearly appeared that this model failed to describe the mechanical properties of ChiNC filled POC nanocomposites. A possible explanation for the failure of the percolation approach resulted from the weakness of inter-ChiNC interactions, for the interactions between ChiNC and POC matrix were much stronger due to the formation of chemical bonds that had been proved in the FTIR analyses.

The typical characteristic of ChiNC/POC system was that the introduction of nanocrystals made the strength and modulus highly improved without losing elongation. The nano-particle-reinforced elastomer exhibiting a concomitant increase in elongation at break and Young's modulus was typically explained by the theory of bound rubber.^{1,24} The bound rubber referred to the macromolecules that can be adsorbed onto the filler's surface and uncoiled at higher stress, thus acting as an extra deformation source to be activated at a high stress, leading to additional elongation in bound-rubber composites. From FTIR and FESEM analyses, the ChiNCs were chemically bonded and uniformly distributed in the POC network, which formed a bound-rubber composite, thus a concomitant increase in the strain at break and Young's modulus occurred. In conclusion, the loading of ChiNCs can highly improve the strength and Yong's modulus of POC matrix without the sacrifice of elongation at break. According to this point, such elastomers with tunable mechanical properties can be designed, of which the elongation can be manipulated by the ultimate crosslinking density depending on the molar ratio of monomers and post-polymerization conditions, and the strength or modulus can be adjusted by the loading of ChiNCs.

The inset in Fig.5 (f) is the optical photos of the nanocomposite films. Evidently, all the films are transparent, but owing to the ChiNCs having color, the nanocomposite films appear light tawny color, and more ChiNC loading results in more deep color.

3.3. Wettability and Swelling Capacity of the Nanocomposites
Chitin is a hydrophilic biopolymer, hence the addition of ChiNCs into POC matrix would possibly affect the wettability of POC, and further the degradability. The static water-contact-angle measurement was used to evaluate the surface wettability of the nanocomposites filled with different amount of ChiNCs. As shown in Table 1, the contact angles of the nanocomposites decreased in comparison to neat POC, implying the nanocomposite had more hydrophilic surface.

The samples of POC, ChiNC/POC (15 wt%) and ChiNC/POC (30 wt%) were selected to study swelling behavior both in PBS and in ethanol. The equilibrium swelling was attained within 1-3 hours, and the maximum swelling degree was presented in Fig. 6.

All the samples had low equilibrium swelling degree in PBS (less than 11%), and a little higher equilibrium swelling degree in ethanol. Furthermore, with increasing ChiNC content, the maximum swelling degree in PBS increased, however, the maximum swelling degree in ethanol decreased, implying the loading of ChiNCs conferred more hydrophilicity on POC network. Sol content has been calculated to be 1-3% for all the samples (data not shown) from ethanol immersion. The relatively small amount of the sol content provided a clear indication of successful polymer network formation from the prepolymer mixture and ChiNC.

4 Conclusions

The ChiNC/POC nanocomposites were prepared by facile casting/evaporation approach. The ChiNC was chemically bonded into POC network, and resulted in a high modulus and strength without the sacrifice of elongation. Thus, the mechanical properties of this system can be tuned by two aspects, one is the ultimate crosslinking density, which can be used to regulate the elongation, and the other is the loading ratio of ChiNCs, which can be used to regulate the strength and modulus. In addition, the loading of ChiNC provided more hydrophilicity to POC network. The equilibrium swelling degree of the nanocomposites in PBS was as low as 11%, which is in favour of *in vivo* usage.

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Notes and references

^a Address, State Key Laboratory For Modification of Chemical Fibers and Polymer Materials, College of Material Science and Engineering, Donghua University, Shanghai 201620, China. Fax: +86 21 6779 2855; Tel.: +86 21 6779 2941; E-mail: jiyali@dhu.edu.cn

^b Address, College of Chemistry, Chemical Engineering and Biotechnology, Donghua University, Shanghai 201620, China

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