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Chitin-natural clay nanotubes hybrid hydrogel

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ABSTRACT

Novel hybrid hydrogel was synthesized from chitin NaOH/urea aqueous solution in presence of halloysite nanotubes (HNTs) via crosslinking with epichlorohydrin. Fourier transform infrared (FT-IR) spectra and atomic force microscopy (AFM) results confirmed the interfacial interactions in the chitin–HNTs hybrid hydrogel. The compressive strength and shear modulus of chitin hydrogel were significantly increased by HNTs as shown in the static compressive experiment and rheology measurement. The hybrid hydrogels showed highly porous microstructures by scanning electron microscopy (SEM). The swelling ratio of chitin hydrogel decreased because of the addition of HNTs. The malachite green's absorption experiment result showed that the hybrid hydrogel exhibited much higher absorption rate than the pure chitin hydrogel. The prepared hybrid hydrogel had potential applications in waste treatment and biomedical areas.

1. Introduction

In recent years, special attention has been drawn to the development and application of biopolymers due to their good biocompatibility, favorable biodegradability, and abundant availabilities [1]. Chitin is a long-chain biopolymer of N-acetylglucosamine, which can be found in many sources throughout the natural world [2]. Chitin is the main component of the cell walls of fungi, the exoskeletons of arthropods such as crustaceans (e.g., crabs, lobsters and shrimps) and insects, the radulas of mollusks, and the beaks of cephalopods, including squid and octopuses. Due to its intrinsic biofriendly properties and abundant availabilities, chitin has been used for several medical and industrial purposes [3]. Because of strong inter/intra-molecular hydrogen bonding, chitin has high degree of crystallization and low solubility in common solvents, which limits its applications [4,5]. Strong acids and polar solvents such as trichloroacetic acid (TCA), dichloroacetic acid (DCA), hexafluoroisopropyl alcohol, and lithium chloride (LiCl)/dimethylacetamide (DMAc) mixtures etc. have been found to dissolve chitin. But these solvents show a low efficiency when dissolving chitin and the dissolution process is usually hard to handle. Until recently, Zhang et al. developed a new method to dissolve chitin in NaOH/urea aqueous solution via freezing/thawing process [6,7]. The urea in alkali solutions can break the hydrogen bondings among the chitin, leading to dissolution of chitin. This new method of dissolving chitin realizes the preparing of chitin hydrogel or aerogel from the transparent chitin aqueous solutions [8]. The prepared chitin hydrogel or aerogel find a vast range of applications, from drug delivery, tissue engineering, heat or sound insulators, to waste treatment materials. The direct dissolution of chitin with NaOH/urea systems, avoiding the deacetylation process (to obtain chitosan), is beneficial to amplify the application of the renewable chitin, which is also favorable to environment protection. Although the chitin hydrogel or aerogel has exhibited good mechanical strength, the mechanical performance should be further improved to expand their application areas so as to lower the cost of the materials.

One of the most promising solutions to enhance the mechanical and thermal performance of polymers is elaboration of nanocomposite or organic-inorganic hybrid materials, namely the uniform dispersion of nanosized filler into a polymer matrix [9,10]. Halloysite nanotubes (HNTs), one kind of natural nanoclays with unique tubular microstructure and high strength, can be employed to prepare the chitin nanocomposites or hybrid materials. HNTs, with a chemical formula of $Al_2Si_2O_5(OH)_4{\cdot}nH_2O$, are a dioctahedral 1:1 clay mineral that appear largely in soils, especially in wet tropical and subtropical regions and various weathered igneous and non-igneous rocks [11]. HNTs have dominantly hollow tubular structure in nano-scale with aspect ratio of ca. 20. The length of tubes ranges from 500 to 1500 nm, while the external diameter

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from 40 to 70 nm and the inner diameter from 10 to 15 nm [12]. HNTs have found applications in many fields, such as bioreactor, time-release capsule, catalysts of polymer degradation, template, and high-tech ceramic applications. In recent years, HNTs have been evaluated as nanofillers for polymers [13]. Attributed to their excellent hydrophilicity and small dimension, HNTs are readily dispersed in water, which is convenient to prepare water-soluble polymers nanocomposites. For example, transparent polyvinyl alcohol (PVA)/HNTs and chitosan/HNTs nanocomposites films have been fabricated via solution casting method [14,15]. Uniformly dispersed nanotubes morphology is obtained in these hydrophilic polymers/HNTs nanocomposite systems. Also, HNTs/polymers nanocomposites exhibit a significant increase in mechanical and thermal properties owing to the good interfacial bonding and/or uniformly dispersed rigid nanotube in the composite systems [16]. As an alternative one-dimensional nanoparticle for carbon nanotubes, HNTs are cheap, abundantly available, environmental-friendly, mechanically strong and biocompatible [17]. Therefore, exploring HNTs for preparing bio-based, renewable and high performance chitin nanocomposites is significant both in theory and practice.

In the present study, chitin–HNTs hybrid hydrogels were successfully synthesized via solution mixing and then crosslinking with epichlorohydrin. Raw chitin was firstly dissolved in the NaOH/urea aqueous solution and then the chitin solution was mixed with HNTs. The chitin–HNTs hybrid hydrogel was prepared at elevated temperature using epichlorohydrin as a crosslinker. The interfacial interactions in the chitin–HNTs hybrid hydrogels were confirmed by Fourier transform infrared spectroscopy and atomic force microscopy. The compressive strength and shear modulus of chitin hydrogel were determined. The microstructure of the chitin–HNTs hybrid hydrogel was observed by scanning electron microscopy (SEM). The malachite green's absorption experiment showed that the hybrid hyrogel exhibits much higher absorption efficiency than pure chitin hydrogel. The relationship between the property of the chitin–HNTs hybrid hydrogel and their microstructures were correlated accordingly. Due to the high mechanical performance and unique structural features of the chitin–HNTs hybrid hydrogel, they had potential applications in waste treatment and biomedical areas.

2. Experimental

2.1. Materials

Chitin powder (K1262) was purchased from Sanland-chem International Inc. and used without further purification. The degree of acetylation (DA) of the chitin was determined by elemental analysis to be 0.98. The halloysites was mined from the deposit of the Hunan province, China, and used after purification according to the reference [12]. The raw HNTs showed a layer spacing of 7.2 Å indicating their high dehydration state. The elemental composition of the used HNTs was determined by X-ray fluorescence (XRF) as follows (wt.%): SiO_2, 58.91; Al_2O_3, 40.41; Fe_2O_3, 0.275; TiO_2, 0.071. The Brunauer–Emmett–Teller (BET) specific surface area was approximately 50.4 m^2/g. Epichlorohydrin (ECH) and malachite green (MG) (chemical formula: $(C_{23}H_{25}ClN_2)_2 \cdot C_2O_4 \cdot 2H_2C_2O_4$) were of analytical-grade and used without further purification.

2.2. Synthesize of the chitin–HNTs hybrid hydrogel

The chitin NaOH/urea solution was prepared according to Zhang's method [7]. The typical dissolution procedure was shown as follows. Chitin powders were dispersed into 8 wt% NaOH/4 wt% urea/88 wt% water mixture with stirring, and then were stored under refrigeration (−80 °C) for 4 h. Subsequently, the frozen solid was thawed and stirred extensively at room temperature. After three freezing/thawing cycles, transparent chitin solutions were obtained by centrifugation. The final concentration of the chitin solution was determined as 2 wt.%. Then the calculated HNTs powders were added into the chitin solution with stirring for 24 h to ensure the good dispersion and the absorption between them. Then 0.1 mL ECH was added as cross-linker to 1 g of the chitin solution and stirred at room temperature for 0.5 h to obtain a homogeneous solution. The solutions were casted into glass tubes with the diameter of 13 mm. The crosslinking reaction was carried out in a vacuum oven at 60 °C for 1 h and the hydrogels were obtained by breaking the glass. Pure chitin hydrogel (CT) was also prepared in the same conditions but without the addition of HNTs. The sample codes of the hybrid hydrogel (CT2N1, CT1N1, CT1N2, CT1N4) stood for the weight ratio of chitin (CT) and the nanotubes (N). For example, the CT1N2 stood for the weight ratio of chitin to HNTs was 1:2 in the hybrid hydrogel. The maximum of HNTs concentration was 80 wt.% (CT1N4), and further increasing the HNTs concentration in the chitin solution leaded not applicably high viscosity to process. All the prepared hydrogels were washed with distilled water to remove alkali, urea, and excess ECH before measurement. The prepared pure chitin hydrogel was transparent, while all the chitin–HNTs hybrid hydrogels were opaque (Fig. 1(a)). This may be due to the relatively large dimension of HNTs compared with the visible light wavelength.

2.3. Characterization

Atomic force microscopy (*AFM*) To evaluate the surface morphology of raw HNTs and chitin–HNTs, a multimode AFM with NanoScope IIIa controller was used (Veeco Instruments). The dilute HNTs dispersion and chitin–HNTs (1/1, w/w) solution were dispersed on a piece of freshly cleaved mica and images were collected under contact mode using a soft cantilever (NP-S20, Veeco, force constant ca. 0.1 nN/nm).

Fourier transform infrared spectroscopy (*FTIR*) FTIR of raw HNTs, ECH, and ECH treated HNTs were recorded in a Bruker FTIR using transmission mode by mixing the samples with KBr in an agate mortar and then pressed into pellets and scanned in transmission model. The FTIR spectra of pure chitin and chitin-HNTs freezing-dried gel were measured using attenuated total reflectance (ATR) model in a Bruker FTIR. ATR was a sampling technique used in conjunction with infrared spectroscopy which enabled samples to be examined directly in the solid without further preparation. Thirty-two consecutive scans were taken and their average was stored. Spectra were taken from 4000 to 400 cm^{-1}. The resolution of the wavenumber was 2 cm^{-1}.

Mechanical properties determinations Compression testing of chitin and chitin–HNTs hybrid hyrogels was carried out using Zwick/Roell Z005 machine under 25 °C. The samples for compression testing were cylinder samples with diameter of 10 mm and thickness of 10 mm. Tests were conducted with a constant strain rate of 2 mm/min and up to failure. The stress–strain curves for every sample were recorded automatically. At least five samples were used to obtained reliable data.

Rheological property measurements Rheological property measurements of the hydrogels were conducted with a Kinexus rotational rheometer (Malvern Instruments, Ltd.) using parallel plates of diameter of 20 mm at 25 ± 0.5 °C. The gap between the two parallel plates was set as 1 mm. Firstly, the dynamic strain sweep from 0.01 to 100% was carried out at angular frequency of 1 Hz. Then, the frequency sweep was performed over the frequency range of 0.001–100 Hz at the fixed strain of 0.5%.

Scanning electron microscopy (*SEM*) Before SEM observation, the freeze-dried hydrogels were sectioned and were sputter coated with 10 nm thick gold–palladium layer using a sputter coater