



Hydrogen bonds of sodium alginate/Antarctic krill protein composite material



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ABSTRACT

Sodium alginate/Antarctic krill protein composite material (SA/AKP) was successfully obtained by blending method. The hydrogen bonds of SA/AKP composite material were analyzed by Fourier transform infrared spectroscopy (FT-IR) and Nuclear magnetic resonance hydrogen spectrum (HNMR). Experiment manifested the existence of intermolecular and intramolecular hydrogen bonds in SA/AKP system; strength of intermolecular hydrogen bond enhanced with the increase of AKP in the composite material and the interaction strength of hydrogen bonding followed the order: OH...Ether O > OH...π > OH...N. The percentage of intermolecular hydrogen bond decreased with increase of pH. At the same time, the effect of hydrogen bonds on properties of the composite material was discussed. The increase of intermolecular hydrogen bonding led to the decrease of crystallinity, increase of apparent viscosity and surface tension, as well as obvious decrease of heat resistance of SA/AKP composite material. SA/AKP fiber SEM images and energy spectrum showed that crystallized salt was separated from the fiber, which possibly led to the fibrillation of the composite fibers.

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1. Introduction

As oil resources become scarcer, high consumption and pollution of synthetic fiber production is facing huge market pressure. Production of biodegradable fiber has been becoming currently a hot issue (Chang, Duan, Cai, & Zhang, 2010; Yang, Ma, & Guo, 2011; Zhou, Ma, Shi, Yang, & Nie, 2011). Regenerative materials have been the new orientation of the development of new materials since environmental protection attracted global attention for decades. Algae, as a kind of renewable biomass resources, has been widely exploited in medicine, modern food industry, spinning and weaving (Dangelico, Pontrandolfo, & Pujari, 2013; Faqeer, 2014; Khan, Huq, Saha, Khan, & Khan, 2010; Senthil Kumar & Vigneswaran, 2013). Alginates are a family of linear unbranched polysaccharides which contain varying amounts of 1,4'-linked β-D-mannuronic acid and α-L-guluronic acid residues. The residues may vary widely in composition and sequence and are arranged in a pattern of blocks along the chain. These homopolymeric regions of β-D-mannuronic

acid blocks and α-L-guluronic acid blocks are inter-dispersed with regions of alternating structure (β-D-mannuronic acid-α-L-guluronic acid blocks) (Khan & Ahmad, 2013; Lee et al., 2007; Turco et al., 2011). It is easy to form hydrogels by chelating with calcium and other divalent metal ions (Murakami et al., 2010; Woraharn, Chaiyasut, Sirithunyalug, & Sirithunyalug, 2010). The molecular structure of the algae is similar to cellulose containing large number of hydroxyl groups. There are intra/intermolecular hydrogen bonds in sodium alginate, which lead to stronger interaction forces (Isogai, Saito, & Fukuzumi, 2011; Park, Chang, Jeong, & Hyun, 2013).

Antarctic krill protein (AKP) is also a kind of renewable biomass resources from ocean. Antarctic krill biomass storage is nearly 6.5–10 billion tons (Gigliotti, Davenport, & Beamer, 2011; Hewitt & Low, 2000; Oehlenschl & Manthey, 1982). But thinking that Antarctic krill cannot be directly used for human consumption due to its high fluorine content (Soevik & Braekkan, 1979; Varshal et al., 1983), krill resources have not been fully exploited as yet. At present, the development and research on Antarctic krill resources mainly focus on the Antarctic krill oil, health care products, spices, animal feed and feed additive products (Bax et al., 2012; Tillander et al., 2014). AKP is rich in hydrogen bond donors and acceptors, such as nitrogen atoms, ether oxygen from protein and benzene ring from phenylalanine, which can form hydrogen bonds with

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hydroxyl groups in algae. AKP can exist in amphoteric aqueous solution and is sensitive to pH, and there are large number of hydroxyl groups in sodium alginate molecules. Therefore, it is reasonable to infer that there are complex interactions in SA/AKP blending system. [Jing et al. \(2013\)](#) have prepared SA/AKP composite fiber through wet spinning technology. Moreover, polyacrylonitrile-Graft-Antarctic krill Protein nanofibers has also been successfully prepared via electrospun ([Jing, Siyang, Yuanfa, Yuyan, & Sen, 2015](#)). The results showed that in the preparation process SA was 5% in concentration. The cross-section of SA/AKP fiber has a jagged shape. Thermal property of SA/AKP fibers is similar to SA fibers. But, there is relatively little research on the effects of SA/AKP molecular interactions on material performance. Our research focused on the weak force of hydrogen bonding. In this work, the types of hydrogen bonds in SA/AKP composite material were first studied and then the relationship between the type of hydrogen bonds and properties of SA/AKP composite material was identified. We can change the hydrogen bond intensity to improve the performance of the material by adjusting the amount of AKP and the pH of the system. The experimental results could provide theoretical basis for the research and development of SA/AKP green composite fiber.

2. Experimental and method

2.1. Materials

Sodium alginate with molecular weight of 3×10^6 – 5×10^6 was obtained from Qingdao Bright Moon Seaweed Group Co., Ltd, China. Antarctic krill protein was prepared via extraction in alkali solution. Hydrochloric acid and sodium hydroxide were analytical grade, from Tianjin Ruiming Chemicals Co., Ltd.

2.2. Preparation of SA/AKP composite materials and fiber

The AKP solution was prepared via putting AKP into 0.5% (w/w) sodium hydroxide solution at 60 °C in a water bath, heating and stirring for 1 h, then adjusting solution pH on a pH-3C pH Meter (Shanghai Scientific Instrument Co., Ltd., China). The SA was added into AKP solution under mechanical agitation, afterward, air bubbles were eliminated under vacuum condition for 24 h. By this method, SA/AKP solutions with the ratios of 10/0, 10/1, 10/2 and 10/3 (w/w) were prepared, and SA/AKP solutions with different pH values (i.e. 6, 7, 8, 9) were obtained at the SA/AKP ratio of 10/2 (w/w). The SA/AKP composite fiber was prepared successfully via wet-spinning method, and The SA/AKP solution was extruded to the 5% (w/w) calcium chloride coagulation bath through spinnerets. Then SA/AKP composite fibers were obtained after stretching, washing and winding.

2.3. Characterization of SA/AKP composite materials

The morphology of the SA/AKP composites at different pH conditions was captured using a scanning electron microscope (SEM) (S-4800, HITACHI, Japan) at the accelerating voltage of 10 kV after sputter-coating with Au. The atomic composition analysis of the SA/AKP composites at different pH conditions was carried out by energy-dispersive X-ray spectroscopy (EDX) adjunct to the SEM.

The nuclear magnetic resonance (NMR) spectra were recorded using an AC 400 instrument (Bruker, Switzerland) in deuterated water (D₂O) at room temperature for chemical structure of SA/AKP materials. Interaction forces of the SA/AKP sample was confirmed by a Nicolet 470 Fourier-transformed infrared spectroscopy (FTIR). The KBr pressed disk technique was used for SA/AKP sample preparation. The scanning range was 4500–400 cm⁻¹ with 64 scans at a resolution of 4 cm⁻¹. Hydrogen bonding strength was taken via six

times infrared spectrum fitting operation, and the standard deviation was calculated by following formula.

$$\sigma = \sqrt{\frac{\sum_{i=1}^n (x_i - \bar{x})^2}{n - 1}}$$

where σ : standard deviation; x_i : the Nth time fitting peak area; \bar{x} : average peak area; n : measurement times.

The thermal properties of composite material were measured using thermogravimetric analysis (TGA-50, Shimadzu, Japan) and 200F3 differential scanning calorimeter DSC (NETZSCH, Germany) which was carried out in N₂ atmosphere from 0 to 300 °C heated at a rate of 10 °C/min. TGA analysis of all the samples were carried out using crimped aluminum pans from the ambient temperature to 700 °C in N₂ flow at a heating rate of 10 °C/min.

The crystal structure of the SA/AKP composites was determined using an X-ray diffractometer (XRD, DIFFRACTOMETER-6000, Japan) with Cu K α over a 2θ range 5–80° with a step size of 4°/min. Tube voltage is 2.5–40 kV. Tube current is 80 mA.

The rheological properties of the SA/AKP blend solution were studied by digital rotational viscometer (DV-C, BROOKFIELD, USA). Test conditions: 40 °C, 12–100 RPM. Surface tension test were applied on Sigma 700 Surface tensiometer (Finland).

3. Results and discussion

3.1. Hydrogen bond of SA/AKP composite material

AKP was obtained via extraction in alkali solution according to literature ([Jing et al., 2013](#)). The SA/AKP composite material was prepared successfully by direct blending in water. There are a lot of hydrogen bond donors and acceptors in AKP and SA. SA/AKP composite material was fabricated successfully based on intermolecular hydrogen bonding. Different types of hydrogen bonding such as OH...OH, OH... π , OH...N, OH...ether O, –OH annular polymer, were formed in the composites. The ownership of different kinds of hydrogen bonding in the infrared spectrum was confirmed according to literature ([Chen, Xuemin, Jinsheng, & Yongjie, 1998](#); [Dagang, Xiaoyu, Yiying, Mindong, & Qinglin, 2011](#); [Painter, Sobkowiak, & Youtcheff, 1987](#)).

The Fourier-transformed infrared spectroscopy of pure SA and AKP was shown in [Fig. 1\(a\)](#). Hydroxyl group of SA is commonly strong and observed at 3404 cm⁻¹ at IR spectra. The peak at 1607 cm⁻¹ is characteristic of the carbonyl group of SA. The peaks located at 1415 cm⁻¹ and 1038 cm⁻¹ in SA are C–H bending vibration absorption and six-member ring stretching vibration absorption. The peak at 3410 cm⁻¹ is clearly observed in infrared spectra of AKP which belongs to N–H and O–H stretching vibration absorption of the stack. Peaks located at 1645 cm⁻¹, 1527 cm⁻¹, 1388 cm⁻¹ and 1238 cm⁻¹ are characteristic of the amide group of protein. There is no new absorption peak in the SA/AKP composites with different mixed ratio in [Fig. 1\(b\)](#), which may be strong hydrogen bonding interaction between molecules of the composites. The broad peak around 3000–3700 cm⁻¹ was smoothed using the Savitzky–Golay method by 15 points in Origin8.0 under six times infrared spectrum fitting operation, with the average of the six times data and the standard deviation calculated. Different types of hydrogen bond were ensured by second derivative spectra shown in [Fig. 1\(c\)](#). As shown in [Fig. 1\(d–f\)](#) and [Table 1](#), assignments, strength and child peak distribution of different types of hydrogen bonding in the broad peak from 3000 to 3700 cm⁻¹ were based on Gaussian fitting. As shown in [Table 1](#), the percentage of intermolecular hydrogen bond increases from 41.1% to 46.0% and percentage of intramolecular hydrogen bond reduces to 55.0% from 51.3%. At the same time, the number of free hydroxyl is nearly unchanged. The data reported here suggest that the interaction between AKP

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