Carbohydrate Polymers 189 (2018) 72–78

Contents lists available at ScienceDirect

Carbohydrate Polymers

journal homepage: www.elsevier.com/locate/carbpol

Effects of sodium salt types on the intermolecular interaction of sodium alginate/antarctic krill protein composite fibers

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ARTICLE INFO

Keywords:
Composite fibers
Sodium alginate
Krill protein
Sodium salt

ABSTRACT

Sodium alginate (SA) and antarctic krill protein (AKP) were blended to fabricate the SA/AKP composite fibers by the conventional wet spinning method using 5% $CaCl_2$ as coagulation solution. The sodium salt was added to the SA/AKP solution to adjust the ionization degree and intermolecular interaction of composite system. The main purpose of this study is to investigate the influences of sodium salt types (NaCl, CH_3COONa, Na_2SO_4) on the intermolecular interaction of SA/AKP composite fibers. The intermolecular interaction, morphology, crystallinity, thermal stability and mechanical properties of SA/AKP composite fibers were analyzed by fourier transform infrared spectroscopy (FT-IR), scanning electron microscope (SEM), x-ray diffraction (XRD), thermogravimetric analysis (TGA). The results show that the types of sodium salt have obvious influences on the content of both β-sheet, intermolecular hydrogen bond, breaking strength and surface morphology in SA/AKP composite fibers, but have a negligible effect on the crystallinity and thermal stability.

1. Introduction

As a pure natural polysaccharide, sodium alginate can be extracted from brown algae and other marine organisms. Alginate salt is often used for the preparation of fiber materials that has a wide range of applications in pharmaceutical industry such as the surgical gauze and wound covering materials due to the good gelling property, hygroscopicity, flame retardancy and biodegradability (Sirviö, Kolehmainen, Liimatainen, Niinimäkib, & Hormi, 2014; Sweeney, Miraftab, & Collyer, 2014). In addition, alginate fiber products have anti-static and electromagnetic shielding ability (Rui, Xiaohui, & Xiaodong, 2014) due to the presence of carboxyl or hydroxyl group, which can form coordination compounds with water polyvalent metal ions, resulting in enhancing the binding force and overcoming the electrostatic repulsion between ions, and forming a conductive particle chain. However, the alginate fiber has some deficiencies, such as poor spinnability, unstable chemical properties, poor dyeability, poor acid and alkali resistance and high production cost.

There are two ways to solve the problems mentioned above. One solution is chemical modification with functional group through carboxylation reaction (Ghahramanpoor, Hassani, Abdouss, Bagheri, & Baghaban, 2011) and hydroxyl reaction (Jeon, Alt, Ahmed, & Alsberg, 2012). Another method is to blend with other polymers. For example, Yadav, Rhee, and Park (2014) mixed graphene oxide (GO)/carboxymethyl cellulose (CMC)/alginate (Alg) to prepare the composite membranes. The tensile strength, Young's modulus and energy storage modulus of GO/CMC/Alg composite membranes were higher than those of CMC/Alg composite membranes. Sibaja et al. (2015) prepared the alginate/chitosan fiber by wet spinning method, and found that composite fibers had antibacterial and better mechanical properties due to the addition of Chitosan. Harper, Barbut, Lim, and Marcone (2013) mixed sodium alginate/protein to get Ca^{2+} crosslinked blend membranes, and found that protein content and species had an obvious impact on mechanical properties, but had a negligible effect on the breaking elongation of composite membranes. Bi, Limin, Jianfeng, and Hengying (2013) mixed collagen/alginate/carboxymethyl cellulose to get blend membrane, and found strong interaction and good compatibility among collagen, sodium alginate and carboxymethyl cellulose. The blending membrane had good mechanical property and thermal stability owing to the strong interaction of Ca^{2+}, hydrogen bonding and electrostatic attraction. Zhang et al. (2014) prepared alginate/feather protein (SA/FK) composite microspheres by extrusion method and found that the interaction of SA/FK system was mainly attributed to electrostatic action and hydrogen bonding. Kulig, Zimoch-Korzycka, Jarmoluk, and Marycz (2016) obtained a sodium alginate–chitosan complex material with variable degree of polyion interactions by complexation of oppositely charged polysaccharides. It found that the thermal decomposition temperature was dependent upon the polymer

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https://doi.org/10.1016/j.carbpol.2018.02.013
Received 12 December 2017; Received in revised form 23 January 2018; Accepted 5 February 2018
Available online 08 February 2018
0144-8617/

ratio and thermal resistance of samples could be significantly improved by increasing chitosan dosage. Marycz, Szarek, Grzesiak, and Wrzeszcz (2014) prepared a sodium alginate hydrogel for cell culture and found that addition of fibrin protein improved material's biocompatibility. Grzesiak, Marycz, Szarek, Bednarz, and Laska (2015) prepared polyurethane/polylactide-based biomaterials to apply in neural regenerative medicine and found that polyurethane–polylactide blend was an optimal composition for culturing and delivery of glial and mesenchymal stem cells.

As a marine organism, antarctic krill contains a large amount of protein (Yang & Xiaofang, 2014). But application of antarctic krill in diet is seriously limited due to the fact that it produces a large amount of fluorine during the fishing process. As a by-product of antarctic krill in deep processing, the krill shrimp powder is often used in the feed industry (Bax et al., 2012; Gigliotti, Davenport, Beamer, Tou, & Jaczynski, 2011). In order to explore high value-added applications for antarctic krill protein (AKP), a series of SA/AKP fiber products (Jing, Xuecai, Weina et al., 2014) were prepared through polyanion properties of SA and polycation properties of AKP by our research group. We also investigated the flame retardancy (Lijun et al., 2015) and dyeability (Lijun, Jing, Mengzhu et al., 2016) of SA/AKP composite fibers, and the effects of pH value and blending ratio on hydrogen bonding (Lijun, Jing, Yue et al., 2016) interaction between SA and AKP. At present, SA/AKP composite fiber is mainly used for the high-end artificial wigs. SA/AKP composites are regard as a substitute for biomass materials, which has a potential application in the biomedicine industry such as nerve catheter and artificial skin due to the good mechanical properties and biocompatibility. Sodium salt plays an important role in regulating the ionization degree of SA/AKP composite solution due to the polyelectrolyte system. Intermolecular interactions are related to the ionization degree. To discover and adjust the regularity of the intermolecular interaction between sodium salt and composite system, the effects of sodium salt types on the intermolecular interaction of SA/AKP composite fibers are studied in this paper.

2. Experimental and method

2.1. Materials

Sodium alginate with molecular weight of 3–5 × 10^6 g/mol was obtained from Qingdao Bright Moon Seaweed Group Co., Ltd, China. AKP was prepared via extraction in alkali solution: 50 g Antarctic krill power was added into 1.5% (w/w) NaOH solution for 6 h at 70 °C. AKP was prepared by isolating non-proteinaceous impurities, adjusting pH of solution, filtration and drying (Jing, Xuecai, Chunfang et al., 2014). Hydrochloric acid, sodium hydroxide, sodium acetate anhydrous, anhydrous sodium sulfate, calcium chloride anhydrous and sodium chloride, purchased from Tianjin Kemiou Chemical Reagent Co., Ltd, China. Acetic acid and sulfuric acid were obtained from Laiyang Kant Chemical Co., Ltd, China. All of chemical agents are analytical grade.

2.2. Preparation of composite fibers

2.2.1. SA/AKP composite solution

AKP solution was prepared via putting AKP into 0.25% (w/w) NaOH solution, adding 0.6% (w/w) different types of sodium salt to adjust the ionization degree and intermolecular interaction of composite system, heating and stirring for 1 h, then adjusting pH of solution by a pH Meter (pHS-3C, Shanghai Scientific Instrument Co., Ltd., China). The SA was added into AKP solution under mechanical agitation, afterward, degassing vacuum for 24 h, to get composite solution.

2.2.2. SA/AKP composite fibers

As illustrated in Fig. 1, the SA/AKP solution was forced through the spinneret into the 5% (w/w) $CaCl_2$ coagulation bath. Then SA/AKP composite fibers with different sodium salt of $1^{\#}$ (containing 0.6% NaCl), $2^{\#}$ (containing 0.6% CH_3COONa), $3^{\#}$ (containing 0.6% Na_2SO_4) were obtained successfully through stretching, secondary solidification, washing, drying and winding (Fourné, 1999, chap. 2).

2.3. Testing

The secondary structure of AKP protein and the intermolecular interaction in SA/AKP composite system were measured using Fourier-transformed infrared spectroscope (FT-IR) (Spectrum-One B, PE company, America), and the KBr pressed disk technique was used for SA/AKP sample preparation. The scanning range was 4500–400 cm^{-1}.

The breaking strength of composite fibers was measured using electronic single fiber strength meter (LLY-06ED, Laizhou Electronic Instrument Co., Ltd., China). Test conditions: the width of the fiber was 10 mm, the stretching speed was 20 mm/min, the ambient temperature was 20 °C and the air humidity was 65%. Every example was measured 10 times and then take average.

The crystal structure of SA/AKP composite fibers was determined using an X-ray diffractometer (XRD) (S-4800, HITACHI, Japan) with 2θ range 10–70° with a step size of 5°/min. Tube voltage is 40 kV. Tube current is 30 mA.

The surface morphology of SA/AKP composite fibers was observed using the scanning electron microscope (SEM) (JSM-6460LV, Electronics Company, Japan) at the accelerating voltage of 10 kV after sputter-coating with Au.

The thermal properties of SA/AKP composite fibers were measured using thermogravimetric analysis (TGA) (Q600, TA Company, America). TGA analysis of all the samples were carried out in N_2 atmosphere from 30 to 700 °C at a heat rate of 10 °C/min.

3. Results and discussion

3.1. FT-IR analysis

The FT-IR of SA and AKP are exhibited in Fig. 2(a). In the FT-IR spectrums of AKP, the absorption peaks located at 1657 cm^{-1} and 1533 cm^{-1} are characteristic of the amide I and amide II bands. In the FT-IR spectrums of SA, the peaks located at 1417 cm^{-1} and 1615 cm^{-1} are −COO− asymmetric stretching vibration and the symmetrical stretching vibration. The peaks located at 2922 cm^{-1} and 3428 cm^{-1} in SA are O−H vibration and C−H stretching vibration on the molecular six-membered ring. As illustrated in Fig. 2(b), there is no new absorption peak in the FT-IR spectrum of SA/AKP composite fibers with different types of sodium salt. It indicates that there is no chemical reaction between SA and AKP. However, absorption peaks produce a small shift, which may be attributed to the strong interaction between molecules of the composites depending on the types of sodium salt.

It has been reported in the literature (Kui, Rong, Jihong, Yingkai, & Jiangning, 2016; Yiqi, Wei, & Ruijin, 2015) that the secondary structure of proteins can be characterized by the amide I band. The more the content of β-sheet is, the better the mechanical properties of the composite fibers become (Helan & Yiqi, 2014; Zhao, Haihui, Xuechen, & Xingxiang, 2017). The broad peak at 1600–1700 cm^{-1} was smoothed using the Savitzky-Golay method by 15 points in Origin 9.1. The peak area ratio (i.e., the ratio of different types of proteins secondary structure) was calculated under subtract straight line and the Gauss peak fitting of peak analyzer. Different types of the secondary structure of proteins in composite fibers were ensured by percentage content, as illustrated in Table 1. Among them, 1620–1630 cm^{-1} represents β-sheet content, 1650–1660 cm^{-1} represents α-helix content, and 1670–1690 cm^{-1} represents random coil content (Zhao et al., 2017). As shown in Table 1, the types of sodium salt have some influence on the secondary structure of composite fibers. The content of β-sheet chain in composite fibers follows the order $1^{\#}$ fiber (14.33%) > $2^{\#}$ fiber (14.13%) > $3^{\#}$ fiber (10.68%) and this is also one of the reasons which affect the mechanical properties of composite fibers.