

BIOCOMPOSITE MEMBRANE MATERIAL, PREPARATION METHOD AND USE THEREOF

Field of the Invention

5 The present disclosure relates to a biocomposite membrane material, preparation method and use thereof.

Background of the Invention

Protein membranes are often used as casings, films for medical devices, etc.

10 Casings are used to extend the shelf life of meat, and are widely used in the processed meat industry. Natural casings were first developed using animal organs such as pig intestines, sheep intestines, and cow intestines. However, natural casings have shortcomings such as different calibers, natural flaws, softness and brittleness, and complicated and time-consuming production and pre-use processing processes, which

15 make it difficult to produce in weight production of automated machines. Various artificial casings are easy to control due to their material characteristics, and can meet the different processing needs of various products, and show more development possibilities. Artificial casings can be divided into two types: edible and inedible. Among them, collagen casings and cellulose casings are very common edible and

20 inedible casings respectively. Collagen casings use pig collagen fibers or cowhide collagen fibers as raw materials and are widely used in the food industry. However, a large number of cross-linking agents with safety risks are usually added during the preparation process. Cellulosic casings are not usually edible, but dietary fiber has been shown to have a variety of physiological functions and is beneficial to health.

25 Combining the advantages of protein and cellulose to prepare casings and reducing the use of additives is the trend in enteric preparation.

Summary of the Invention

Directed against the above problems with the existing technology, the present

30 disclosure provides a biocomposite membrane material, specifically a cellulose derivative-protein/gelatin casing and a cellulose derivative-protein/gelatin film. The biocomposite membrane material provided by the present disclosure solves the problems of numerous additions, residues, and poor safety in the protein casings and cellulose derivative-protein film, which caused by using cross-linking agents. The

biocomposite membrane material can adapt the characteristics of the casing to meet different needs by combining protein and cellulose derivatives.

In a first aspect, the present disclosure provides a biocomposite membrane material, which comprises a dialdehyde cellulose compound and a biomaterial,
5 wherein the biomaterial is selected from a collagen or a gelatin.

In some embodiments, the dialdehyde cellulose compound comprises a dialdehyde cellulose and/or a dialdehyde carboxymethyl cellulose.

In a second aspect, the present disclosure provides a method for preparing a biocomposite membrane material, which comprises mixing a dialdehyde cellulose
10 compound and a collagen or a gelatin in the presence of a solvent to form a mixture, and extrusion molding the mixture.

In some embodiments, the dialdehyde cellulose compound comprises a dialdehyde cellulose and/or a dialdehyde carboxymethyl cellulose.

In some embodiments, a weight concentration of the dialdehyde cellulose
15 compound is 2%-20%, such as 2%, 5%, 10%, 15%, 20% or any value between them.

In some embodiments, a weight concentration of the collagen is 5%-40%, such as 5%, 10%, 15%, 20%, 25%, 30%, 35%, 40% or any value between them.

In some embodiments, a weight concentration of the gelatin is 5%-40%, such as 5%, 10%, 15%, 20%, 25%, 30%, 35%, 40% or any value between them.

20 In some embodiments, a weight ratio of the dialdehyde cellulose compound to the collagen or the gelatin is 1:(0.5-5), such as, 1:0.5, 1:1, 1:2, 1:3, 1:4, 1:5, or any value between them.

In some embodiments, the solvent comprises water.

In some embodiments, the step of extrusion molding comprises extruding and
25 inflating to obtain a tubular casing or extruding to obtain a film.

In some embodiments, the dialdehyde cellulose compound is prepared by a method comprising the following steps:

(1) dispersing the cellulose compound in water or an acid solution to obtain a cellulose compound suspension;

30 (2) performing oxidation reaction between the cellulose compound suspension and a periodate salt to obtain a reaction product;

(3) performing a solid-liquid separation and drying on the reaction product after the oxidation reaction.

In some embodiments, the method further comprises adding an alcohol

compound to a reaction solution of the cellulose compound suspension and the periodate salt to terminate the oxidation reaction.

In some embodiments, the cellulose is dispersed in water. Preferably, a weight ratio of the cellulose to the water is 1: (1-50), such as, 1:1, 1:5, 1:10, 1:20, 1:30, 1:40, 1:50 or any value between them.

In some embodiments, the carboxymethyl cellulose is dispersed in the acid solution. Preferably, a weight ratio of the carboxymethyl cellulose to the acid solution is 1:(5-25), such as, 1:5, 1:10, 1:15, 1:20, 1:25 or any value between them.

In some embodiments, the acid solution is 0.1N sulfuric acid solution.

In some embodiments, a weight ratio of the periodate salt to the cellulose compound is 1: (0.3-10), such as, 1:0.3, 1:0.5, 1:2, 1:4, 1:6, 1:8, 1:10 or any value between them.

In some embodiments, the periodate salt is a sodium periodate.

In some embodiments, a molar ratio of the alcohol compound to the sodium periodate is 1: (0.3-10), such as, 1:0.3, 1:0.5, 1:2, 1:4, 1:6, 1:8, 1:10 or any value between them.

In some embodiments, the alcohol compound is selected from an ethylene glycol.

In some embodiments, the dialdehyde cellulose is prepared by the following steps:

(1) dispersing the cellulose: mixing the cellulose and water in a fixed weight ratio with at least 1 times the weight of water, and stirring continuously to form a suspension;

(2) oxidizing the cellulose: adding the sodium periodate in a weight ratio of 1: (0.3-10) to the cellulose into the suspension, and stirring the reaction continuously;

(3) terminating the oxidation reaction: adding the alcohol solution with a molar ratio of 1: (0.3-10) to the sodium periodate into the reaction solution and continue stirring; this step can be skipped in the continuous production process;

(4) purifying and drying the dialdehyde cellulose: filtering under reduced pressure to obtain a solid product, washing the solid product with water several times, and drying to obtain the dialdehyde cellulose.

In some embodiments, the dialdehyde carboxymethyl cellulose is prepared by the following steps:

(1) dispersing the carboxymethyl cellulose: mixing the carboxymethyl cellulose and 0.1N sulfuric acid solution at a weight ratio of 1: (5-25), and stirring continuously

to form a suspension;

(2) oxidizing the carboxymethyl cellulose: adding sodium periodate in a weight ratio of 1: (0.3-10) to carboxymethylcellulose into the suspension, and stirring the reaction continuously;

5 (3) terminating the oxidation reaction: adding the alcohol solution with a molar ratio of 1: (0.3-10) to the sodium periodate into the reaction solution and stirring continuously;

(4) purifying and drying the dialdehyde carboxymethyl cellulose: dialyzing the liquid product in water, evaporating under reduced pressure and drying to obtain the
10 dialdehyde carboxymethyl cellulose.

In some embodiments, the cellulose-protein composite material is prepared by the following steps:

(1) stirring and mixing: stirring and mixing the protein (containing ~60% w/w or more moisture) and the dialdehyde cellulose suspension (2% w/w or more) or
15 dialdehyde carboxymethyl cellulose solution (2% w/w or more) in a mixer;

(2) molding: extruding and inflating the mixture to obtain a tubular casing, or preparing a film by a film-making method;

(3) drying and plasticizing: drying the tubular casing or the film.

In some embodiments, the cellulose-gelatin composite material is prepared by
20 the following steps:

(1) stirring and mixing: stirring and mixing the gelatin solution (10% w/w or more) and the dialdehyde cellulose suspension (2% w/w or more) or dialdehyde carboxymethyl cellulose solution (2% w/w or more) to form a dough in a mixer;

(2) extrusion molding: extruding and inflating the mixture to obtain a tubular
25 casing, or preparing a film by a film-making method;

(3) drying and plasticizing: drying the tubular casing or the film.

In a third aspect, the present disclosure provides use of the biocomposite membrane material according to the first aspect or the biocomposite membrane material prepared by the preparation method according to the second aspect in
30 medical devices or food processing.

In the present disclosure, the cellulose is oxidatively modified into dialdehyde cellulose firstly. The dialdehyde cellulose can produce excellent cross-linking with proteins and has low biological toxicity. Alternatively, the carboxymethyl cellulose is oxidatively modified to the dialdehyde carboxymethyl cellulose, which has similar

properties to the dialdehyde cellulose. Then, the mixture of the dialdehyde cellulose or dialdehyde carboxymethyl cellulose and collagen is extruded and inflated to obtain a tubular casing, or a cellulose derivative-protein casing or a cellulose derivative-protein film prepared by a film-making method. In addition, the cellulose derivative-gelatin can also be prepared using similar methods. The biocomposite membrane material provided by the present disclosure not only avoids the problems of numerous additions, residues, and poor safety caused by use of cross-linking agents, but also improves the tensile strength and elongation at break of the biocomposite membrane material.

Examples and drawings are provided below to aid understanding of the present disclosure. However, it should be understood that these examples and drawings are only used to illustrate the present disclosure and do not constitute any limitation. The actual scope of the invention is set forth in the claims. It is understood that any modifications and changes may be made without departing from the spirit of the invention.

Brief Description of the Drawings

Fig. 1 shows the Fourier Transform infrared spectroscopy of the cellulose (Cellulose) and dialdehyde cellulose (DC) in Example 1.

Fig. 2 shows the Fourier Transform infrared spectroscopy of the carboxymethyl cellulose (CMC), dialdehyde carboxymethyl cellulose (DCMC) 0.5 and dialdehyde carboxymethyl cellulose (DCMC) 1 in Examples 2 and 3.

Fig. 3 shows photographs of the collagen-DCMC membrane (upper) and the collagen-DC membrane (lower) of Example 2 and Example 1.

Detailed Description of the Embodiments

In order to make the purpose, technical solutions and advantages of the present disclosure more clear, the present disclosure will be further described in detail below with reference to the examples. The exemplary described here are only used to explain the present disclosure and are not intended to constitute any limitation on the present disclosure. Furthermore, in the following description, descriptions of well-known structures and techniques are omitted to avoid unnecessarily confusing the concepts of the present disclosure.

Example 1. Preparation of the collagen-dialdehyde cellulose (collagen-DC)

film

(1) 10g of cellulose was added to 100mL of deionized water and stirred with an electromagnetic stirrer to form a suspension. 13.2g sodium periodate was added to the suspension and stirred continuously. The reaction was carried out in the dark at 50°C for 5 hours. Then, 1.7 mL of ethylene glycol was added to the reaction solution for 0.5 hours. The product was washed several times with deionized water and filtered under reduced pressure. Finally, the product was dried. The dialdehyde cellulose (DC) was obtained. The Fourier Transform infrared spectroscopy of the cellulose (Cellulose) and dialdehyde cellulose (DC) are shown in Fig. 1.

(2) 5g collagen (containing ~90% w/w moisture) and 5g DC suspension (10% w/w) were stirred and mixed. A small amount of the stirred product was covered with cooking paper, put into a dough press and extruded in a decreasing thickness manner. The collagen-dialdehyde cellulose (collagen-DC) membrane was obtained, as shown in Fig. 3 (lower).

Example 2. Preparation of the collagen-dialdehyde carboxymethyl cellulose (collagen-DCMC) film

(1) 8 mL of 5N sulfuric acid was added to 400 mL of deionized water, stirred continuously and 20.0 g of carboxymethyl cellulose was added. After the carboxymethyl cellulose was evenly dispersed, 200mL of sodium periodate solution (0.1g/mL) was added to the carboxymethyl cellulose dispersion. The solution was heated to 40°C over water, protected from light and stirred continuously. After 4 hours of reaction, 2.6 mL of ethylene glycol was added and the reaction was continued for 0.5 hours. The product was dialyzed against deionized water using a dialysis bag (MWCO 3500Da) for two days. Finally, the product was evaporated under reduced pressure to a viscous liquid and dried at 40°C. The dialdehyde carboxymethyl cellulose (DCMC 0.5) was obtained. The Fourier Transform infrared spectroscopy of the carboxymethyl cellulose (CMC) and dialdehyde carboxymethyl cellulose (DCMC) 0.5 are shown in Fig. 2.

(2) 5g collagen (containing ~90% w/w moisture) and 5g DCMC solution (10% w/w) were stirred and mixed. A small amount of the stirred product was covered with cooking paper, put into a dough press and extruded in a decreasing thickness manner. The collagen-dialdehyde carboxymethyl cellulose (collagen-DCMC) film was obtained, as shown in Fig. 3 (upper).

Example 3. Preparation of the collagen-dialdehyde carboxymethyl cellulose (collagen-DCMC) film

(1) 8 mL of 5N sulfuric acid was added to 400 mL of deionized water, stirred continuously and 20.0 g of carboxymethyl cellulose was added. After the carboxymethyl cellulose was evenly dispersed, 200mL of sodium periodate solution (0.1g/mL) was added to the carboxymethyl cellulose dispersion. The solution was heated to 40°C over water, protected from light and stirred continuously. After 4 hours of reaction, 2.6 mL of ethylene glycol was added and the reaction was continued for 1 hour. The product was dialyzed against deionized water using a dialysis bag (MWCO 3500Da) for two days. Finally, the product was evaporated under reduced pressure to a viscous liquid and dried at 40°C. The dialdehyde carboxymethyl cellulose (DCMC 1) was obtained. The Fourier Transform infrared spectroscopy of the carboxymethyl cellulose (CMC) and dialdehyde carboxymethyl cellulose (DCMC) 1 are shown in Fig. 2.

(2) 5g collagen (containing ~90% w/w moisture) and 5g DCMC solution (10% w/w) were stirred and mixed. A small amount of the stirred product was covered with cooking paper, put into a dough press and extruded in a decreasing thickness manner. The collagen-dialdehyde carboxymethyl cellulose (collagen-DCMC) film was obtained, as shown in Fig. 3 (upper).

Test Example 1. Aldehyde Group Content Test

The aldehyde group content of the dialdehyde carboxymethyl cellulose (DCMC) and dialdehyde cellulose (DC) was tested, and the results are shown in Table 1.

Table 1 Aldehyde group content of DCMC and DC after modification reaction (n=3).

Sample	aldehyde group content (mmol/g)
DCMC 0.5	0.45 ± 0.13
DCMC 1.0	1.12 ± 0.10
DC	3.28 ± 0.25

Test Example 2 Tensile strength (TS) and elongation at break (EB) test of film

The tensile strength (TS) and elongation at break (EB) of the films prepared in

Examples 1-3 were tested, and the results are shown in Table 2.

Table 2 Tensile strength (TS) and elongation at break (EB) of the film

Sample	TS (MPa)	EB (%)
Example 1	26.70 ± 4.13	102.74 ± 0.17
Example 2	30.28 ± 5.06	103.28 ± 1.04
Example 3	34.76 ± 8.17	108.68 ± 0.96
Cellulose casing	23.49 ± 5.04	105.55 ± 0.80
Collagen casing	21.26 ± 1.68	134.03 ± 1.85

- 5 The technical solution of the present disclosure is not limited to the above-mentioned specific examples. All technical variations made based on the technical solution of the present disclosure fall within the protection scope of the present disclosure.

Claims

1. A biocomposite membrane material, comprising a dialdehyde cellulose compound and a biomaterial, wherein the biological material is selected from a collagen or a gelatin.
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2. The biocomposite membrane material according to claim 1, wherein the dialdehyde cellulose compound comprises a dialdehyde cellulose and/or a dialdehyde carboxymethyl cellulose.
3. A method for preparing a biocomposite membrane material, comprising mixing a dialdehyde cellulose compound and a collagen or a gelatin in the presence of a solvent to form a mixture, and extrusion molding the mixture.
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4. The method according to claim 3, wherein the dialdehyde cellulose compound comprises a dialdehyde cellulose and/or a dialdehyde carboxymethyl cellulose.
5. The method according to claim 3 or 4, wherein a weight concentration of the dialdehyde cellulose compound is 2%-20%; and/or
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a weight concentration of the collagen is 5%-40%; and/or
a weight concentration of the gelatin is 5%-40%; and/or
a weight ratio of the dialdehyde cellulose compound to the collagen or the gelatin is 1: (0.5-5); and/or
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the solvent comprises water.
6. The method according to any one of claims 3 to 5, wherein the step of extrusion molding comprises extruding and inflating to obtain a tubular casing or extruding to obtain a film.
7. The method according to any one of claims 3 to 6, wherein the dialdehyde cellulose compound is prepared by a method comprising the following steps:
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(1) dispersing the cellulose compound in water or an acid solution to obtain a cellulose compound suspension;
(2) performing oxidation reaction between the cellulose compound suspension and a periodate salt to obtain a reaction product;
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(3) performing a solid-liquid separation and drying on the reaction product after the oxidation reaction;
optionally, the method further comprises adding an alcohol compound to the reaction solution of the cellulose compound suspension and the periodate salt to terminate the oxidation reaction.

8. The method according to claim 7, wherein the cellulose is dispersed in water, preferably, a weight ratio of the cellulose to the water is 1: (1-50); and/or

the carboxymethyl cellulose is dispersed in the acid solution, preferably, a weight ratio of the carboxymethyl cellulose to the acid solution is 1: (5-25); and/or

5 the acid solution is 0.1N sulfuric acid solution.

9. The method according to claim 7 or 8, wherein a weight ratio of the periodate salt to the cellulose compound is 1: (0.3-10); and/or

a molar ratio of the alcohol compound to the sodium periodate is 1: (0.3-10); and/or

10 the alcohol compound is selected from ethylene glycol.

10. Use of the biocomposite membrane material according to claim 1 or 2 or the biocomposite membrane material prepared by the method according to any one of claims 3 to 9 in medical devices or food processing.