Sisal Fiber Reinforced Collagen Biocomposites*

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Abstract: This paper presents an investigation on the preparation and properties of an environmentally friendly biocomposite based on collagen hydrolysate (CH) and sisal fibers (SF). Collagen hydrolysate was crosslinked by glutaraldehyde (GTA) and plasticized by glycerol to improve the mechanical performance. The influences of GTA content, CH concentration and glycerol content on the swelling ratio of the modified collagen were investigated. Alkali treatment was applied to sisal fiber to remove the non-cellulose materials and to induce cellulose fibers fibrillation. With modified CH as the matrix and alkali treated short sisal fiber as reinforcing agent, SF/CH biocomposites were prepared by a solvent-casting method. Morphologies of the samples were characterized by using scanning electron microscopy (SEM). It was found that alkali treatment improves the surface structure of SF and decreases the fiber diameter. Alkali treatment made it easy for CH to penetrate into the cavities of SF due to the removing of cementing substances on the inner surface of the lumens. The influence of sisal fiber treatment, fiber content and fiber length on the mechanical properties of the biocomposites was discussed. It was found that the mechanical properties were improved greatly when the sisal fiber mass fraction is 15% with the fiber length of 7–8 mm.

Key words: collagen hydrolysate; sisal fiber; biocomposite; swelling ratio; mechanical properties

1 Introduction

The relatively greatest proportion of collagen waste is from leather making. A lot of studies have been done on the extraction and use of the collagen from leather making. Collagen hydrolysate (CH) derived from leather processing is a kind of hydrolyzed product. The three top collagen strands are partially or completely separated into globular domains, containing a different secondary structure to the normal collagen random coils, due to the poor mechanical properties. The mechanical properties can be improved by adding chemical reagents to make linkages between molecules and intermolecular. Another way to improve the mechanical properties is the introduction of fiber-like materials to obtain a new composite. The fiber-protein composites with functionality have broad applications. There are many researches on fiber-like materials reinforced composites [1-5]. Natural fibers such as fibers of cotton, ramie, jute, flax, sisal, and wood can be a renewable and cheaper substitute for synthetic fibers, and have numerous advantages, such as low cost, low density, high toughness, acceptable specific strength properties, ease of separation, and biodegradability [6-12].

This paper presented an investigation on the preparation and properties of an environmentally friendly biocomposites based on collagen hydrolysate (CH) and sisal fibers (SF). CH was crosslinked by glutaraldehyde (GTA) and plasticized by glycerol to improve the mechanical performance. The influences of GTA content, CH concentration, and glycerol content on the swelling ratio of the modified collagen were investigated. The influence of sisal fiber treatment, fiber content and fiber length on the mechanical properties of the biocomposites was discussed.

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2 Experimental

2.1 Materials

Collagen hydrolysate (industrial grade) is supplied by Xinxiang Biological Chemical Co Ltd. Sisal cellulose fibers with the diameter of 100μm are supplied by Guangxi Sisal Company, China. 50% Glutaraldehyde solution (GTA), NaOH and glycerol are analytic grade.

2.2 Sisal fibers (SF) surface modification

The chopped SF and a 10 % solution of NaOH were put into a stainless steel vessel at 25℃ and the mixture was stirred for 1 h. Afterward, the sisal fibers were washed thoroughly with water to remove any excess NaOH until the pH of the washed water was 7.0. And then, they were vacuum dried.

2.3 Modification of CH and the preparation of biocomposites

The powdery CH was dissolved into 40 ml distilled water, and the solution with some glycerol was stirred at 60℃ to get a homogeneous solution. The pH of the solution was adjusted with 30% NaOH to 9.0. And then, some dose of 50% GTA was dropwise added in the solution under a continuous stirring, and the mixture was vigorously stirred and fully reacted for 1 h. Finally, the mixture was poured into an open mould and then, fully dried in the blast drying oven at 60℃. The modified CH, glycerol and SF were added into a flask in the water bath at 60℃, under a good stirring. After about 1 h, the mixture was poured into polypropylene mould, and then dried as described above.

2.4 Swelling ratio

The modified CH samples (20 mm × 20 mm × 1.5 mm) were swollen in water and equilibrated in PBS (pH 7.2) at room temperature for 12 h. The samples were removed quickly blotted with filter paper to remove excess surface water and weighed immediately. The samples were then washed with the demonized water to remove the excess buffer salts and dried in blast drying oven at 80℃ for 24 h, and then weighed. The swelling ratio was calculated as

\[ Q = \frac{m_1}{m_2} \times 100\% \]

Where \( m_1 \) and \( m_2 \) were the weights of the wet and the dried samples, respectively.

2.5 SEM study and mechanical tests

The composite samples were observed by scanning electron microscopy (Quanta 200, FEI, Holland). The accelerating voltage applied was 5 KeV. The samples were cryofractured to observe the sample cross sections. All the samples were sputter-coated with gold before examination. Mechanical tests were carried out using CMT5104 testing machine. The sample effective size was 25.0 mm × 6.5 mm. Tensile testing was performed at an extension rate of 50 mm/min.

3 Results and discussion

3.1 Swelling ratio

The influence of glutaraldehyde content on the swelling ratio of modified CH is shown in Fig. 1. From Fig 1, it was found that with increasing the glutaraldehyde content in the composite, the swelling ratio decreases first and then increases. The result indicated that the short-range cross-linkage occurred in the self-organized units to restrict water intrusion into CH. Consequently, water amount in the composite decreased at low GTA concentration because GTA molecules were consumed mainly in the molecule chain. Even if they are used for intermolecular cross-linkage, only short chains are formed because of little excess of GTA. However, with GTA amount increasing, intermolecular cross-linkage with long GTA
chains increased and maintained large amounts of water because the GTA chain between the self-organized units resisted the dehydration pressure as schematically illustrated in Fig. 2.\(^\text{[14]}\).

**Fig. 1 Influence of glutaraldehyde content on the swelling ratio of modified CH**

**Fig. 2 Schematic drawing of GTA cross-linked CH**

**Fig. 3 Influence of CH concentration (a) and glycerin content (b) on the swelling ratio of modified CH**

The influence of CH concentration on the swelling ratio of modified collagen is shown in Fig. 3a. The swelling ratio decreased with increasing the collagen concentration. The cross-linkage may occur within the molecular chain when the CH concentration was low to get a soluble resulted modified CH. The cross-linking reactions may take place between the macromolecules at high collagen concentration to get networks in the modified CH, which restricted the movement of the molecules and decreased the swelling degree.

The pure CH films were brittle with less flexible, and plasticizers is usually needed to improve the physical properties. Glycerol is the most widely used plasticizers, which is hydrophilic and can be mixed with water at any ratio. The influence of glycerin content on the swelling ratio of modified CH is shown in Fig. 3b. The swelling ratio was increased and the crosslink degree was decreased with the addition of glycerin.

### 3.3 Morphologies of sisal fiber and the composites

**Fig. 4 Surface contour of sisal fiber, (a) untreated; (b) alkali treated. (1000x)**

**Fig. 5 Cross sectional morphologies of SF/CH composites, (a) untreated sisal fibers; (b) alkali treated sisal fibers**

This surface modification process usually greatly affects the morphology, mechanical properties and thermal degradation of natural fibers. Alkali treatment is the common method to produce high-quality
fibers. Moreover, alkali treatment increases the number of possible reactive sites and allows better fiber wetting.

Fig. 4 shows the surface morphology of the natural and alkali modified SF. It can be seen that the surface of sisal fiber was wrapped with some “cementing substances” before alkali treatment, which made the epidermal cells of sisal fiber combined with neighboring cells closely. Alkali reagents has an effect on the chemical composition of the fibers, the degree of polymerization and the molecular orientation of the cellulose crystallites due to “cementing substances” like lignin and hemicelluloses that were removed during the treatment process.

Fig. 5 shows the cross sectional morphologies of SF/CH composites, where the SF mass fraction was 15%. The untreated fibers formed the hollow structure in composites, where the untreated sisal fibers could not be wetted by the modified CH (Fig. 5a). Alkali treatment removed “cementing substances” and produced a rough surface topography. The porous of fibers was filled with modified CH (Fig. 5b), which indicated that the treatment improved the interfacial adhesion between fibers and modified CH. The modified CH solution could penetrate into the microspores of SF to form mosaic structure morphology and to improve the mechanical property of composites.

### 3.4 Mechanical properties

<table>
<thead>
<tr>
<th></th>
<th>Tensile strength (MPa)</th>
<th>Young's modulus (MPa)</th>
<th>Elongation at break (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SF untreated</td>
<td>0.9</td>
<td>7.6</td>
<td>33</td>
</tr>
<tr>
<td>SF treated with alkali</td>
<td>1.7</td>
<td>19.9</td>
<td>57</td>
</tr>
</tbody>
</table>

**Note:** SF mass fraction 10%, fiber length 7~8mm.

As shown in Tab 1, the alkali treated SF/CH composites were better than untreated SF/CH composites on tensile strength, Young's modulus and elongation at break. This indicated that the alkali treated sisal fiber was a kind of good reinforcement to modified CH. Alkali treatment increased the effective surface area available for wetting by the matrix resin. Therefore, increasing the fiber aspect ratio by reducing the fiber diameter and getting a rough surface topography may improve the fiber/CH interface adhesion and increase the mechanical properties.

![Fig. 6 Influence of sisal fiber content on the mechanical properties of the SF/collagen composites](image)

The influence of SF content on the mechanical properties of the SF/CH composite (the length of the sisal fiber: 7~8mm) is shown in Fig. 6. With the increase of sisal fiber content, the tensile strength (Fig. 6a), Young's modulus (Fig. 6b) are increased first and then decreased. The elongation at break, however, was decreased (Fig. 6c), which was in line with the changes of mechanical properties of general natural
fiber reinforced polymer composites. Sisal fibers with good mechanical properties could share tensile stress when the composites were being stretched. As the content of the sisal fibers increased, more fibers shared the tensile stress to improve the tensile strength and Young’s modulus greatly. On the other hand, the limit deformation of sisal fibers made the elongation at break decrease. When the mass fraction of sisal fiber above 15%, the fibers could not distribute evenly and the defects of the composite increased, which limited the improvement of mechanical properties.

![Graphs showing influence of fiber length on mechanical properties](image)

**Fig. 7 Influence of sisal fiber length on the mechanical properties of the sisal fiber/collagen composites**

Some factors may have influences on the fiber-like reinforcement, such as the fiber properties, content, aspect ratio and the adhesion between fibers and matrixes. Among these factors, the fiber aspect ratio is the most important one. The shear stress between fibers and matrix should be greater than or equal to fiber tensile yield stress to make the fibers with a good reinforcement effects. So, the fiber aspect ratio must be greater than or equal to critical value, called fiber critical length. In this research, different length fibers were added into modified CH to study the effects of fiber aspect ratio on the composite mechanical properties. Fig. 7 shows the influence of sisal fiber length on the mechanical properties of the sisal fiber/CH composites. The chosen lengths of fibers were 3–4 mm, 7–8 mm, 11–12 mm, the fiber mass fraction all was 15%. When the length of sisal fiber was 7–8 mm, the tensile strength and Young’s modulus were ideal, indicating that the fibers with this length range have good reinforcement effects. Generally speaking, in the case of composite, the fiber end could not transfer the stress, and the fiber length should be greater than the effective length for the fibers to share the maximal stress. With the same fiber content, the number of longer fiber ends was smaller than the short ones, so the chances to encounter the cracks were more for longer fibers. The chances of cracks termination were more. On the other hand, the longer fiber would enamel each other together and distribute unevenly. The defects increased due to the stress could not transfer to matrix. Therefore, the composites had not ideal mechanical properties when longer fiber (11~12 mm) added.

4 Conclusions

Collagen hydrolysate could be modified at the temperature of 60°C and the pH of 9.0. The swelling ratio decreased with increasing the collagen concentration. The swelling ratio increases and the crosslinking decreases with the addition of glycerin. The decreasing network structures and the increasing degree of freedom yields increased swelling ratio. Alkali treatment leads to a rough surface topography and results in better fiber matrix interface adhesion to increase the mechanical properties. The mechanical properties of composites were improved dramatically when the sisal fiber mass fraction was 15% and the fiber length was 7–8 mm.
References