A method for the process of collagen modified polyester from fish scales waste

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**Abstract**

In this study, we introduced a novel polymerization method of polyester using collagen peptides derived from fish scale waste. After the extraction process of collagen peptide from fish scales, putting collagen peptide, ethylene glycol and Benzenedicarboxylic acid into a container, and mixing them to form a mixture; heating the mixture for executing an esterification reaction, to product esters and water; heating the esters, and stirring the esters via a mixer; in a specific period, decreasing the pressure in the container for executing a polycondensation reaction; decreasing the pressure in the container to a second pressure, and stirring the esters via the mixer, to produce a collagen modified polyester.

Collagen peptides are rich in glycine, proline, and hydroxyproline, and by forming a triple helix structure, such as that of the copolyester, gain better hydrophilicity, antistaticity, and ductility. As a result, the produced collagen modified polyester fiber keeps the characteristics of the traditional polyethylene terephthalate fibers including strength, durability, and resistance to wrinkle and shrink. However, the supramolecular collagen modified polyester containing animal collagen peptides has naturally a soft touch and champagne-like color. Consequently, it can be used as a suitable material for skin-friendly functional clothes with or without additional dying. In brief,

- This study introduces a novel method for collagen modified polyester.
- Upcycled fish scale waste brings the sustainable benefits of circular economy.
- Collagen modified polyester provides a new direction for future technological development in the textile industry.

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Specifications table

| Subject Area: | Materials Science |
|---------------|-------------------|
| More specific subject area: | Textile Material |
| Method name: | Supramolecular polymerization for collagen modified polyester |
| Name and reference of original method: | NA |
| Resource availability: | NA |

Background

Polyester commonly refers to polyethylene terephthalate (PET) whose forming substance is any long-chain synthetic polymer composed of at least 85% by weight of an ester, dihydric alcohol and terephthalic acid. The advantages of polyester include durable, lightweight and anti-wrinkle. The disadvantages of polyester include airtightness and a harder touch. The hygroscopicity of polyester fiber is so poor that the clothing made from polyester fiber makes the skin sticky, clammy and uncomfortable. As a result, polyester fibers and various textile fibers are usually blended or interwoven products, which compensate for the shortcomings of pure polyester fiber fabrics. For example, polyester and cotton blends are common in polo shirts. In addition, polyester and rayon blends are common in men and women suits. Blended or interwoven polyester products are usually more skin-friendly. Besides, application of moisture management chemicals is used to improve the comfort and esthetic properties of polyester fibers [1]. Alkaline and enzyme hydrolysis, plasma, and grafting are popular methods for modifying the chemical and physical characteristics of polyester fabrics for improving their moisture management property [2].

In the food industry, collagen is widely used as a nutritional supplement in the food industry. Recently, due to the mad cow and other problems, collagen extracted from animals has gradually been replaced by other sources [3]. One of the alternative collagen sources is aquaculture waste material (fish skin and scales) [4–7]. Compared to collagen from animals, collagen from fish scales has advantages such as fat-free, antibiotic-free and prion-free [7]. Consumers often take collagen in nutritional supplements. The nutritional value of collagen peptides from fish scales has also been widely studied [8,9]. Rather than using collagen from scales as a food source, we conceived its application as textile material. Collagens are composed of three α-chains that assemble into complex hierarchical fibers or other structures [10]. We developed a method of producing collagen modified polyester with fish scale-derived collagen in order to improve the properties of common polyester fibers [11].

The extraction process of collagen peptide from fish scales

The methods to extract collagen peptides from fish skins and scales have been investigated [6,7,12] Fig. 1. Illustrates the process of producing collagen peptide from fish scales [13].

Step 1 (Washing): Wash fish scales with purified water.
Step 2 (Drying): Dry fish scales with cooling fans.
Step 3 (Freeze-drying): Send fish scales into a cold dried chamber. Quick freeze under vacuum conditions.
Step 4 (Smashing): Micronize fish scales by mechanical crusher
Step 5 (Enzyme treatment): Add enzyme to the finely crushed fish scale material, and perform enzyme treatment under warm water.
Step 6 (Filter): After centrifugal filtration of the hydrolyzed liquid, it is dried into a powder.
Washing  Freeze-drying  Enzyme treatment
Drying  Smashing  Filter

Fig. 1. The process of Collagen peptide from fish scales.

Fig. 2. The stages of supramolecular polymerization. (a) mixing of raw materials and catalysts, (b) Introducing nitrogen into the container and stirring the mixture, (c) Heating the mixture for executing an esterification reaction from 210 °C to 270 °C, (d) Decreasing the pressure to 20 torr in the container for a polycondensation reaction, (e) Decreasing the pressure to 3 torr in the container and forming copolyester material and (f) the produced bionic polyester pellets. The values of pressure are not limited thereto and can be changed in accordance with the needs.

**Process of producing collagen modified polyester materials**

The materials for producing the proposed collagen modified polyester include collagen peptides derived from fish scales, benzenedicarboxylic acid, ethylene glycol and catalysts. The molar ratio of collagen peptides and Benzenedicarboxylic acid was (0.47–0.60):(1.14–1.26). The benzenedicarboxylic acid was terephthalic Acid (TPA) or iso-phthalic Acid (IPA), or a combination of TPA and IPA. The catalysts were Sb$_2$O$_3$ and TiO$_2$ and the ratio range of ppm concentration between Sb$_2$O$_3$ and TiO$_2$ was (160–360):(0–60).

The entire process of producing collagen modified polyester is illustrated in Fig. 3 including the three steps:

Step 1 (Supramolecular polymerization): The proposed supramolecular polymerization is an adjusted procedure of normal polymerization method (Fig. 2).

Step 2 (POY Extrusion): The extrusion process includes the melting of polyester chips to form a syrup-like solution which is put in a spinneret and forced through its tiny holes to produce POY (Partially oriented yarns).

Step 3 (Draw texturing): The draw texturing process makes collagen modified silk POY become the collagen modified silk DTY (Draw textured yarns).
Conclusion

In summary, we introduced a new process for producing collagen-modified polyester from fish scale waste. This produced material has excellent deodorant and moisture regain activity, and is friendly to the skin. The collagen extracted from fish scales helps to reuse aquaculture waste. The manufacturing process changes the molecular structure of the polyester, and gives it a natural champagne gold color. The produced collagen modified polyester material can be used in many products such as base fabrics, socks, tops, denim fabrics, outerwear, bedding, etc.

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Declaration of Competing Interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests. This research was sponsored by Camangi Corporation (Taiwan) and may lead to the development of products that may be licensed to Camangi Corporation (Taiwan), in which we have a business and/or financial interest. We have disclosed those interests fully to SAGE Publishing, and have in place an approved plan for managing any potential conflicts arising from this arrangement. The trade name of the proposed bionic silk polyester fiber is “UMORFIL T”

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