Available online at www.sciencedirect.com
SCIENCE DIRECT
Polymer 46 (2005) 11193–11194
polymer
www.elsevier.com/locate/polymer

Polymer Communication

Gel-spinning and drawing of gelatin

Ryohei Fukae [a,*], Asuka Maekawa [a], Osamu Sangen [b]

[a] School of Human Science and Environment, University of Hyogo, 1-1-12, Shinzaikehoncho, Himeji 670-0092, Japan
[b] Faculty of Engineering, Himeji Institute of Technology, 2167, Shosha, Himeji 671-2201, Japan

Received 14 March 2005; accepted 2 October 2005
Available online 24 October 2005

Abstract

Gelatin fibers can be prepared by the gel-spinning method using dimethyl sulfoxide as a solvent. The use of the method and the drawing in a gel state were effective in inducing segmental orientation in gelatin fiber. The fibers showed high values for the mechanical properties of tensile strength of 180 MPa and Young's modulus of 3.4 GPa.

Keywords: Gelatin; Fiber; Gel-spinning

1. Introduction

Producing fibers from gelatin could widen the application field. As collagen fibers have attracted attention as a useful material for tissue-engineering applications, the preparation of a gelatin fiber has attained greater importance. In its preparation, more efficient purification of starting material is possible, compared to collagen. There have been several attempts to prepare the gelatin fiber; for example, the wet-spinning of concentrated gelatin aqueous solution followed by the cross-linking treatment of the obtained fiber with glutaraldehyde (GTA) etc., and the wet-spinning of gelatin crosslinked with GTA in aqueous or organic (e.g. dimethyl acetic amide) solution [1–3]. With such spinning procedures, however, it is probably difficult to prepare the gelatin fiber with sufficient drawability.

We have succeeded in preparing segmentally orientated gelatin fibers with high mechanical strength by the gel-spinning method using dimethyl sulfoxide (DMSO) as a solvent. In this report, the gel-spinning process and the physical properties of the obtained fibers are described.

2. Experimental

2.1. Material and treatment

Type A gelatin (Sigma-Aldrich Co., Ltd) prepared from porcine skin was used. Number- and weight-average molecular weights of the gelatin were estimated by gel permeation chromatography to be ca. 1.8×10^4 and ca. 6.2×10^4, respectively. Heat-treatment was carried out for 1 h under an inert atmosphere, at a constant tension of the fiber. Chemical crosslinkings were carried out by the immersion of the fiber in a 2.5 wt% glutaraldehyde solution in phosphate buffer at pH 7.4.

2.2. Gel-spinning of gelatin

A 10% gelatin-DMSO solution maintained at 60 °C was used for the spinning. Gel fiber was formed when the solution was extruded into a methanol bath held at −20 °C through a single nozzle 0.3 mm in internal diameter with an air gap of 5 mm. The fiber was rolled up and immediately drawn to required multiple of its original length. The drawn fiber was immersed in methanol for a week for the extraction of the solvent.

2.3. Measurements

Tensile tests were run on the fibers of 20-mm gauge length at a crosshead speed of 20 mm/min with a Tensilon Universal Tester RTC-1350A (Orientec Co. Ltd). The tensile strength and Young's modulus were evaluated from the stress–strain curves. The dynamic storage modulus, the loss modulus and the loss tangent were measured at 110 Hz and at a heating rate of 2 °C/min with a dynamic viscoelastic analyzer DVE-V4 (UBM Co. Ltd). Wide-angle X-ray diffraction patterns were recorded on an imaging plate for 40 min with a Rigaku RINT-2000 diffractometer under nickel-filtered Cu Kα radiation (40 kV, 100 mA).

* Corresponding author. Tel.: +81 792 92 9389; fax: +81 792 93 5710.
E-mail address: fukae@shse.u-hyogo.ac.jp (R. Fukae).

0032-3861/$ - see front matter © 2005 Elsevier Ltd. All rights reserved.
doi:10.1016/j.polymer.2005.10.001

Table 1
Mechanical properties of gelatin fibers

Draw ratio	Treatment after drawing	Tensile strength (Mpa)	Young's modulus (GPa)
–	–	28	0.7
4	–	81	1.9
8	–	180	3.4
4	Heated at 180 °C	79	1.9
	Heated at 220 °C	82	1.7
4	Crosslinked with GTA	112	1.9

3. Results and discussion

Table 1 shows the mechanical properties of the prepared gelatin fibers. Tensile strength (σ_b) and Young's modulus (E) of the undrawn fiber are 28 MPa and 0.7 GPa, respectively. The values of σ_b and E increase by drawing, and reach 180 MPa and 3.4 GPa when the fiber is drawn to eight times its original length.

Nagura et al. have reported that the gelatin fiber, which is prepared by wet-spinning of the concentrated gelatin aqueous solution (20 wt%) and subsequently heat-treated at 150 °C for 3 h, shows a σ_b value of 130 MPa and an E value of 7 GPa [3]. However, there is no reference to the drawability of the spun fibers. As to the gelatin specimen having no plasticizer, there are very few studies of the changes in properties by drawing. Bigi et al. have prepared water-cast films of gelatin, and noted the properties of the films drawn in a mixture of water and ethanol [4,5]. In their report, the values of σ_b and E also increase with the draw ratio, and these values were found to be 15 and 150 MPa, respectively in drawing the film to twice the original length, and 30 and 250 MPa when drawn to three times the original length. They have mentioned that the improvement in the mechanical properties by drawing is due to inducing segmental orientation in gelatin film.

In our study, the gel-spun fiber was found to be drawn to eight times its original length. The value of σ_b of the drawn fiber is approximately six times that of the drawn film sample reported by Bigi et al., and the value of E is approximately fourteen times greater. The use of the gel-spinning process and the drawing in a gel state are considered to be effective in inducing segmental orientation in gelatin fiber. Wide-angle X-ray diffraction patterns of gelatin fibers are shown in Fig. 1. The molecules of gelatin have been thought to form a pseudo-crystalline structure similar to the triple-helix structure of natural collagen in its gelation [6]. Compared with undrawn fiber, the lattice spots are located near the equatorial axial line in the drawn fiber. This suggests that the crystalline form can align along the drawing direction, which improves the mechanical properties of the fiber.

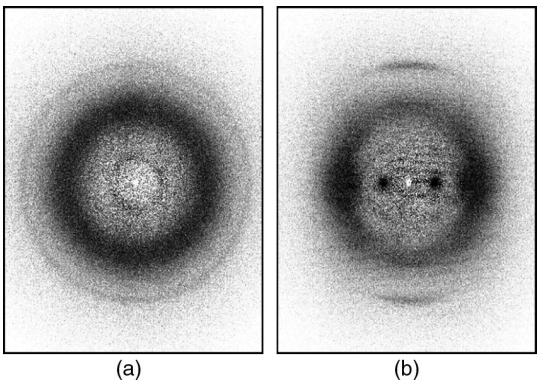

Fig. 1. Wide-angle X-ray diffraction patterns of gelatin fibers: (a) undrawn fiber; (b) fiber drawn to four times its length.

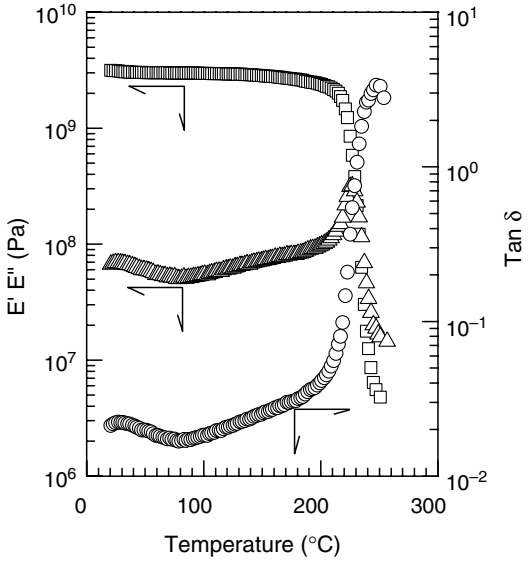

Fig. 2. Temperature dependencies of the dynamic storage modulus (E'), the loss modulus (E'') and the loss tangent (tan δ) for the gelatin fiber drawn to four times its length.

Temperature dependencies of the dynamic storage modulus (E'), the loss modulus and the loss tangent of the fiber drawn to four times its length are shown in Fig. 2. The value of E' is approximately 3 GPa at room temperature. The change in E' is extremely small below ca. 200 °C, and E' decreases rapidly beyond 200 °C. The fiber drawn to four times its length is soluble in water at approximately 35 °C. When the fiber is heat-treated at 180 °C, it is insoluble in water at 40 °C. In contrast, fiber heat-treated at 220 °C or fiber treated with GTA for 24 h is insoluble even in water at 90 °C.

References

[1] Tokura S, Tamura H., Jpn Patent 1999; 3 086 822.
[2] Yokota H, Gotoh Y, Ohkoshi Y, Nagura M. Fiber Prepr Jpn 2001;56:141.
[3] Nagura M, Yokota H, Ikeura M, Gotoh Y, Ohkoshi Y. Polym J 2002; 34:761.
[4] Bigi A, Panzavolta S, Roveri N. Biomaterials 1998;19:739.
[5] Bigi A, Bracci B, Cojazzi G, Panzavolta S, Roveri N. Biomaterials 1998; 19:2335.
[6] Veis A. The macromolecular chemistry of gelatin. New York: Academic Press; 1964.