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Temperature effect on the recovery process in stretched *Bombyx mori* silk fibers

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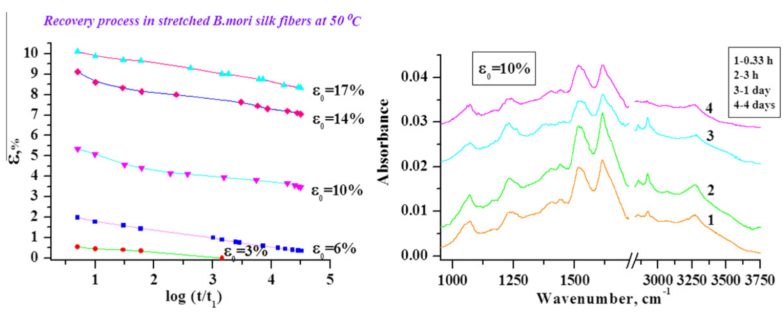
HIGHLIGHTS

- A complete recovery from 3% strain was observed after 3 days at room conditions.
- Deformations induced by stretching the silk fiber up to 6% strain are reversible.
- Increasing temperature up to 125 °C led to a better recovery and lower ε_{rd}.
- A linear equation between ε and log t was proposed for the recovery process.
- Changes in the hydrogen bonds greatly contribute to recovery process.

GRAPHICAL ABSTRACT



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ABSTRACT

The recovery process in stretched *Bombyx mori* silk fibers at different strain levels from 3% to 17% was investigated at room conditions during long period of time from 5 min to 20 days and more. How the temperature affects the recovery process in the silk fibers stretched at room conditions was examined at temperatures from 25 to 125 °C. The results of the recovery process at 25 °C revealed that although the recovery process from strain values higher than 3% strain continued slowly which caused quite high remaining deformation, a complete recovery from 3% strain was observed after 3 days. However, better recovery process was observed with increasing temperature which led to lower remaining deformations. For instance, a complete recovery from 6% strain was observed after 144 h and 3 h for the recovery process at 100 °C and 125 °C, respectively which indicates an important result that the deformations induced by stretching the silk fibers up to 6% strain are reversible and increasing temperature affects the velocity of this process significantly. The recovery process expressed in the strain (ε) and logarithm time coordinates showed a linear dependence for which a linear equation was proposed. Thus, this linear equation enables to estimate the required time for a complete recovery from different strain levels and remaining deformation at any stage of the recovery at different temperatures. The ATR-FTIR spectra of the stretched silk fibers during the recovery process revealed some changes in the absorbance ratios and shifts in the positions of the bands assigned to C_α–C, N–H stretching vibrations, and the Amide III mode. It was suggested that new formation of the hydrogen bonds between polypeptide chains especially in amorphous regions and the changes in the intra-sheet hydrogen bonds in β-sheet crystalline regions greatly contribute to the recovery process.

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Introduction

Bombyx mori (*B. mori*) silk fibers thanks to their high mechanical properties [1–6], as well as other properties such as biocompatibility and biodegradability are used especially in textile industry, material, and medical sciences such as blood vessel engineering in different material forms ranging from silk fibers and fabrics to biomedical sutures, biocomposite films, and silk microtubes [7–16]. Silkworm thread called silk bave consists of 2 single brins having the diameter of approximately 9–10 μm coated by a sericin protein which can be removed with a degumming process [17,18]. Two silk fibroin cores consist of many fibrils each of which is composed of ca. 1000 microfibrils with a diameter of ≈10–15 nm [18]. *B. mori* silk is a semicrystalline polymer which consists of crystalline (β-sheet crystals) and non-crystalline (amorphous) domains [3]. The primary structure of polypeptide chains which are arranged in an antiparallel manner in β-sheet crystals is a repeating amino acid sequence of $(\text{Gly-Ala-Gly-Ala-Gly-Ser})_n$ [18,19]. The β-sheet crystals are stabilized by intra-sheet hydrogen bonds between carbonyl oxygens and amide hydrogens of neighboring polypeptide chains and by inter-sheet Van der Waals interactions occurring between the hydrophobic side chains [1,19]. On the other hand, in amorphous regions polypeptide chains which do not contribute in β-sheet formation also contain amino acids with bulky and polar side-chains such as tyrosine, valine and acidic amino acids with low content [3,16,20]. Amorphous flexible chains connecting β-sheet crystals contribute to the elasticity of the silk fiber considerably, while the β-sheet crystals are responsible for the high strength and stiffness of the fiber [18].

It is obvious that during the usage of silk fibers in different forms, they can be exposed to high loads and stress which lead to the changes in mechanical properties as well as other properties. These structural changes depend on the time of loading or straining and affect the usage performance and characteristics of the silk fibers. Thus, the determination of the recovery properties of the structure and predicting the recovery processes in long period of time are quite important for determining and enhancing the usage performance of the stretched silk fibers after removal of the applied load or tension. Although there are some studies on the stress-relaxation and creep behaviors of silk fibers [6,21–24] and the structural changes of silk fibers under tension by only raman spectroscopy [25,26], almost there is not any study which investigates the recovery process of stretched *B. mori* silk fiber as a silk bave and the temperature effect on these processes in different period of time from minutes to several days. Thus, in the present study, the recovery process of *B. mori* silk fibers being stretched at different strain level (ε_0) ranging from 3% to 17% at room conditions for 10 min in which stress-relaxation occurred and the influence of temperature on these processes in long period of time was investigated by means of tensile testing method. The recovery processes in longer times than those used in the experiments were predicted by introducing linear equations of strain (ε) with respect to logarithm time. Responsible structural changes during the recovery process were also discussed by analyzing spectral results obtained using Attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR).

Materials and methods

Materials

B. mori silk fibers were obtained from silkworm silk cocoons which were taken from Koza Han in Bursa, Turkey. Following the degumming method described earlier [6], the silk fibers were obtained in the form of bave consisting of two individual brins. The degummed silk baves (filaments) were dried at room conditions (T = 25 °C; RH = 60%) for 1 day prior to the mechanical and spectroscopic experiments.

Methods

Method for mechanical measurements

Single silk fibers in the filament (bave) form of 10 cm gauge length were extended at different strain levels ranging from 3% to 17% on a Lloyd tensile testing machine LF Plus (AMETEK Lloyd Inst., UK) with a crosshead speed of 100 mm/min at room conditions (T = 25 °C; RH = 60%) and fixed for 10 min during which stress-relaxation occurred for each strain level. After the stretched silk fiber was released from the stretched position and removed from the tensile testing machine, the recovery process was investigated by measuring carefully the present part of the applied strain on the sample length with a sensitive vernier at different times. In order to see the temperature effect on the recovery process in stretched silk fibers, as soon as the silk sample stretched at room conditions was taken from the tensile testing machine, it was immediately put in a thermal chamber and kept at different temperatures ranging from 25 to 125 °C. At different time intervals, the same sample was taken from the thermal chamber and as soon as the recovery measurement was carried out quickly, the same sample was immediately put again in the thermal chamber. The recovery process in the length of the test sample at both room and different temperatures was investigated in the wide period of time ranging from minutes to 20 days and more.

Method for ATR-FTIR spectroscopic measurements

The ATR-FTIR spectra of the silk samples were carried out on a Perkin-Elmer Fourier transform spectrometer "Spectrum One" (Perkin Elmer, Inc. USA) utilizing the ATR (Attenuated Total Reflectance) cell at different times during recovery processes at room conditions. The silk sample containing approximately 40 individual filaments which were placed very close and parallel to each other was pressed on top of the ATR plate after being covered by another top plate. The spectra of the samples were recorded in the 650–4000 cm^{-1} range at a resolution of 4 cm^{-1} with 4 scans for each measurement. Following the same experimental procedure, The ATR-FTIR spectra of the silk samples kept at different temperatures from 25 to 100 °C which were already stretched at different ε_0 at room conditions were also recorded at different times during the recovery process.

Results and discussion

Results

Recovery processes in stretched B. mori silk fibers

Stress–strain curve of the *B. mori* silk filaments obtained at room conditions and the applied strain levels used for stretching the silk fiber in the experiments are shown in Fig. S1.

Typical stress–strain curve of silk fiber consists of an elastic initial region up to 1–2% strain and following a yield point at around 5%, a plastic deformation region in which main deformations and reorganization processes of the structural units, that is, the straining of macromolecular chains, especially in amorphous regions and the orientation of structural elements such as β-sheet microcrystals in stretching direction as well as destruction and some bond breakages at high strain levels occur as discussed earlier [6].

After different ε_0 from 3% to 17% was applied to the silk sample and it was fixed for 10 min during which the stretched silk fiber underwent a stress-relaxation process and obtained more stretched and oriented polypeptide chains and segments, in order