Mechanical Properties of *Bombyx mori* Silk Yarns Studied with Tensile Testing Method

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ABSTRACT: The mechanical properties of *Bombyx mori* silk yarns and baves were investigated with tensile testing method. After silk yarns were pre-extended at different strain levels and fixed for a while followed by recovery process, the tensile characteristics were examined in detail. It was commonly observed that low preliminary extensions up to 2–3% do not cause the changes of the mechanical properties and stress-strain curves because they result in small structural changes and distortions, which were recovered within relatively short time (∼ 1 min) in recovery process. However, pre-extension values >3% strain lead to great changes of the mechanical properties and fibre structure, i.e., the changes of the shape of stress-strain curve where additional transition point was observed, increase in the rigidity and stress at rupture, but decrease in extensibility as a result of orientation and destruction of the fibre structure especially in the amorphous region. It was stated that silk fibre consists of two distinct deformation regions, namely first linear region extending up to 2–3% strain and the second region beyond 2–3% strain where the main reorganization processes of the fibre structure, that is, the straining of macromolecular chains especially in the amorphous regions, the orientation of structural units such as β-sheet microcrystals in stretching direction, and the destruction of macromolecules take place. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 113: 2514–2523, 2009

Key words: fibres; mechanical properties; structure-property relations; strain; stress

INTRODUCTION

Silks generally defined as spun fibrous proteins polymer secretions are synthesized by a variety of organisms including silkworms, spiders.[1–6] There are several silkworms such as *Bombyx mori*, Atlas, Eri, Tussah, Muga, etc. The worm of the moth *B. mori* that lives exclusively on the leaves of white mulberry tree has been intensively studied in the world. From the structural point of view, silk fibre in the form of either mono filament (brin or bave) or yarn mainly consist of silk fibroin surrounded by a cementing layer of sericin. Silk fibroin is defined as a semicrystalline polymer of natural fibrous protein having the two important phases: crystalline and amorphous.[7] Crystal phase is represented by β-sheet structure stabilized by intrasheet hydrogen bonds occurring between the amide hydrogen and carbonyl oxygen on adjacent chain and intersheet van der Waals interactions occurring between the hydrophobic short side chains of amino acids such as glycine and alanine.[6,8,9] The amorphous phase is a noncrystalline form consisting of irregular structure formed by the molecules having an amino acid sequence that does not participate in β-sheet formation and micro voids.[9] According to Kaplan,[8] silk can consist of helical, β-sheet (chain axis parallel to the fibre axis) or cross-β-sheet (chain axis perpendicular to the fibre axis) secondary structures depending on the organism. He also stated that chain-chain interactions in silks include extensively intrachain and interchain hydrogen bonding. It is obviously known that these two types of noncovalent interactions, that is, hydrogen bonding and van der Waals dominantly determine the structural and mechanical characteristics of silk fibres.

As for the application of silk filaments or yarns in industrial areas, they are well known to be extensively used in textile industry and engineering to produce textile materials with different purpose from simple cloth to bullet-proof vests and parachutes.[2] The other application fields of silk fibres are biomedical and composite materials[10–16] in which silk fibres are used as a base to reinforce whole material structure.

In literature, there are many researches to determine mechanical properties and deformation process of silk filaments and yarns under different factors such as temperature and relative humidity,[7,9,17–22] as well as a few studies devoted to examine stress-

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relaxation and creep-recovery properties of silk yarns.[1,19,23–26] However, there is almost no research that estimates how tensile characteristics of silk fibre changes after the application of pre-extension at different levels. In most cases, the deformation of polymeric materials leads to the changes of its mechanical properties due to structural changes. It is interesting to estimate a correlation between extension level and the character of the changes of mechanical properties after pre-stretching. Also such researches are important and fundamental to understand the deformational process of the natural silk fibres and establish structure-property relationship.

Thus, this study aimed to investigate the tensile properties of *B. mori* silk yarns and their changes after application of preliminary extension at different strain levels and on the basis of these data, to define a relationship between mechanical properties and structural changes.

PREPARATION OF SAMPLES AND EXPERIMENTAL METHODS

Materials

In this study, *B. mori* silk baves opened from cocoon and silk yarns consisting of several filaments taken from Bursa (Turkey) and Baku (Azerbaijan) having a linear density of 3.40 Tex and 3.35 Tex, respectively, were used. These two types of *B. mori* silk yarns with close linear density were chosen to study to see whether or not they will show similar mechanical characteristics after the effect of preliminary extensions (strain history) as well as those of unstressed fibres and to provide a good statistics for the generalization of results, even though they were produced by silkworms which were grown and fed in different geographical regions that may result in the changes of mechanical characteristics.

In this study, silk fibres were degummed and prepared with a similar method described earlier[9,27–30] as follows: the cocoons were first boiled in 0.33% (w/v) soapy water for 30 min. Then, the baves were opened gently from cocoon and washed in distilled water for 1 h. These degummed fibres were then kept in ethyl alcohol for 6 h to remove any residual fatty matters and sericin completely. Later, they were rinsed in distilled water again and dried at room condition.

Similarly, the silk yarn samples had been produced as follows: the silkworm cocoons were degummed in boiling distilled water for 30 min. Then, several baves from different cocoons were pulled together gently with a pair of tweezers and reeled on a pulley. These silk yarns were rinsed in distilled water for 1 h and dried under room conditions.

The average diameters of baves were determined with a polarization microscope as 14 ± 1 μm. The average diameters of the yarn samples were determined as 47 ± 3 μm after the measurements at 15 different points along the sample of 50 mm with a digital micrometer.

Experimental methods and measurements

Scanning electron microscopy (SEM) measurements of studied silk baves and yarns were carried out on a JEOL JMS 5410 LV microscope with an applied voltage of 15.0 kV.

The tensile, stress relaxation and recovery tests of the silk baves and yarns were carried out under room conditions on a tensile tester "Instron-1122" with the constant crosshead speed of 50 mm/min. The gauge length of the samples was chosen as 50 mm.

To investigate the effect of preliminary extension on the tensile characteristics of silk yarns, we carried out short-term stress relaxation of 4 min and after recovery process of 4 min. The period of 4 min for each process was thought to be adequate for the experiments to see the changes of mechanical characteristics, because the stress relaxation and recovery process continue very slowly after the first 3–4 min which do not change mechanical properties considerably in time. In these processes, samples were extended at different level of strain and fixed constant for 4 min during which the stress relaxation occurs as shown in I and II regions of Figure 1 illustrating the stress-relaxation at 8% strain and recovery processes of Bursa silk yarns as an example. Then, after the removal of the extension effect, as depicted in III region of Figure 1, it is followed by a recovery process for 4 min.

After the effects of preliminary extension and recovery process the mechanical properties of silk yarn samples were investigated by means of observing stress-strain curves again. That is, as soon as the average diameter of the strained fibre was determined by a digital micrometer, the same sample was tested in the tensile tester to get stress-strain curve with the same experimental conditions. Ten to 15 samples were tried in each tensile test and each stress relaxation and recovery tests.

RESULTS AND DISCUSSION

Mechanical properties of unstressed *B. mori* silk fibres

The SEM images of original *B. mori* silk baves and yarns are shown in Figure 2. Here, it is seen that although the silk bave consists of two single brins together that are difficult to be opened separately

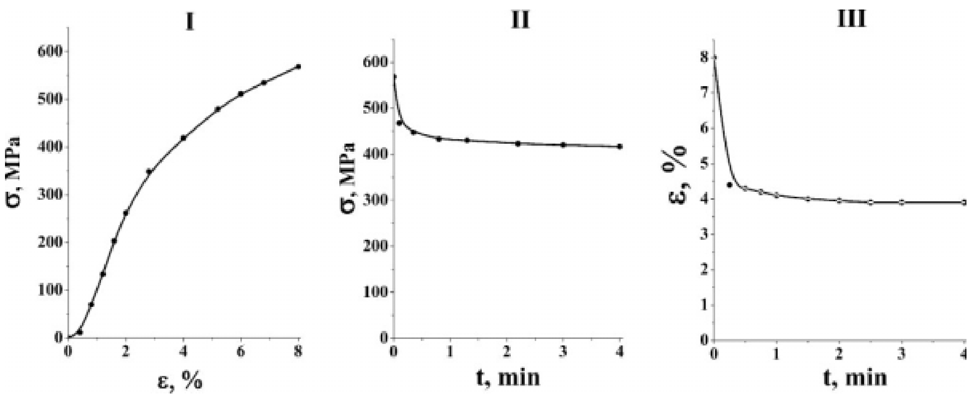

Figure 1 An experimental plot of Bursa silk yarn for the description of the method for the investigation of stress relaxation and recovery processes for silk yarns: I, stretching at a constant rate up to 8% strain; II, stress-relaxation process for 4 min at the fixed extension level; III, recovery process for 4 min.

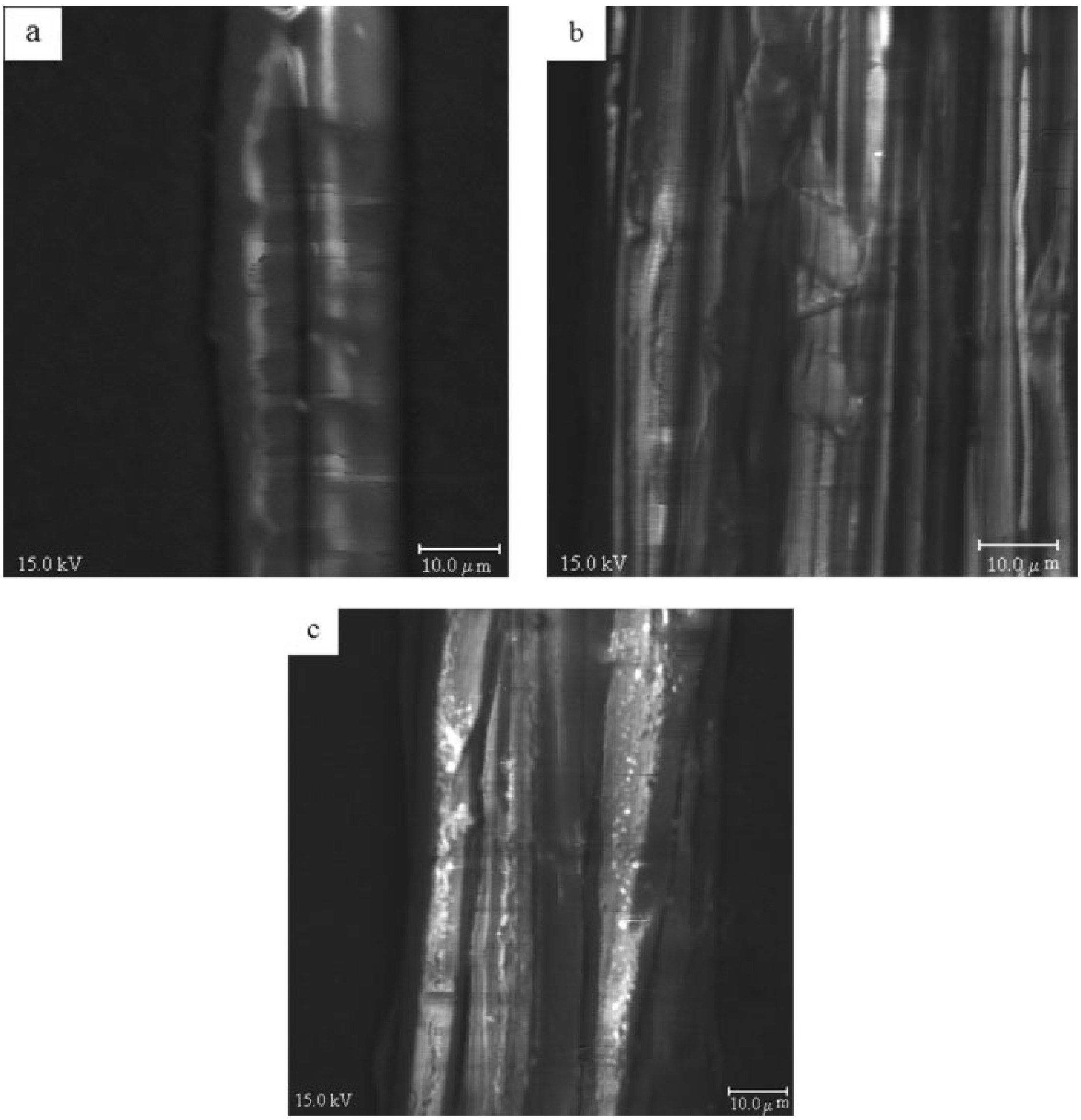

Figure 2 SEM images of studied silk fibres: (a) Silk bave; (b) Bursa silk yarn; (c) Azerbaijan silk yarn.

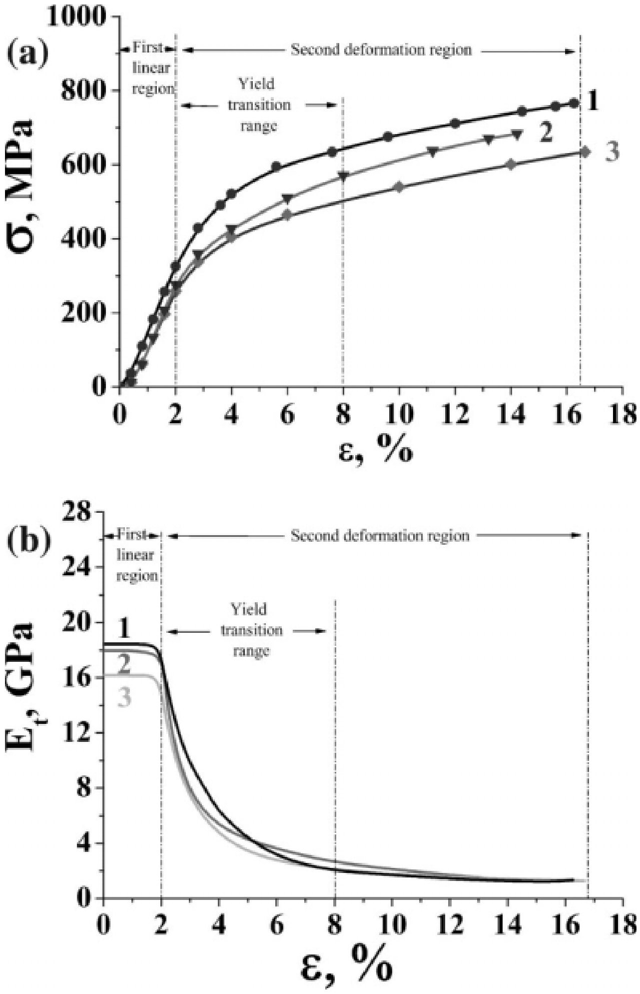

Figure 3 (a) Stress σ and (b) tangent modulus E_t versus strain ε curves of silk fibres: 1-silk bave; 2-Bursa silk yarn; 3-Azerbaijan silk yarn.

from a silk cocoon, silk yarns consist of several silk monofilaments (baves).

From the results of tensile tests, the stress-strain curves of *B. mori* silk baves and yarns and tangent modulus E_t defined as $d\sigma/d\varepsilon$ by differentiating stress with respect to strain on stress-strain curve at room conditions ($T = 20°C$; 65% relative humidity (RH) were shown in Figure 3. The average values and standard deviations designated by σs with sub-index of tensile characteristics of these fibres are listed in Table I. It is seen that all silk bave and yarn samples consisting of several mono filaments have the same kind of stress-strain curve and similar tensile characteristics consistent with the literature.[9,10,27,31] All tested samples gave stress values at rapture changing in the region of $634 \leq \sigma_b \leq 766$ MPa, initial modulus (E_i) of 16–19 GPa, and breaking extension (ε_b) of 15–17%.

To define yield point we used the dependence of tangent modulus versus strain, that is, $E_t(\varepsilon)$ where the point of intersection of the tangents to the two distinct regions of the curves was attributed with yield point. Strain and stress values of yield point determined by this method are in a good agreement with values determined by Coplan's construction as mentioned.[31] However our method enables us to investigate transition point and deformation regions on the stress-strain curve more carefully. Thus, we estimated the yield strains for the obtained stress-strain curves of different silk yarns and bave as ∼5% strain with both Coplan's construction as shown in Table I and our method as seen in Figure 3(b). Although we defined the yield point, we can see that the yield transition is not well marked and appears in the elongation range $2–3\% \leq \varepsilon \leq 8\%$. Starting from the quite high value of modulus after yield transition the curves obtain lower slope, hence lower values of modulus reaching a limit or constant value of $E_t \cong 1.5$ GPa as noticed in Figure 3(b). So we can commonly observe two deformation regions: the first linear region having modulus of ∼16–19 GPa and the second region containing the yield transition range, after which the modulus becomes ∼10 times lower.

On the basis of obtained diagrams of *B. mori* silk fibres and data in the literature,[8,9,28] we can suppose that high rigidity in the first linear region is related with the resistance of most oriented structural elements and β-sheet microcrystals which represent 60% of the total volume of the fibre and have higher elastic modulus than that of amorphous phase. Although stretching, due to the weakening of Van der Waals interactions and breaking of hydrogen bonds between amorphous molecules, amorphous molecules and entanglements start to straighten

TABLE I
Average Values of Tensile Characteristics of Studied Silk Fibres

	Initial modulus, GPa		Yield point values				Rupture values			
			Y. strain, %		Y. stress, MPa		R. strain, %		R. stress, MPa	
Fibre name	E_i	σ_{Ei}	ε_1	σ_{ε_1}	σ_1	σ_{σ_1}	ε_b	σ_{ε_b}	σ_b	σ_{σ_b}
Silk bave	19.36	1.80	5.7	0.52	591	30.58	16.26	0.59	766	31.23
Bursa silk yarn	17.20	1.24	4.8	0.32	460	28.28	14.20	1.79	683	58.0
Azerbaijan silk yarn	15.90	1.0	4.8	0.65	431	44.19	16.70	0.26	634	49.53

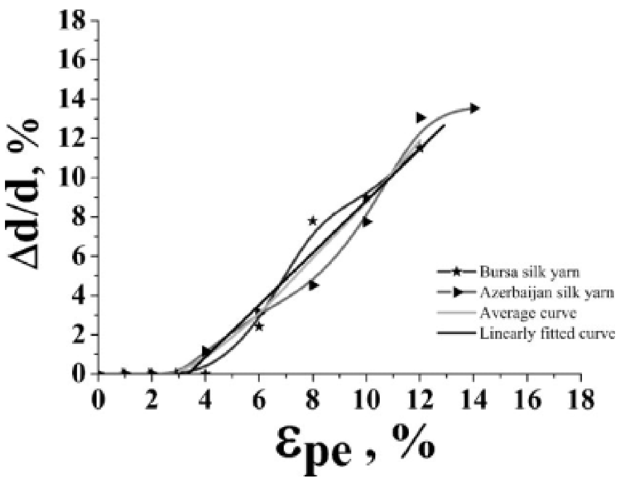

Figure 4 Percent decrease in diameter (*d*) of the yarn sample versus preliminary extension (ε_{pe}) curves.

along stretching direction at around yield transition. Then, with increasing extension, supermolecular structural elements such as β-sheet microcrystals are oriented and destruction processes occur.

Mechanical properties of *B. mori* silk fibres after the application of preliminary extensions

To see how tensile properties and structure of *B. mori* silk yarns will change depending on strain history or previous deformation due to preliminary extension (ε_{pe}), we extended yarns and fixed them at constant deformation (ε_{pe}) for 4 min, during which stress-relaxation process was occurring. After the removal of the deformation (ε_{pe}), recovery experiments of 4 min were carried out. The samples pre-extended at different levels were subsequently tested again at tensile testing equipment to see how mechanical characteristics change.

We saw that after the effect of preliminary extension, the average diameters of the yarn samples decreased. The changes of the diameter (*d*) of the samples depending on the level of preliminary extension (LPE) for both Bursa and Azerbaijan silk yarns are shown in Figure 4. As an approximation, we fitted a linear curve for the average curve in Figure 4 and introduced the following simple linear function to calculate the decrease on the diameter:

$$\Delta d/d, \% = 1.32\varepsilon_{pe} - 4.44 \qquad (1)$$

Here, in the region of $\varepsilon_{pe} > \sim 3.4$ %, the new diameter of the yarn sample can be determined easily for the calculation of stress and this approach can also be considered to be useful for the calculations of mechanical values of the strained silk yarns in textile industrial applications. Here, we suppose that the average diameter of silk yarn sample decreases by an amount equalling the additions of decrease on the diameter of each monofilament, because it is known that the diameter of each mono filament decreases while it is stretched. We assume that the decrease on the diameter of each monofilament may be caused by the reorganization of disordered amorphous regions during stretching. It is worth noting that such disordered amorphous regions form 40% of fibre structure,[9] thus we can also suppose that such regions have important effects on the mechanical properties of silk yarns especially in the second deformation region.

After the yarns were pre-extended at different deformation levels for 4 min in stress relaxation process, the recovery of the applied strain on the length of the sample was recorded during recovery process. The recovery process of the *B. mori* silk yarns from different LPE are shown in Figure 5. This process enabled us to determine and estimate residual deformation (ε_r), which are related to great structural changes of the sample after the application of preliminary extensions. The last value of deformation obtained at 4 min of recovery process was taken as a residual deformation (ε_r) from applied initial strain (ε_{pe}). In Figure 6, the dependence of ε_r with respect to LPE is given.

As we can see from Figures 5 and 6, pre-extension <2% does not cause any residual deformation, because the pre-extended silk fibre recovered completely from small deformations of bond length and angles on macromolecules. However, LPE >2% leads to high residual deformation caused by significant structural changes. These structural changes may be as a consequence of the orientation process of structural units such as β-sheets and stretching of amorphous chains. As a result of these processes, some chemical bonds may be broken and result in very high residual deformation which can take very long time to recover completely. Because of very high

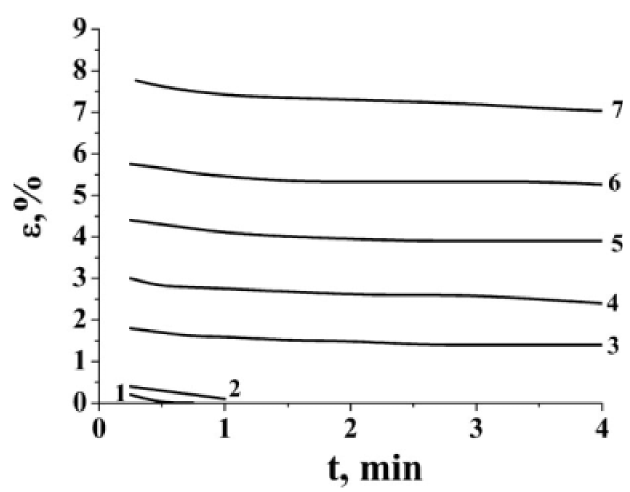

Figure 5 Recovery process of *B. mori* silk yarns from different pre-extension levels: 1% (1); 2% (2); 4% (3); 6% (4); 8% (5); 10% (6); 12% (7).

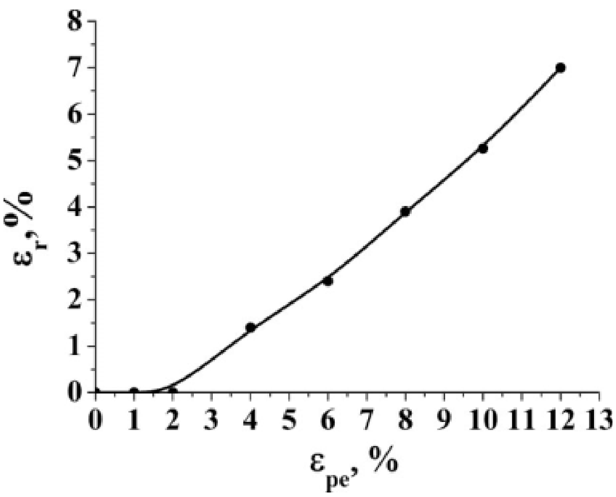

Figure 6 Relationship between residual deformation (ε_r) of *B. mori* silk yarns and the levels of preliminary extension.

residual deformation and great structural changes, we observed different stress-strain curves and mechanical properties as we are going to discuss.

Here, for the values of LPE > ∼2% strain we saw an almost linear relationship between residual deformation (ε_r) and LPE (ε_{pe}), which can be described with the following linear function:

$$\varepsilon_r = 0.68\ \varepsilon_{pe} - 1.48 \quad (2)$$

The obtained stress-strain curves of Bursa and Azerbaijan silk yarns after they were exposed to the preliminary extensions during 4-min intervals are given in Figure 7. Besides, the tangent modulus versus strain curves is shown in the Figure 8. The changes of the average values of tensile characteristics and new transition points due to previous deformation (strain history) and corresponding standard deviations are tabulated in Tables II and III for Bursa and Azerbaijan silk yarns, respectively. It is clearly seen that the changing of mechanical properties for both silk types have similar tendency correlated with LPE. Here, it was noticed that while LPE gets higher, the stress at rupture gets higher, but breaking extension decreased.

It is known that silk fibres have high initial modulus and rigidity in initial state due to high degree of crystallinity about 60%.[9] However, it is worth noting that initial modulus E_i does not change much even at very high pre-extension values.

When we examine these new stress-strain curves obtained after different strain history we can see that preliminary extensions in the region $0 < \varepsilon_{pe} \leq$ 2–3% do not cause big changes on the tensile properties, that is, the shape of the stress-strain curves and mechanical characteristics of these pre-extended yarns are similar to that of the unstressed one. We obtained the same changing tendency from the estimation of diametral changes and residual deformation. Thus, we can conclude that deformation in this region is connected with small structural changes which can be recovered easily within relatively short time (∼1 min).

LPE >3% causes significant changes of mechanical properties: yield point shifts from ∼5% to higher values around 6–8% (Tables II and III), breaking extension decreases whereas stress at rupture calculated considering new diameters of the sample which may be regarded more meaningful for industrial applications increases as it is also seen in Figure 9. Especially, when LPE ≥10%, the stress at rupture increased at around 10–20%, whereas the breaking extension decreased dramatically at around 50–60%.

The examination of the tangent modulus of strained yarns (Fig. 8) showed the increasing of rigidity in the elongation range of $3\% < \varepsilon \leq 8\%$. Moreover, one of the most interesting characteristics for strained yarns was noticed: after the application of preliminary extensions ≥8% a new transition

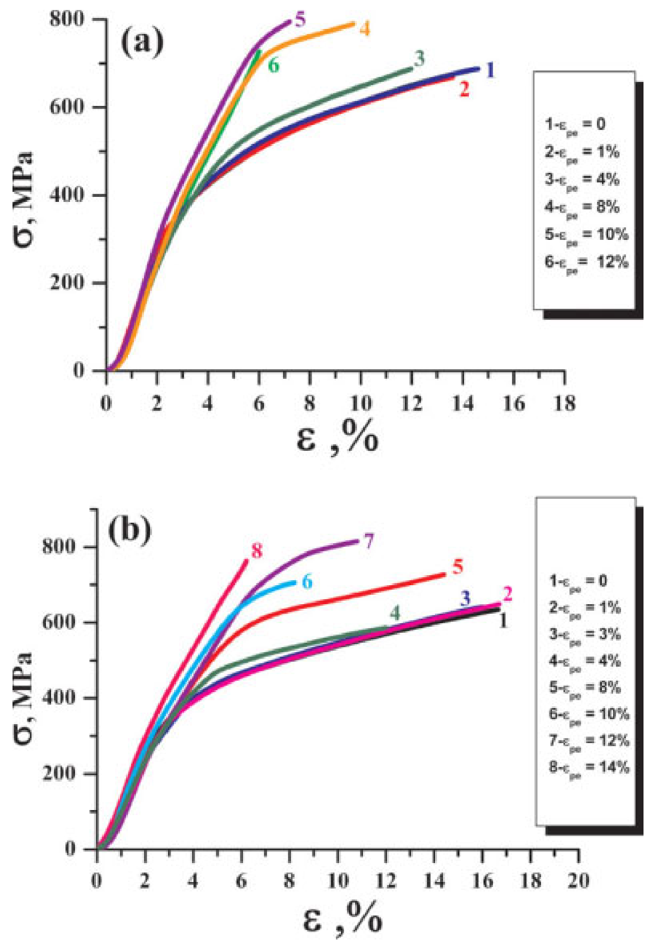

Figure 7 Stress-strain curves of (a) Bursa and (b) Azerbaijan silk yarns after stress relaxation for 4 min at different pre-extension levels (ε_{pe}) followed by recovery process for 4 min. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

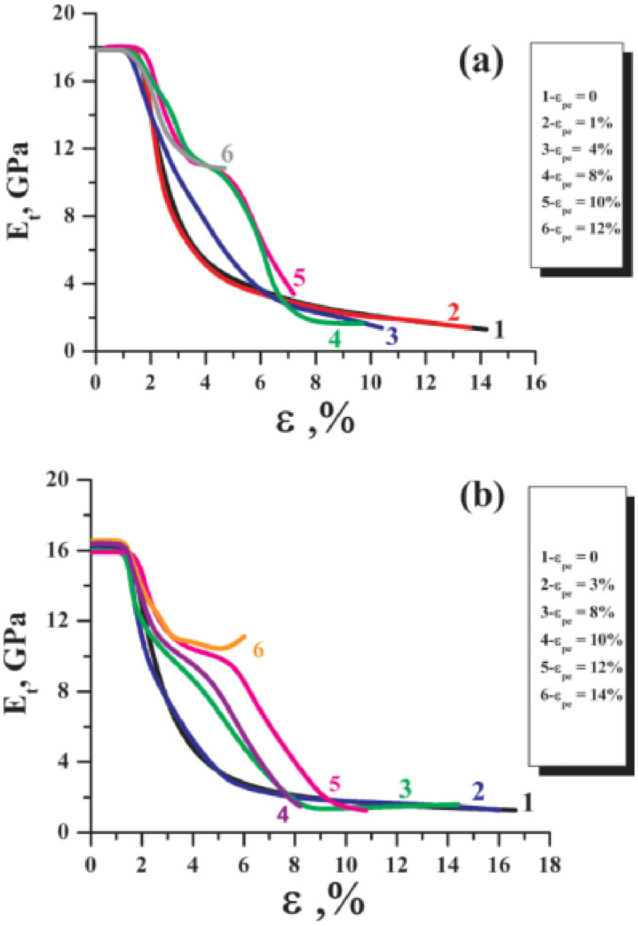

Figure 8 Tangent modulus E_t versus strain curves of (a) Bursa and (b) Azerbaijan silk yarns after the application of preliminary extension (ε_{pe}) at different levels. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

point appears in the elongation range of ~2–3%. We assume that this transition point may appear as a result of orientation and destruction process, that is, the breaking of some chemical bonds which is going to be discussed later.

It was observed that LPE ≥12–14% strain which are quite close to breaking extensions leads to the disappearance of the yield point. We assume that at these very high pre-extension values, destruction processes become more intense. However, the initial modulus does not change much with increasing LPE, because a great amount of β-sheet microcrystals keep their strength constant. Therefore, it is clearly seen that extension or strain history on silk yarns causes great changes of the mechanical properties depending on elongation level as it was described.

From the structural point of view, Figure 10 illustrates how the microstructure of the silk yarns changes with the intensity of the deformation, that is, LPE. Here, Figure 10(a) shows the microstructure of the silk fibre in the initial state where nonoriented β-sheet microcrystals are connected with amorphous flexible chains. In this scheme, it should be noticed that although most of amorphous chains connect β-sheet microcrystals in fibre axis, some chains connect some β-sheet microcrystals in horizontal direction. Besides, some entanglements are formed due to irregular matching and connection of β-sheet microcrystals with amorphous chains. These entanglements and macromolecular chains connecting β-sheet microcrystals in horizontal direction will restrict the straining of macromolecules and their orientation in the fibre axis during stretching.

When the preliminary deformation in the range of $0 < \varepsilon_{pe} \leq 3\%$ which falls into the first linear region are applied to the fibre, small structural changes which are the deformation of bonds angles and length in the β-sheet microcrystals as well as in amorphous chains are seen. That is why the state of β-sheet microcrystals and amorphous chains become almost the same as those in the original one as seen in Figure 10(b). In recovery process, the fibre recovers back completely within 1 min without any residual deformation, because such deformations are elastic and reversible.

However, when the fibres are exposed to preliminary extensions in the range of $3\% < \varepsilon_{pe} < 8\%$ and fixed for the time of stress relaxation process, we suppose that as schematized in Figure 10(c),

TABLE II
Tensile Characteristics of Bursa Silk Yarns After the Application of Preliminary Extensions

LPE	Initial modulus, GPa		Yield point values (first transition) Y. strain, %		Y. stress, MPa		Second transition Strain, %		Stress, MPa		Rupture values R. strain, %		R. stress, MPa	
ε_{pe}, %	E_i	σ_{Ei}	ε_1	σ_{ε_1}	σ_1	σ_{σ_1}	ε_2	σ_{ε_2}	σ_2	σ_{σ_2}	ε_b	σ_{ε_b}	σ_b	σ_{σ_b}
0	17.2	1.24	4.8	0.32	460	28.28	–	–	–	–	14.2	1.79	683	58.0
1	16.7	0.95	4.8	0.49	463	20.24	–	–	–	–	13.6	1.58	669	22.01
4	17.0	0.72	5.8	0.60	541	64.81	–	–	–	–	11.9	0.90	687	54.03
8	17.1	0.53	6.6	0.49	730	14.65	2.8	0.14	363	19.67	9.7	1.88	789	34.61
10	19.2	1.79	6.0	0.15	742	47.97	2.3	0.07	346	31.92	7.2	0.52	795	48.52
12	16.0	2.07	–	–	–	–	2.4	0.13	305	44.21	6	0.68	727	69.45

TABLE III
Tensile Characteristics of Azerbaijan Silk Yarns After the Application of Preliminary Extensions

LPE	Initial modulus, GPa		Yield point values (first transition)				Second transition				Rupture values			
			Y. srain, %		Y. stress, MPa		Strain, %		Stress, MPa		R. strain, %		R. stress, MPa	
ε_{pe}, %	E_i	σ_{Ei}	ε_1	σ_{ε_1}	σ_1	σ_{σ_1}	ε_2	σ_{ε_1}	σ_2	σ_{σ_2}	ε_b	σ_{ε_b}	σ_b	σ_{σ_b}
0	15.9	1.0	4.8	0.65	431	44.19	–	–	–	–	16.7	0.26	634	49.53
1	14.3	0.66	4.8	0.74	419	26.83	–	–	–	–	16.7	1.08	649	53.37
3	13.9	1.57	4.8	0.28	432	62.0	–	–	–	–	16	1.41	641	70.94
4	13.8	1.20	4.9	0.28	466	31.33	–	–	–	–	12	1.04	586	19.72
8	14.5	0.76	6.6	0.15	603	40.50	2.4	0.54	280	46.60	14.4	0.65	727	40.11
10	17.06	1.36	6.3	0.10	657	41.07	2.0	0.14	267	21.44	8.2	0.36	700	47.69
12	15.3	1.23	8.0	0.07	757	40.44	2.4	0.12	279	23.45	10.8	0.70	815	33.41
14	17.3	1.50	–	–	–	–	2.3	0.58	334	72.96	6.2	0.88	763	36.86

realignment or orientation of macromolecular segments, that is, the orientation of macromolecules in the amorphous phase and stretching of entanglements take place with the orientation of β-sheet microcrystals in the direction of stretching, ie., fibre direction in Figure 10. Moreover, we also expect that some β-sheet microcrystals start to slide relatively to each other in small distances. In this orientation process, due to approaching of macromolecules to each other, intermolecular interactions, that is, noncovalent interaction such as hydrogen bonds increase. Consequently, due to orientation and stretching, the macromolecules become more strained and the structure becomes more oriented and rigid. With increasing LPE in this range, the processes of orientation and straining of macromolecules and β-sheet microcrystals become more intense. During the recovery process in this preliminary extension range, due to these severe structural changes in the microstructure, very high residual deformations which can influence the mechanical properties of these strained silk fibres were observed as we have discussed earlier.

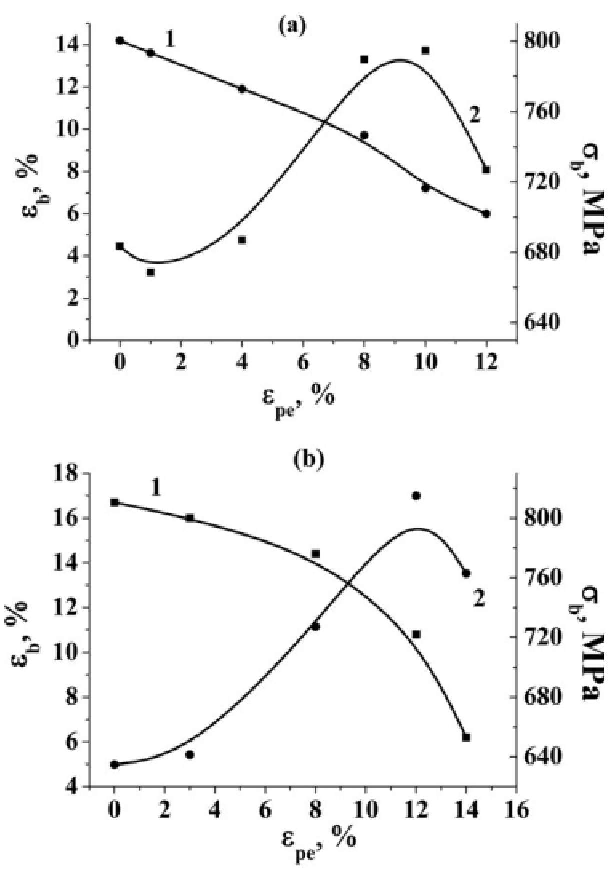

Figure 9 The changes of breaking extension ε_b (1) and stress σ_b (2) values versus preliminary extension curves for (a) Bursa and (b) Azerbaijan silk yarns.

When preliminary extensions in the range of $\varepsilon_{pe} \geq$ 8% are applied to the silk fibre, as depicted in Figure 10(d), the amorphous chains become more stressed and strained and slight deformations of β-sheet microcrystals can be expected. At the same time, the sliding of structural elements such as β-sheet microcrystals increases. During this stretching and stress-relaxation process, as a result of breaking of some chemical bonds in more stressed macromolecular chains in amorphous regions, destruction process starts at $\varepsilon_{pe} \cong$ 8%. When the LPE increases up to close to breakage extensions of the fibre, the destruction process gets more intense and the number of broken bonds increases. In the subsequent recovery process, because the recovery of such more oriented and strained macromolecular chains as well as recombination of broken bonds will take very long time, the fibre obtains higher residual deformations and a number of more strained macromolecular chains which cannot be elongated much. Thus, the strained silk yarn broke at lower extensions as we have seen earlier.

Consequently, our results concerning the influence of preliminary extension, that is, how the structure and mechanical properties change with the intensity

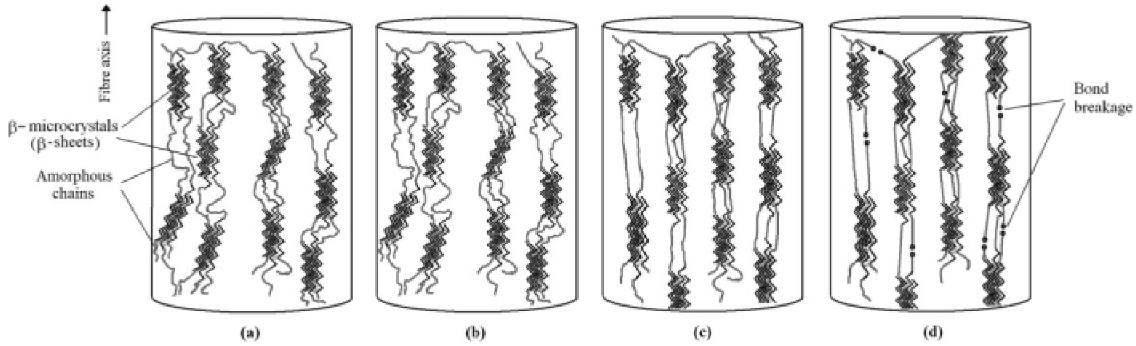

Figure 10 The scheme for the microstructural changes of the silk fibre after the application of preliminary extensions at different levels: a) $\varepsilon_{pe} = 0$ (unstressed silk fibre); b) $0 < \varepsilon_{pe} \leq 3\%$; c) $3\% < \varepsilon_{pe} < 8\%$; d) $\varepsilon_{pe} \geq 8\%$.

of applied deformation helped us to understand the deformation process more clearly and interpret the stress-strain curve of silk fibres as follows: we assume that the first linear region, where elastic or quasi elastic deformations take place, extends up to 2–3% strain and the second region beyond 2–3% strain can be attributed to the orientation processes of macromolecules and β-sheet microcrystals in straining direction and destruction process of macromolecules. In this region, the main reorganization processes of the fibre structure take place, that is, entanglements and amorphous chains are unfolded and then strained during stretching and orientation process of structural units such as β-sheet microcrystals occurs. During stretching and orientation process, breakage of some chemical bonds on more strained amorphous chains can start. We assume that especially after 8–10% strain, the destruction of macromolecules becomes more intense, that is, the number of broken chemical bonds increases and the sliding of molecular and supermolecular structural elements continues with this process.

CONCLUSIONS

Both silk bave considered as a monofilament and silk yarns taken from different places showed almost the same tensile characteristics and stress-strain curves. The preliminary extensions at different levels led to the significant changes of both physical and mechanical properties of *B. mori* silk yarns. It was observed that the diameter of silk yarns decreased linearly with LPE higher than $\sim$ 3.4%. The examination of tensile properties of silk yarns revealed that with increasing LPE, the stress at rupture showed an increasing tendency, whereas the breaking extension decreased greatly. Especially, when LPE $\geq$10%, the stress at rupture increased at around 10–20%, whereas the breaking extension decreased dramatically at around 50–60%. Moreover, it was observed that the initial modulus remained almost constant even after the application of high pre-extension values. Based on the results from the recovery processes, silk yarns had quite high residual deformation after preliminary extension >2–3% where almost a linear relationship between residual deformation and LPE was observed.

Furthermore, considering all the results, we tried to interpret the stress-strain curve of silk fibre more clearly. We assumed that the first region is elastic or quasi elastic region ranging from 0 up to 2–3% strain and the second region beyond 2–3% strain represents the main reorganization processes of the fibre structure, that is, the straining of macromolecular chains especially in the amorphous regions and the orientation of structural units such as β-sheet microcrystals in stretching direction together with destructions of macromolecules. We supposed that especially after 8–10% strain, the destruction of macromolecules becomes more intense, that is, the number of broken chemical bonds increases.

Considering the extensive applications of silk fibres especially in textile industry to produce silk-based clothes and material science to create novel silk-based composite materials and their utilization in medicine as well as in the production of bullet-proof vests and parachutes, we believe that the determination of the changes of the mechanical characteristics and the structure of silk fibres subjected to stress relaxation and recovery processes is quite important and useful for the analysis of the changes of mechanical characteristics and the deformation properties of the whole silk-based material subjected to any extension or stress at different levels for a period in exploitation times. Furthermore, very high residual deformations caused by high preliminary extensions and a very slow recovery process of silk fibres can cause undesirable physical properties and deformations of silk-based clothes and materials if they are exposed to any stretching or extension in the production stages or daily uses. Besides, these very high residual deformations and slow recovery of the silk fibres will certainly affect the reusability of such silk-based materials or silk fibres themselves.

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