STUDY OF PROPERTY & STRUCTURAL VARIANTS OF MULBERRY AND TASAR SILK FILAMENTS

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Abstract

The tensile behaviour of fully degummed filaments of two commercial varieties of silk produced in India, namely mulberry (Bombyx mori) and tasar (Antheraea mylitta), has been investigated in dry and wet state. The tensile properties were correlated with the structures and morphologies of these two varieties of silk. The tenacity and elongation at break of these silks were not significantly different in dry and wet state; however, a slight reduction in initial modulus was noticed in wet state. The stress-strain behaviour of mulberry silk filament was different from that of tasar in that it demonstrated a characteristic yield point, lower modulus and elongation at break twice as high as that of mulberry. The characteristic stress-strain behaviour of theses two varieties of silk was correlated with density, birefringence, orientation index, sonic modulus and amino-acid composition. Poor orientation and less order in tasar are related to the higher percent of bulky groups present in fibroin.

Key words:

mulberry silk, tasar silk, silk filaments, tensile properties, structural properties

Introduction

In spite of a large number of man-made fibres overwhelming the textile arena, silk indeed still commands a considerable respect, as its emotional and prestigious aura is still incomparable. Although in use for centuries, it is one of the least researched fibres. Today China and India are the major production centres. In the Indian subcontinent, silk is receiving renewed and focussed attention, from the point of view of production, processing and properties. The present study is an attempt to understand the two important commercial varieties produced in India, namely mulberry *(Bombyx mori*) and tasar (*Antheraea mylitta*), in respect of their structure and property.

Earlier research [1,2] has shown that these two fibres exhibit distinctly different tensile behaviours. These studies have shown that among the fibres, mulberry is weakened considerably in wet state, while the stress-strain behaviour of both is largely modified upon wetting. In an aqueous medium, inter-molecular hydrogen bonds would break, and in turn lead to a certain drop in tenacity and/or modulus; but such a large reduction in tensile properties tends to show that fabrics/garments cannot be home laundered or machine-washed without damage or distortion. However, the reality is far different from this; silks can be machine washed at 40-60ºCprovided one uses appropriate washing procedures, such as the use of neutral detergents.

Are these fibres weakened to such an extent in wet state? Is the residual sericin in any way responsible for this behaviour? These were some of the questions which motivated the present study. It was considered of interest to study the tensile behaviour of fully degummed fibres in dry and wet state, and to investigate the structure and morphology of these two commercial varieties of silk.

Experimental investigation

Materials

(a) Yarns

Commercial mulberry (multivoltine) and thigh-reeled tasar yarns were collected from the Central Silk Technological Research Institute, Bangalore and the Raw Material Bank, Chaibasa, Bihar, India.

(b) Filaments

Raw silk filaments were obtained after reeling mulberry and tasar silk cocoons.
The mulberry cocoons were taken in a wire mesh cage and cooked in the first pan at 65±5ºC for one minute, then in the second pan at boiling point for about one and half minutes, and finally at 65±5ºC for one minute. The cooked cocoons were hand-brushed at boiling in order to obtain the true end of the filament. Due to the hard and compact nature of the tasar cocoons, these were cooked with 10% ethylenediamine at 80ºC for 50 min. The cocoons were individually deflossed by hand. The mulberry and tasar cocoons were then reeled on a wrap reel, and continuous filaments were collected in the form of hanks. These were then degummed with 25% Marseilles soap (on the weight of the material) at boil for 90 min. at a liquor ration of 50:1. The degummed hanks were washed, dried and conditioned at tropical atmospheric of 27±2ºC and 65±2% RH (according to ISO139-1973IE, s.2.3.1) for 48 hours. The filaments thus obtained were evaluated for their mechanical and structural properties.

Evaluation

Tensile properties

The tensile properties were measured on an Instron 4301 Universal Tensile Tester (interfaced with an IBM PC) at tropical atmospheric of 27±2ºc and 65±2% RH, at a gauge length of 5 cm and strain rate of 1 cm/min. In order to study the mechanical behaviour in wet state, the samples were soaked in distilled water for 30 min., and then tested for mechanical properties.

Structural properties

The density was measured using a Davenport Density Gradient Column. The column was prepared using carbon tetrachloride (Density 1.6 g/cc) and n-heptane (density 0.7 g/cc). An average of 10 readings was reported. All the measurements were made at 25ºC.

The birefringence was measured by the compensator method. A single filament was placed on a glass slide and covered with an immersion oil between them. Birefringence was evaluated using a polarised microscope with a compensator, and calculated using the following expression :

$\Delta n = 6.18 \times (a+b) / d \times 1000$, where, d=the filament diameter in microns, (a+b)=phase difference (nm)

The wide angle X-ray diffractograms of the finely powered samples were obtained on a Philips X-ray diffractometer (Model PM 203 A) between 2θ values ranging from 10º to 35º at a scan rate of 3º/min using CuK_α radiation (λ = 1.54A). The voltage and current of the X-ray source were 40 KV and 30 mA respectively.

To study the orientation index, a parallel bundle of filaments of reasonable thickness was fixed on an aluminium frame with an appropriate slit. This was placed perpendicular to the path of X-ray beam. The orientation index was obtained from the azimuthal scans at 2θ = 20.6º for mulberry and 20.3º for tasar using the method described elsewhere [3].

The sonic modulus was measured on a PPM-5R Dynamic Modulus Tester with a sound pulse of longitudinal waves at a frequency of 5 KH_z. The scanning speed was 6.4 cm/min. The total length scan was 10.2 cm in each cycle. An average of 15 scans was reported.

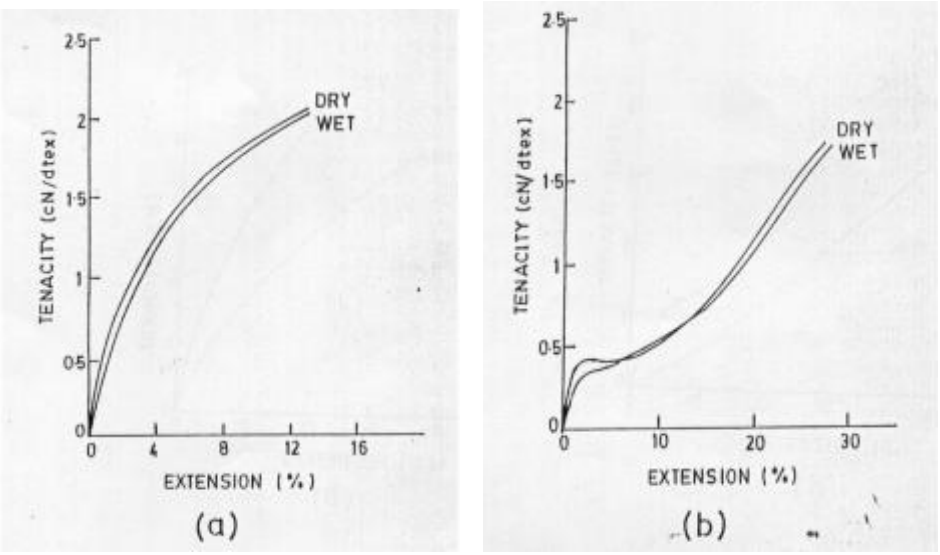
The amino acid composition of the degummed silk filaments of *Bombyx mori* and *Antheraea mylitta* were analysed using the Waters Pico Tag system. The hydrolysis of the silk filaments was carried out at 110ºC using 4M methanesulphonic acid containing 0.2% (w/v) tryptamine (Sigma P/N M4141) for 24h; the analysis was carried out as per the Waters Pico Tag Method [4].

Results and discussion

Effect of wetting on mechanical properties

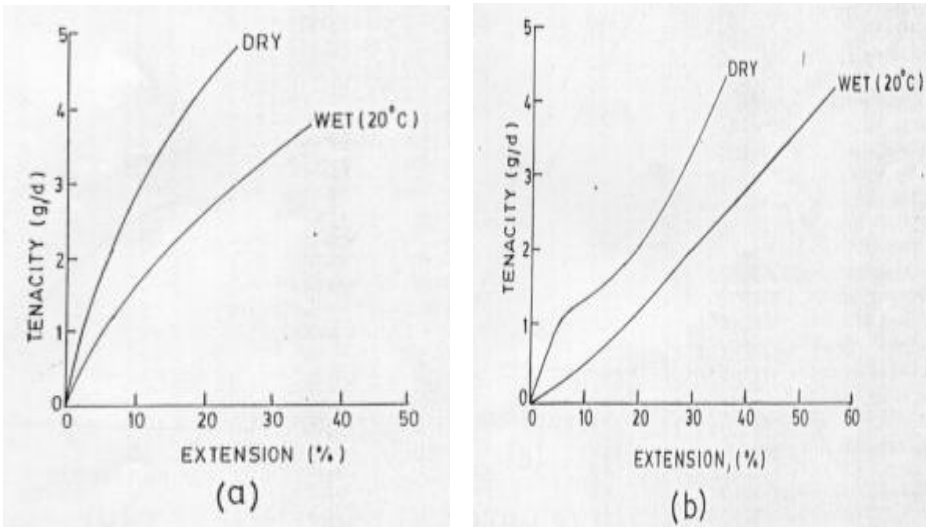
The mechanical properties of fully degummed mulberry and tasar, in both dry and wet state, are presented in Table 1.

It is very interesting to note that for both these filaments, the tenacity and elongation at break are not significantly different in dry or wet state. This is in contradiction with the observations of earlier work [1,2]. However, a slight reduction in modulus may be noted. A glance at the typical tensile behaviour reveals that the stress-strain curve of these two varieties is distinctly different, in that tasar shows a clear yield point and very high elongation compared to the mulberry filament (Figure1a & Figure1b). This has also been observed by earlier workers. However, wetting does not seem to significantly change the tenacity and extension at break. However, a slight reduction in yield stress is perceptible in both the wetting cases , more so in the case of tasar. This behaviour in wet state does not fall into line with the observations of earlier researchers. For the sake of clarity, it is worth reproducing the previous results from literature. Figure 2a, Figure 2b and Fig 3a, Figure 3b as adapted from literature [1,2] tend to show that wetting considerably modifies both the fibres. However, it is not very clear as to the extent of residual sericin present in yarns used in these studies.



Mulberry Tasar

Figure 1. Stress-strain behaviour of fully degummed silk filaments (Fibroin) in dry and wet conditions

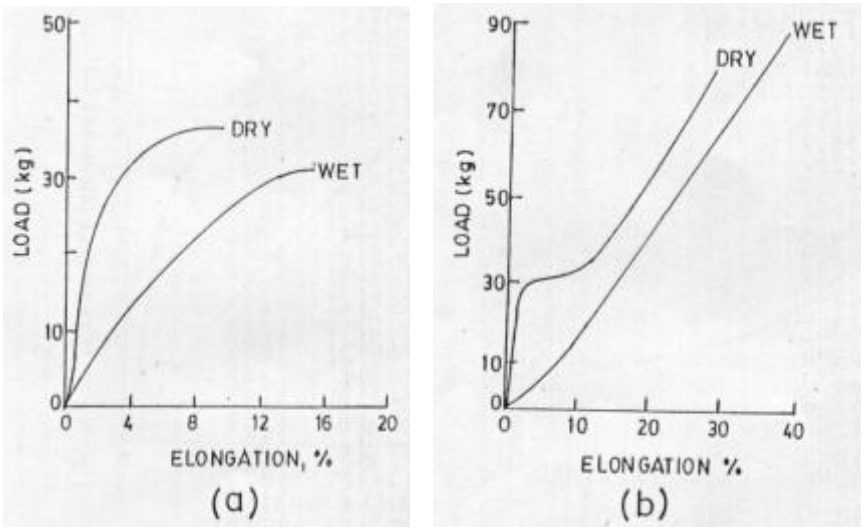


Mulberry Tasar

Figure 2. Stress-strain behaviour of silk yarns in dry and wet conditions (adapted [1])

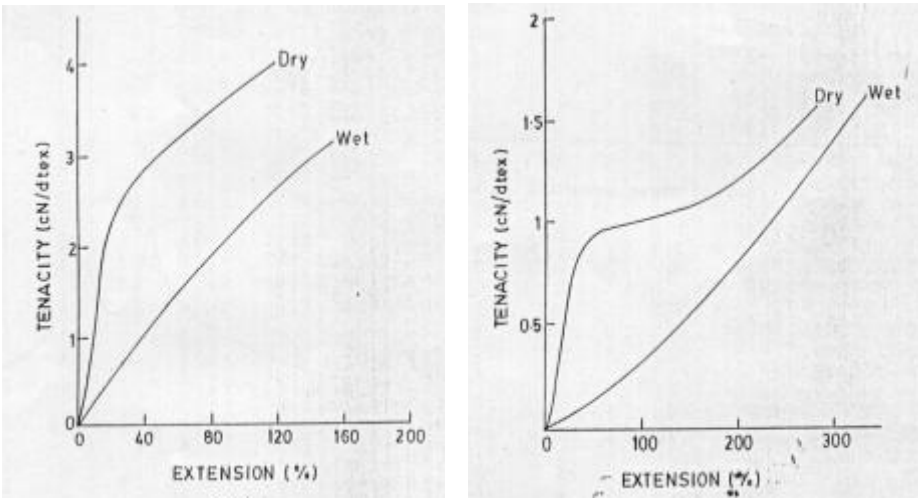
To investigate this, it was decided to test the commercially available yarns of both these varieties. It is interesting to note (Figure 4a & Figure 4b) that the tensile behaviour of the yarns is vastly modified upon wetting. This is due to the fact that both these yarns had residual sericin (mulberry 20.70% and tasar 5.48%). On wetting, the sericin weakens (as expected), and allows interfilament slippage, which

in turn leads to a drastic reduction in mechanical properties. The change in tensile behaviours may thus be related to the presence of sericin. On the other hand semi-crystalline fibroin, the main fibre, does not undergo drastic modification upon wetting. A slight reduction in the yield stress of fully degummed single filaments (Figure 1a and Figure 1b) may be due to the breakdown of some inter-molecular hydrogen bonds, limiting the initial resistance to tensile deformation. Thereafter, further deformation leads to molecular readjustment under tensile loads, and the fibre in wet state almost behaves similar to the one in dry. This is clearly indicated from the tenacity and breaking extension values (Table 1).



Mulberry Tasar

Figure 3. Load-elongation curves of silk yarns in dry and wet conditions (adapted [2])



Mulberry Tasar

Figure 4. Stress-strain behaviour of commercial silk yarns in dry and wet conditions

Structure-Property Correlation

As pointed out earlier, the stress-strain behaviour of mulberry silk filament is different from that of tasar, in that tasar (a) demonstrates a characteristic yield point (Figure 1b), (b) has a significantly lower modulus (Table 1) and (c) shows elongation at break about twice as high as that of mulberry (Table 1). However, the tenacity of mulberry filaments is higher, but only marginally so. These differences in mechanical properties must correlate with the structural features of these filaments. True comparisons become difficult because the amino acid composition and sequencing of fibroin in

both these varieties are different. However, lower modulus and higher extension in tasar do indicate poor orientation and crystalline order.

Table 1. Mechanical properties of mulberry and tasar silk in dry and wet condition

Properties	Mulberry		Tasar	
	Dry	Wet	Dry	Wet
Tenacity, cN/dtex	1.9 ± 0.2	1.8±0.3	1.6±0.3	1.7±0.3
Elongation at Break, %	13.5±3.7	13.3±4.8	29.9±5.9	27.7±6.6
Initial Modulus, cN/dtex	49.5±16.8	42.5±18.6	34.3±5.3	24.5±4.6

Figure 5 depicts the wide-angle X-ray diffractograms of these varieties. Mulberry shows a distinct peak at 2θ = 20.6º, while tasar shows two distinct peaks at 20.3º and 17.1º respectively. It has been shown by earlier research that the unit cell dimensions of *Bombyx mori* L and *Antheraea mylitta* D differ, which causes this characteristic difference [5]. Though Tsukada et al [6] have calculated the degree of crystallinity by drawing base lines using methods suggested by Herman & Weidinger [7] and Sakurada et al [8], in the absence of any well-established procedure to produce standard amorphous samples, particularly of tasar, it may be more appropriate to rely on density values. However, Izuka [9] reports that *A. mylitta* D has a crystallinity of 39.5% compared to that of *Bombyx mori* L of 41.1%.

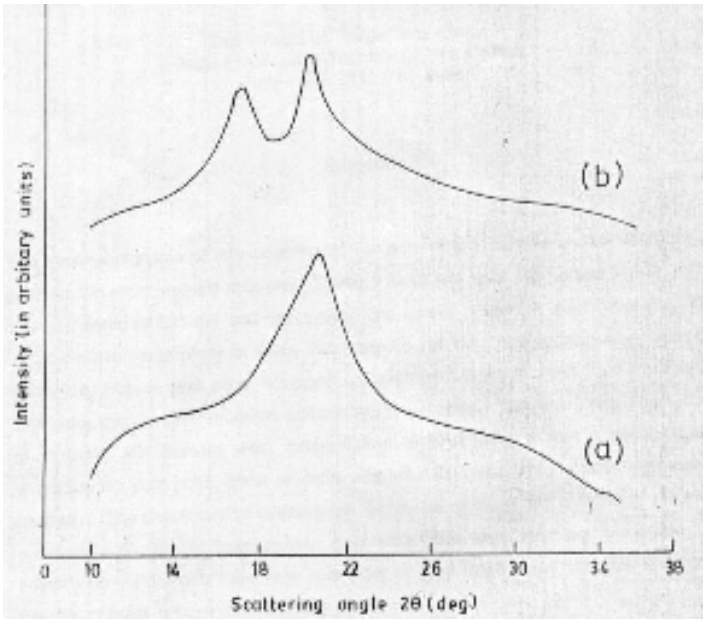


Figure 5. Wide angle X-ray diffractograms of degummed silk fibroins
a) Mulberry b) Tasar

The higher density of mulberry, compared to tasar (Table 2), suggests a relatively poor degree of order of tasar. This may be responsible for the lower modulus and typical yield behaviour of tasar yarn.

Table 2. Structural properties of mulberry and tasar silk

Type of silk	Density g/cm^3	Birefringence △n	Orientation index %	Sonic modulus cN/dtex
Mulberry	1.3525	0.0539	85	112.2
Tasar	1.3033	0.0165	61	73.7

The breaking extension is more closely related to the overall orientation of the ordered and disordered regions. It may be noted (Table 2) that the birefringence, index of orientation and sonic modulus values for mulberry filament are significantly higher than those of tasar. This clearly indicates that

tasar is more disordered at molecular and morphological levels, leading to an overall lack of order. During tensile stress, the unoriented entangled chains open, leading to higher extension.

Table 3. Amino acid composition of mulberry and tasar silk fibroin (% moles of amino acid)

Amino acid	Mulberry	Tasar
Glycine	43.08	30.04
Alanine	27.61	37.09
Serine	9.62	9.94
Tyrosine	4.58	4.93
Aspartic & glutamic Acid	2.69	5.28
Arginine, histidine & tryptophan	2.55	8.05
Others	9.87	4.67

The lack of orientation and order may be related to the inability of molecular chains to pack together closely during fibre development. In the present case, the composition and sequencing of the amino acids in fibroin can affect the close packing of chains. Table 3 gives the amino acid composition of these two varieties of silk. It may be noted that tasar has a higher percentage of alanine and amino acids with large residues. Lucas at al [1] also showed that the ratio of number of amino acids with bulky side groups to the number with short side chains in tasar is almost twice that of mulberry silk. Upon stretching, the molecular segments in the amorphous regions will flow more easily if they contain more bulky side groups. This is what is clearly reflected in the stress-strain behaviour of tasar silk, which has an elongation at break almost twice as high as that of mulberry.

Conclusions

Though a slight decrease in modulus of both the silks results in wet condition, there is virtually no change in ultimate tenacity and elongation, suggesting that they can be safely wet-processed and laundered. However, if sericin is present, the tensile behaviour of the yarn is largely modified in wet conditions. The characteristic stress-strain behaviour of tasar is due mainly to less order and poor orientation, which in turn may be related to the higher percent of bulky groups present in its fibroin.

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