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DEGUMMING CHARACTERISTICS OF SILK FILAMENTS SPUN UNDER VARIED CLIMATIC CONDITIONS OF TEMPERATURE AND RELATIVE HUMIDITY

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ABSTRACT
Silk is composed of two proteins viz., sericin and fibroin. In-vitro studies confirmed that structure formation of fibroin varied with the speed of casting. On the other hand, structural deformations and advancement in the structure of sericin was observed with the variation in the time required for settling. Prolonged duration in settling will result in the formation of compact structures. Sericin being hydrophilic, the settling duration increased with an increase in the moisture content. Silkworms being poikilothermic exhibit greater fluctuation in their physiological activities in response to the variations in the environmental conditions. During cocoon spinning, the speed increases with increase in the temperature resulting in shorter spinning durations. On the contrary, though relative humidity has no significant effect on the physiological behaviour of silkworms, cocoons spun under higher humidities are characterized by low reelability and lower silk recovery percentages. The present study correlates the implications of physiological behaviour of silkworm as a consequence of variation in the environmental conditions of temperature and relative humidity on the structure formation of fibroin and sericin, In turn, on the degumming behavior of silk filaments. Significant variation in the trend for degumming weight loss percentages was observed among different categories of filament produced. It is inferred that the in-vitro behavioural characteristics of silk proteins, more or less remain applicable to in-vivo conditions also.

KEY WORDS: *Bombyx mori L,* degumming, Relative humidity, temperature, silk filament

INTRODUCTION

Silk has its unique properties with regard to strength, elongation and luster. Its superior qualities can never be compared with other natural textile fibres (Gurumurthy, 1989). Silk is composed of two proteins viz., Fibroin and Sericin. Fibroin, which is the actual fibre part, forms the core of the filament and sericin ensheathes it. The sericin has its own significance during the processing stages like Reeling, Twisting and Weaving of silk. Infact, the presence of sericin is found significant during the construction of cocoon shell by the silkworm (Xiaosong, 1975). Sericin contributes to about 12 – 30% of the weight of the cocoon fibre. The quality and quantity of sericin greatly varies from one species to other and also across different breeds of the same species. Mulberry silk offers highest sericin content (23-30%) when compared to non-mulberry silks (12-18%) (Venugopal, 1991). Indian multivoltine varieties have higher sericin content when compared to bi-voltine varieties or their hybrids (Radha and Muthukrishnan, 1976). It is also noticed that sericin is much higher in the outer layers when compared with middle and inner layers of the cocoon shell (Gulrajani, 1992).

Sericin is a globular protein seen in the form of pellets adhering to the outer surface of fibroin in a irregular fashion. They possess adhesive or gelatin like characteristic (Komatsu, 1980; Minagawa, 1981). The qualities of sericin are distinct from fibroin. The molecules of sericin are not compatible to form the fibre along with the fibroin due to their low molecular weight, high water content and more number of hydrophilic amino acids.

The sericin of the cocoon filaments exists in 4 different forms classified as sericin –I, -II, -III & -IV based on their solubility in hot water (Komatsu, 1975). They are said to be distributed one above the other in the respective order (though not distinct) over the fibroin with sericin-IV being closely associated with the fibroin. The order of solubility decreased from outer to inner layer (Shimizu, 1980; Wang *et al*., 1985). The arrangement of sericin molecules in the silk fibre has been categorized into α-helical and β-structure and sericin with high β-structure (crystalline structure) content offered greater resistance to their removal (Zhu *et al*., 1998).

The silk fibre formation from their native liquid state, as determined by Foa (1912) and Hiratsuka (1916), is due to coagulation of fibroin molecules brought about by mechanical transformations at point of spinneret during cocoon spinning. Silkworm generally spins at a rate of 0.4 – 1.5 cms per second. Silk pulled at a speed of 2 cms per second showed higher ordered nature of fibroin (Kataoka, 1975b).

Besides, the structural deformation of fibroin molecules during spinning, sericin which is non-fibrous part of the silk filament, also exhibits structural deformations as against spinning speed (Wu *et al*., 1931). However, the transformation of lower order random coil sericin to highly ordered β-structure is been influenced more through repeated moisture absorption and desorption. The quantum of β-structures increased with increasing exposure durations to higher humidity during spinning (Kataoka, 1977b). Formation of more of β-structures in sericin influenced the structure transformations from sericin-I to sericin-II, -III or –IV.

Silkworms being poikilothermic, exhibits greater fluctuation in their physiological activities in response to variations in the environmental conditions (Jolly, 1987). Higher temperatures during cocoon spinning resulted in higher spinning speeds, impairing with the structural characteristics of silk proteins in silk filaments. Ogiwara (1951) opined that analysis of these relationships were important to improve the quality of silk filaments / raw silk. On the contrary, though relative humidity has no significant effect on the physiological behaviour of silkworms, cocoons spun under higher humidity are characterized by low reelability and lower silk recovery percentages due to increased sericin strength and high gumming force (Zhu *et al*., 1998).

The dissolution behaviour of sericin is greatly altered by its percentage crystallinity. The sericin with higher crystallinity offers greater resistance to their removal and vice-versa (Zhu *et al.,* 1998). Sericin –IV fraction is said to be closely associated with fibroin, does not dissolve easily when compared with its other fractions (Shimizu, 1980), indicating higher degree of crystallinity for this fraction.

The concomitant release of sericin during the process of degumming largely depends on the structural features of sericin and their interaction with the agents used for their removal. The degumming process is been effected through the utilization of alkaline media or through the usage of proteolytic enzymes. In the alkaline method of degumming, the serine and threonine bonds are hydrolyzed, consequently bringing out the degradation of sericin. Owing to the chemical composition and structural stability, fibroin is least affected under such a condition (Das, 1991). Inappropriate use of chemicals, especially the alkali, during degumming has led to severe loss in weight as well the strength (Shukla *et al.,* 1992). Thus control over the application of alkali should be positive in order to achieve the quality of excellence (Chakraborthy *et al.,* 1997). Since enzyme degumming is based on the cleavage of specific bond characteristic to sericin, the application of the same to degum the silk has proved to produce better results in their finished products. The proteolytic enzyme of bacterial origin has been recommended for a better result (Gulrajani, 1992).

In the present investigation, degumming behavior of filaments produced under varied climatic conditions was studied in detail. Consequently, the implications of degumming agents and treatment duration on strength and weight loss were assessed. Process efficacies in degumming each of the class of filaments were determined.

MATERIALS AND METHODS

Silkworms of variety PM x NB_4D_2 (multi x bi hybrid), were subjected to spin the cocoons under varied climatic conditions of temperature and relative humidity (RH), keeping other factors such as air and light constant. The treatments followed were:

Control -Normal Temperature (25±1°C) and Normal RH (65%)

T1 -High Temperature (35±1°C) and High RH (95%)

T2- High Temperature (35±1°C) and Low RH (45%)

T3- Low Temperature (15±1°C) and High RH (95%)

T4- Low Temperature (15±1°C) and Low RH (45%)

The cocoons thus obtained were conditioned at 25°C and 65% RH for 2 days and utilized for the preparation of filaments (Minagawa, 1960) on an epprouvette. Filaments from middle layer were only selected for degumming and subsequent analysis of mechanical properties.

A. Degumming Analysis

The filaments obtained from the above case were subjected to degumming test by employing Soap-Soda and Enzyme methods. The concentration and duration of treatment were as follows:

1. Degumming using Soap-Soda

(i) Soap 5 gm/l + Soda (i) 0.25 g/l, (ii) 0.5 g/l, (iii) 0.75 g/l

Treatment Duration : (a) 30 mins., (b) 45 mins., (c) 60 mins.

(ii) Soap 7.5 gm/l + Soda (ii) 0.5 g/l, (iii) 0.75 g/l

Treatment Duration: (a) 30 mins. (b) 45 mins., (c) 60 mins.

A material : liquor ratio of 1:60 was used and a treatment temperature of 90±1°C was employed. The pH of the bath was maintained at 9.0 to 9.5 during each of the treatment.

2. Degumming using bacterial enzyme (Alkalase)

(1)Enzyme – (i) 2 g/l, (ii) 4 g/l, (iii) 6 g/l

Treatment Duration: (a) 60 mins., (b) 90 mins., (c) 120 mins.

A material: liquor ratio of 1:60, treatment temperature of 50°C to 55°C and a pH of 8 – 8.5 were employed. The auxiliaries Sodium Carbonate (0.5 g/l) and non-ionic surfactant (0.1 g/l) used, were kept constant for all the treatments.

B. Determination of mechanical properties (Strength and Elongation)

The mechanical properties with respect strength and elongation of degummed filaments obtained from each of the treatments were determined on a 'Instron-4061 Tensile Tester' by adopting standard test methods for tensile properties of single textile fibres prescribed by American Standards for Testing and Materials – 1996

The results obtained from the above experiments were statistically analyzed, compiled and interpreted.

RESULTS AND DISCUSSION

The degumming weight loss of the filaments spun under varied environmental conditions of temperature and relative humidity are placed in fig 1 and fig 2.

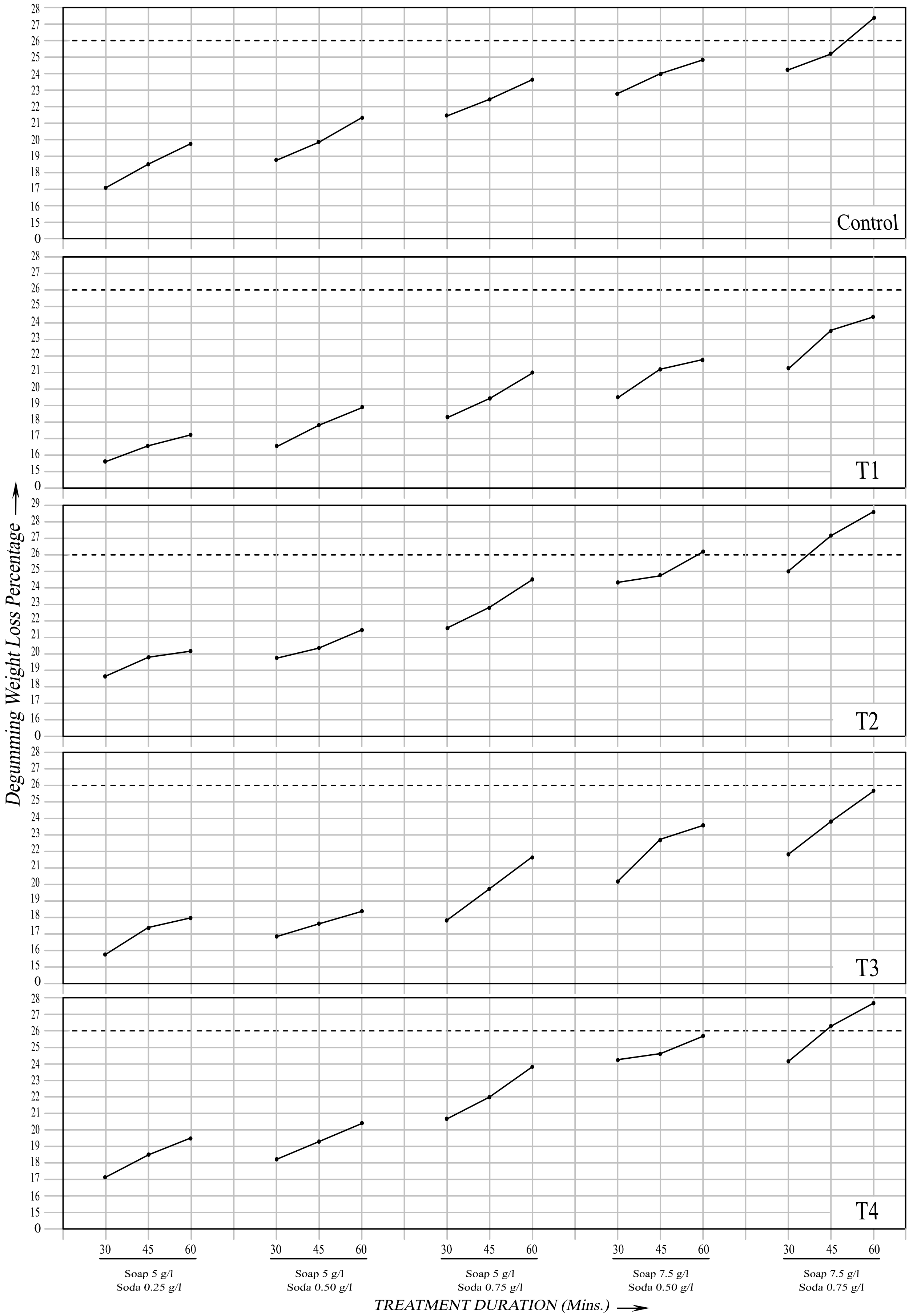

Fig.1. Degumming behaviour of silk filaments spun under varied environmental conditions of temperature & relative humidity (VAR - PM x NB4D2

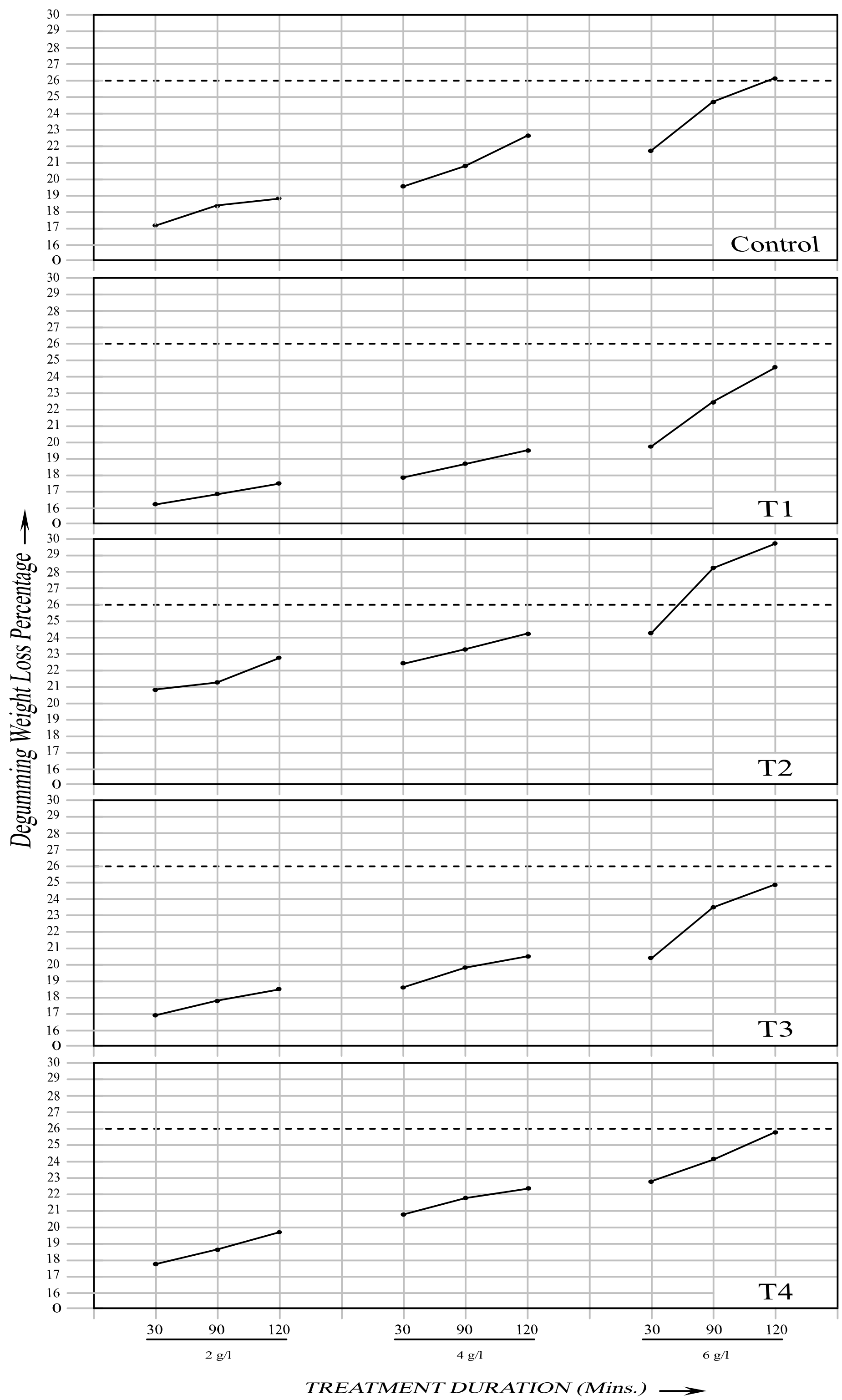

Fig.2. Degumming behaviour of silk filaments (using Enzyme) spun under varied environmental conditions of temperature & relative humidity (VAR - PM x NB4D2)

Irrespective of the degumming agent, the increase in the concentration of degumming agent and the treatment duration increased the weight loss percentage. Especially, the increase in the concentration of soda had a profound influence over the degumming loss percentage in soap-soda degumming method. The ease of removal of sericin increased with increase in the concentration of soda. These results are in confirmation with the work carried out by Fischer and Fischer (1937), Demoyanovski and Korchagin (1937) and Hillman (1932).

There existed a variation in the degumming loss percentage behaviour of the filaments from different treatments. At a relatively higher concentration of degumming agents, the weight loss percentage for the filaments from treatments T2 and T4 was significantly higher and was observed to be beyond the nominal degumming weight loss percentage. On the contrary, the filaments from the treatment T1 and T3 showed a significant lower degumming loss for the respective concentration and degumming time durations when compared with the filaments from treatments T2 and T4. The difference in the behaviour could be attributed to the variation in the structure of sericin as a consequence of influence of environmental factors which could be correlated to the fact that higher humidity influenced the formation of higher order structures in sericin (Kataoka, 1977) and the formation of such structures in the filaments offered greater resistance towards its removal (Zhu *et al*., 1992).

Similarly, it can be noticed from fig 1 and fig 2 that the degumming weight loss percentage of the filaments from treatment T2 was significantly higher at their respective stages of degumming when compared to that of the filaments from treatment T4 suggesting lower degree of orientation of sericin molecules under high temperature and low humidity conditions, ultimately leading to formation of higher degree of amorphous structures in the sericin in these filaments (Kataoka, 1977). The lower order structures so formed are easily degraded by degumming agents (Komatsu, 1975), ultimately, resulting into higher degumming losses.

Among the soap-soda and enzyme degummed sets, significant variation in the degumming behaviour could be noticed. In case of soap-soda degumming method, for a given particular concentration, the efficiency of degumming tends to decrease with the passage of time and is more apparent in case of filaments from treatment T1 and T3. However, the degumming weight loss percentage increased with increasing degumming duration when enzyme was used. These results implies the effectiveness of enzymes in silk degumming irrespective of the quality of fibre and has been proved from the earlier works of Sonwalker and Prabhu (1992), Chopra and Gulrajani (1994), Das (1991) and Venugopal (1991).

Thus it is clear to observe that, the kinetics of degumming as a consequence of various degumming agents at different concentrations and time durations is not the same for different categories of filaments and this exclusively dependent on the structural features of sericin as characterized by the spinning environmental conditions.

Degumming is a process carried out to facilitate removal of sericin and obtain the desirable properties of the silk with which it is associated, without impairing with the fine structure of fibroin. Irrespective of the quality of the fibre, commercial silk degumming is restricted either to a standard degumming weight loss percentage or a standard degumming method to mark the completeness of the process. However, from the above results, it is evidenced that the degumming process to be carried out in accordance to quality of raw silk filament.

The implications of using either a standard degumming procedure or standard weight loss percentage is been further explored in this study. The mechanical properties viz., tenacity and elongation % were considered to mark the efficacy of the degumming. The strength and elongation % values of degummed filaments from different treatments are placed in the Fig. 3 and Fig. 4.

In general, the strength of the filaments decreased and elongation percentage increased with an increase in the concentration of degumming agent and the degumming duration. However, higher concentrations (soap 7.5 g/l, soda .75 g/l; enzyme 6 g/l) involving higher treatment duration, reduced the strength and elongation percentage values for all the categories of filaments and it was more significantly higher for the filaments from the treatment T2 and T4. The above results imply that the filaments from treatment T1 and T3 had their fibre forming molecules in a more ordered form (crystalline) and were less prone to the attack of degumming agents unlike the filaments from treatment T2 and T4. These results are in confirmation with the works carried out by Nagura (1980), Setoyama (1982) and Min et al., where in high humidity favoured the formation of crystalline structures in fibroin. On the other hand, fibroin casted at low temperature and low humidity showed a higher degree of chemical degradation due to low crystalline order regions.

Among the low humidity treatment sets (T2 and T4), filaments from treatment T2 showed relatively a better strength retention (2.34 g/d and 2.21 g/d for soap-soda and enzyme respectively) over the filaments from treatment T4 (2.10 g/d and 2.01 g/d for soap-soda and enzyme respectively). These results suggest that there exists a better orientation of the fibroin molecules in the filaments from treatment T2 rather than in the filaments from treatment T4. This fact could be well supported by the work of Kataoka 1975b, wherein it was indicated that higher spinning speeds favoured the formation crystalline structures in fibroin. Higher temperature during spinning increased the speed with which the cocoon was constructed due to increased physiological activity of the silkworm and is true in the case of treatment T2.

The degumming behaviour of soap-soda degumming method is quiet different from that of enzyme method. This is more evident when their degumming weight loss percentage at higher concentrations of degumming agents (7.5 g/l soap & 0.75g/l soda; 6 g/l enzyme) and resultant mechanical weight loss percentage of filaments from treatment T2 and T4 are compared. Under the longest degumming durations, the enzyme degummed filaments of treatment T2 besides undergoing higher degumming weight loss (29.8%), exhibited a better retention of strength (2.21 g/d) and elongation (17.86%) properties when compared with the soap-soda degummed set where in the degumming weight loss percentage was 28.6% with strength of 2.34 g/d and elongation of 17.89%. On the contrary, in the case of filaments from treatment T4, the soap-soda degummed sets exhibited poor retention of strength (2.10 g/d) and elongation (16.02 %) on account of high degumming weight loss (27.7%) when compared with enzyme degummed set wherein the degumming weight loss was 25.9% with strength of 2.2 g/d and elongation of 18.83%. The trend remained the same for the average values obtained across the different treatment duration for the above mentioned concentration.

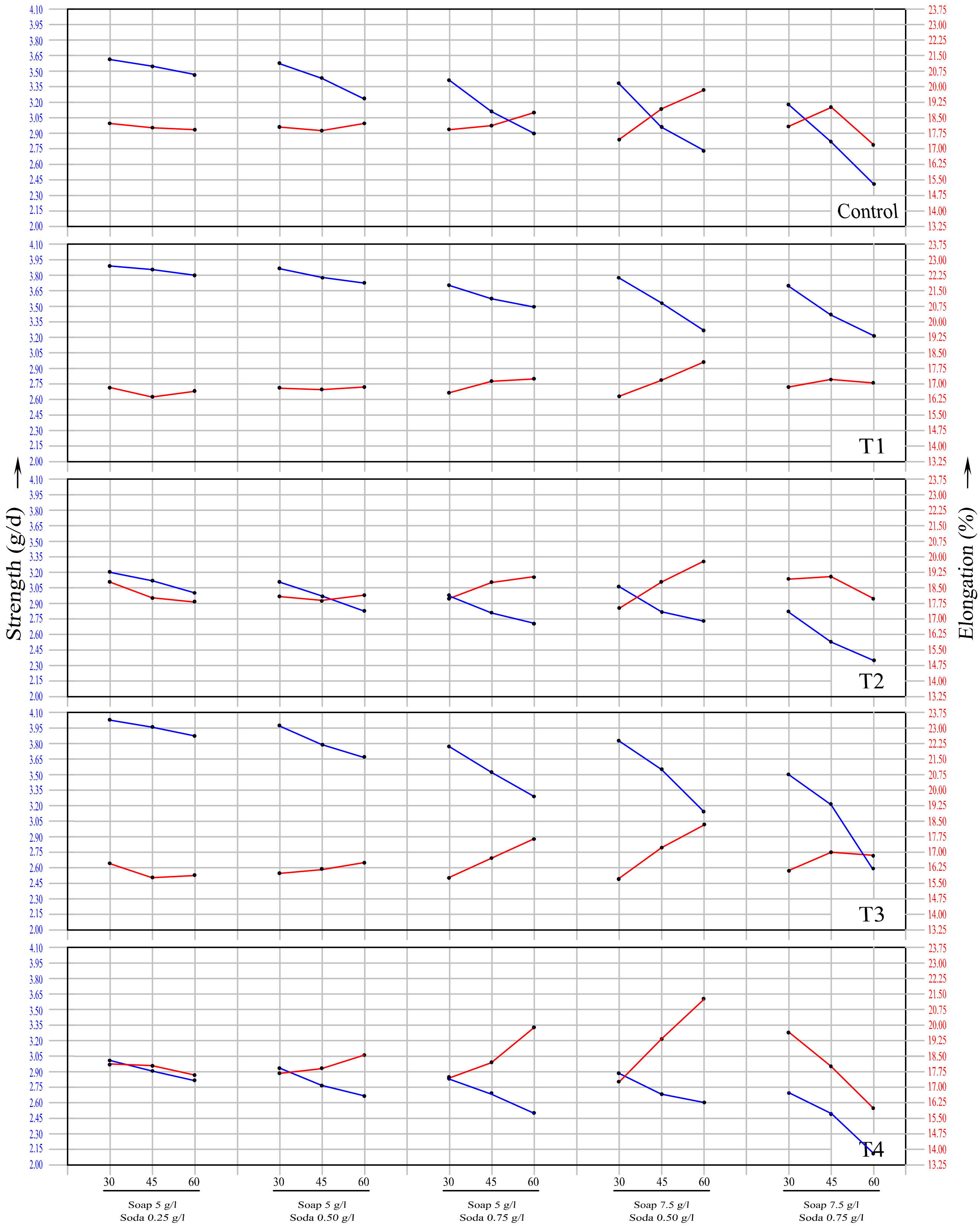

Fig 3 Mechanical properties of silk filaments degummed using Soap-Soda

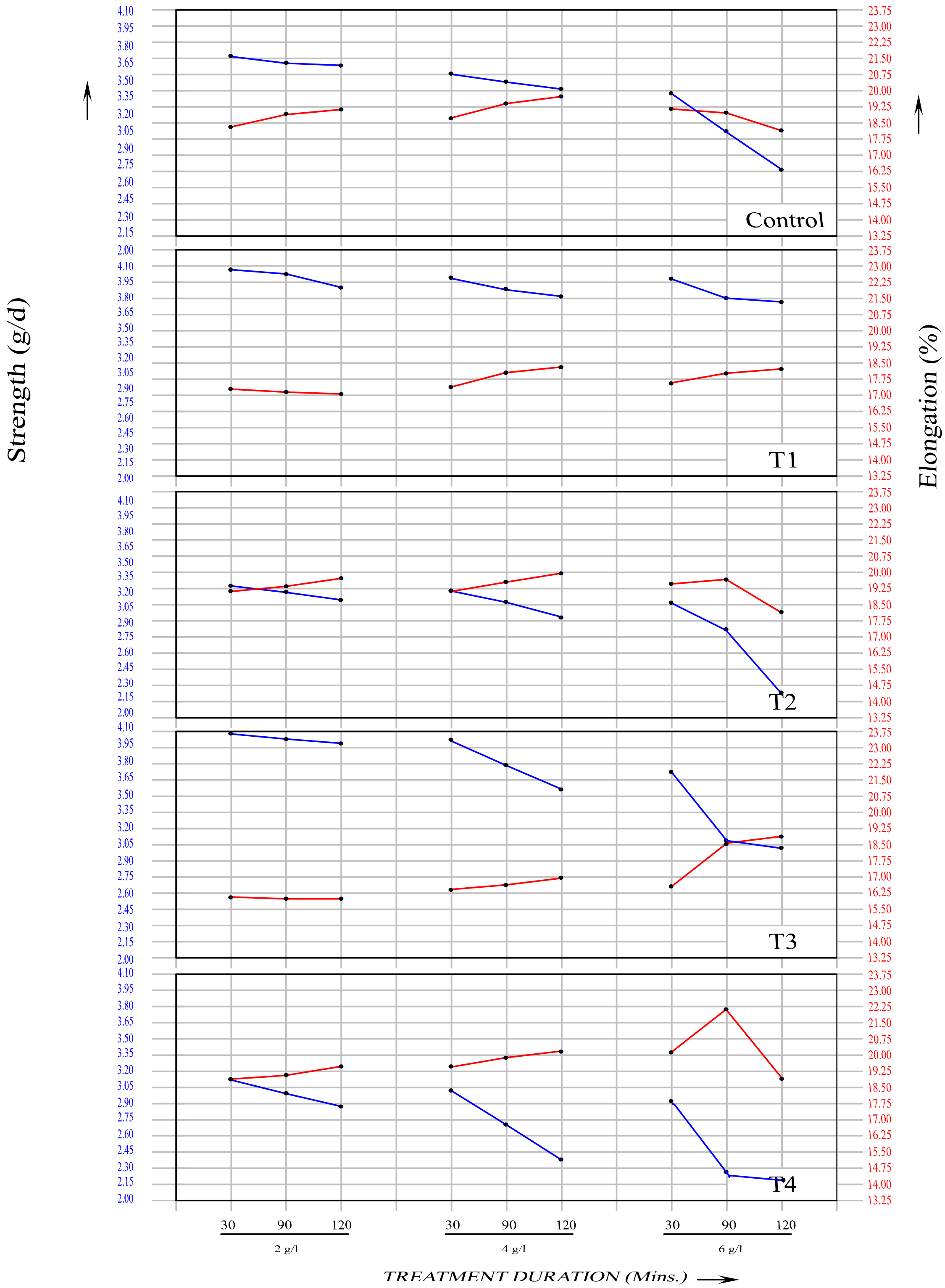

Fig 4 Mechanical properties of silk filaments degummed using enzyme

The above result confirms that the action of enzyme is more specific in removing sericin, especially at the interstitials of the fibre matrix unlike soap-soda which is non-specific and could have degradative effects on fibroin especially at higher concentration and prolonged treatment durations. These results are in confirmation with the work carried out by Zhu et al., 1994, Min *et al.,* 1997, Lee et al., 1986, Gulrajani, 1992. However, higher concentration and prolonged treatment with enzyme also caused degradative effect on fibre with severe loss in strength and elongation

values (Chopra and Gulrajani, 1994). This is been evidenced in the filaments from treatments T4 followed by T2 where in the tenacity and elongation values decreased drastically with a progress in the degumming time when higher concentration of enzyme (6 g/l) was used.
Thus in view of the above results, the following conclusions was drawn:

1. The temperature and relative humidity during cocoon spinning influenced separately the structure formation of sericin and fibroin
2. The structure development in silk fibre is no doubt a two phase system. However, formation of super-lattice structures between fibroin and sericin could not be ruled out.
3. Degumming is a process essentially required to remove sericin without destructing the fine fibrillar structure of fibroin. Inappropriate degumming methods and concentration of degumming agents could have serious implications on the qualitative aspects of finished product besides making the process uneconomical.
4. Besides restricting the degumming process to a nominal degumming weight loss percentage or a common degumming method, degumming procedures based on certain qualitative aspects of fibre is found essential.

Thus, from the above work, it is imperative to note that structural features of silk filaments could vary for cocoons from different environments and processing of such fibres could be challenging. Implementation of degumming process as appropriate to the quality of the fibre could lead to the manufacture of economical and robust quality end products.

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