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Research Paper

Characterization of Bivoltine and Nistari Silk Fibres Using Basic Analytical Tools

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The structural, thermal and mechanical behavior of two types of silk fibres namely Bivoltine and Nistari were studied using FTIR, XRD and DMTA. The chemical constituents like C=O, C-N stretching and N-H sites of these fibres were identified using Fourier Transform Infrared (FTIR) Spectroscopy. X-ray diffraction (XRD) measurements reveal that among the two silk varieties the Bivoltine is found to be more crystalline compared to Nistari fibre. In the present investigation we have made use of Dynamic Mechanical Thermal Analysis (DMTA) to look into the glass transition temperature (T_g) of these fibres and it is confirmed that the glass transition temperature (T_g) of Bivoltine silk (78ºC) is higher than Nistari silk (67ºC). Also small percentage change is observed in the storage modulus of these two fibres. From their visco-elastic property and glass transition temperature, Bivoltine silk is more suitable for silk fabrication than Nistari silk.

Key Words: Bivoltine; Nistari; XRD; DMTA

1. Introduction

Natural polymers like silk fibres are a continuous high molecular weight fibrous protein consisting of many kinds of amino acids. These are produced by different species of silkworm of which the principal species is bombyx mori, or the mulberry silkworm [1-3]. It has been shown that depending on the conditions of the sample preparation, silk fibres in solid state exist in different conformations. In its natural state raw silk from silkworm contains a number of constituents other than the fibre [4-7]. The main ones are silk grease, water-soluble material derived from perspiration and contaminants such as dirt and vegetable matter picked up from the pastures [8-10]. A Nistari silk fibre is another variety of popular Indian silk fibre dispersed in the eastern part of India. These contaminants are removed during processing. Clean silk with other animal fibres belongs to a group of proteins know as keratins. Unlike cotton and the majority of synthetic fibres, wool and silk does not have a homogeneous structure. wool and silk fibres have highly complex physical and chemical compositions that have evolved over millions of year to protect sheep and silk worm from extremes of heat and cold [11-13]. From the application point of view, these are excellent biomaterials for enzyme immobilized membranes used as biosensors. This property is due to the insolubility of the silk and immobilization of enzyme. Motivated by the interesting aspects of silk fibres mentioned above and their potential application it is worthwhile to investigate the structural changes in the silk fibres [14-16]. The structure of silk is shown in Fig. 1.

2. Experimental

Popular Indian silk fibres strands like Bivoltine and Nistari of required length and diameter has been reeled

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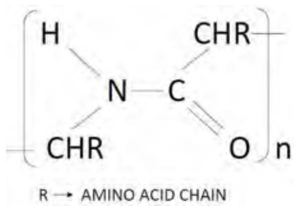

Fig. 1: Structure of Polypeptide Chain

out using respective cocoons by mechanical method. The filament of Bivoltine is long and usually white in colour. The total filament of a cocoon of this race is 1200-1500m and has a higher denier compared to Nistari. The Bivoltine and Nistari races do have higher tensile strength [17]. The amount of sericin content in bivoltine is less compared to Nistari races [18]. Also, Bivoltine fibre shows significant improvement in crystalline size with annealing temperature by rearrangement of protein molecules while retaining its fibre features [17]. The cocoon of Nistari silk is small in size and its characters are not as good for reeling compared to Bivoltine races. The total length of the filament of a cocoon is 500-600 m and has a lesser denier compared to Bivoltine races. The usual colour of the filament is golden yellow and possesses higher lustre property compared to Bivoltine races [19]. Similar to Bivoltine fibres, Nistari fibres show significant improvement in crystal size value with annealing temperature. The amount of sericin content in Nistari fibre is more compared to Bivoltine [18] races (approximately 25%) suggesting that the protection of the fibroin in this type is more, so that it cannot be easily damaged like the Bivoltine fibres. FTIR and DMTA spectra were taken from Bangalore Analytical Research Centre, Pvt., Ltd., Peenya, Bangalore. XRD measurement was done using model Jeol 8030, the voltage and current applied for the instrument is 40 kv and 20 mA, target element used is CuKα.

3. Results and Discussion

3.1. FTIR Analysis

FTIR spectra taken for Bivoltine and Nistari silk fibres are present in Figs. 2 and 3. The amide-I band at 1700-1600 cm^{-1} is characteristic to the peptide C=O stretching, revealing whether the carbonyl groups participate in the bonding or not. The frequency downshift can be explained by the decrease in the double bond character of the carbonyl group in the presence of bonding, i.e., an increased electronegative character of the oxygen atom. Furthermore, the bonding at the peptide amines can be studied based on the FTIR amide-II band at 1500-1580 cm^{-1}, which

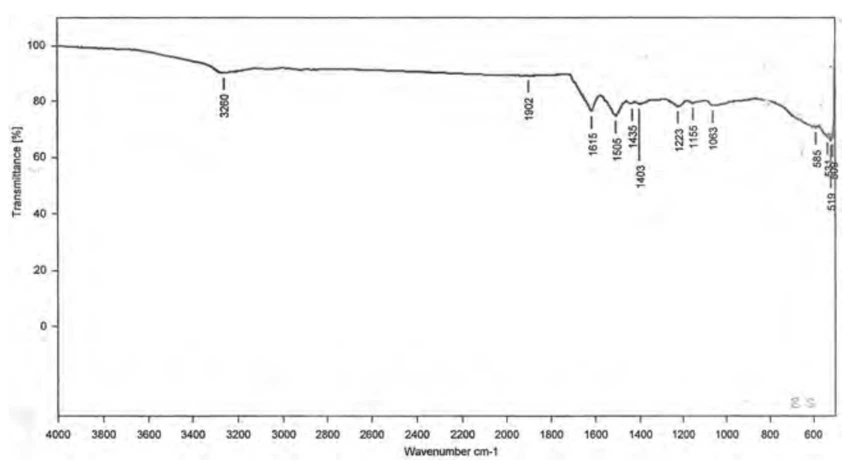

Fig. 2: FTIR Graph of Bivoltine Silk Fibre

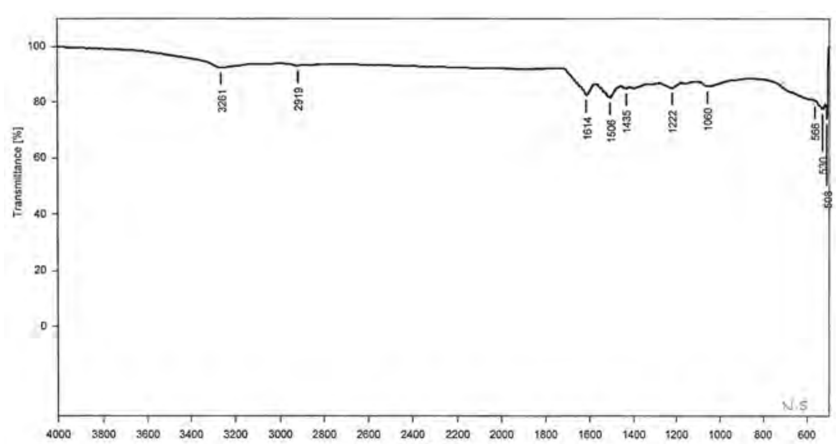

Fig. 3: FTIR Graph of Nistari Silk Fibre

is characteristic to both C-N stretching and N-H in plane bending. Bivoltine silk shows amide-I band at 1615 cm^{-1}. Amide-II band occurs at 1505 cm^{-1}. When there is bonding at N-H site in a peptide, there will be upshift in wavenumber. Nistari silk shows Amide-I band at 1614cm^{-1}. The amide-II band occurs at 1506 cm^{-1}, when there is bonding at N-H site in a peptide [20-24].

3.2. XRD Analysis

A typical XRD scan of Bivoltine fibre and Nistari fibres are presented in Figs. 4 and 5. Bivoltine XRD plot reveals that this fibre is not fully amorphous in nature and shows semicrystaline behaviour. XRD scan of Nistari fibre indicates a more amorphous nature compared to Bivoltine races [1].

3.3. DMT Analysis

DMTA scan of the experimental samples are presented in Figs. 6 and 7. Bivoltine is having 34 megapascal storage modulus and it is almost constant upto 40°C beyond which it decreases as shown in Fig. 6. It is found that Nistari has 110 mega Pascal storage modules which is shown in Fig. 7. From the study of graph the storage modulus decreases sharply upto 67°C and then the change in storage modulus is very small. It reveals that Nistari is more amorphous than Bivoltine [10, 11, 25].

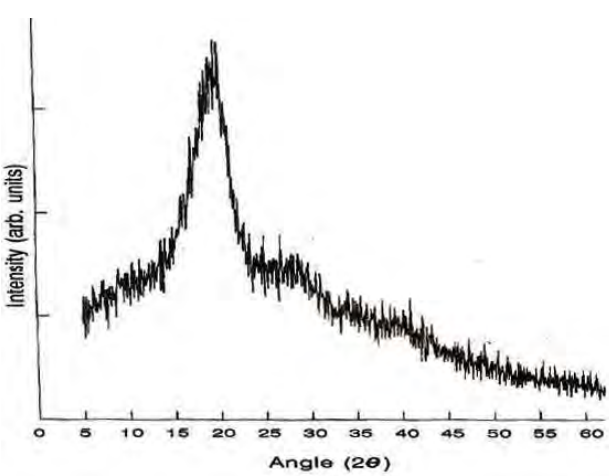

Fig. 4: XRD Scan of Bivoltine Silk Fibre

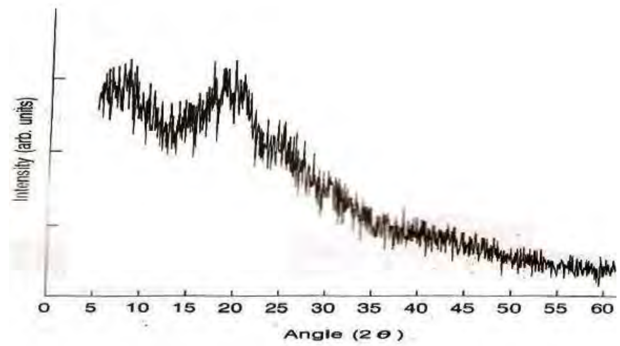

Fig. 5: XRD Scan of Nistari Silk Fibre

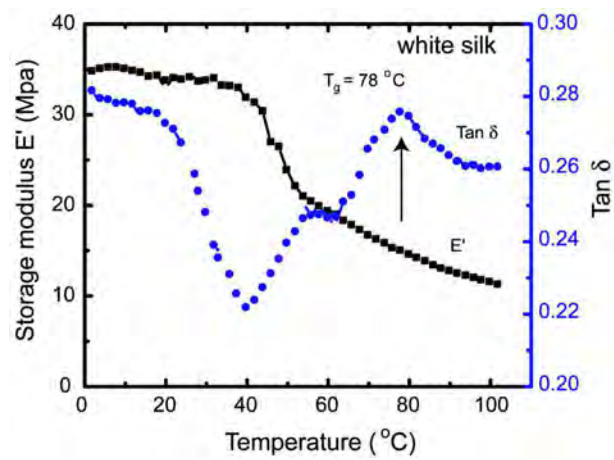

Fig. 6: DMTA Scan of Bivoltine Silk Fiber

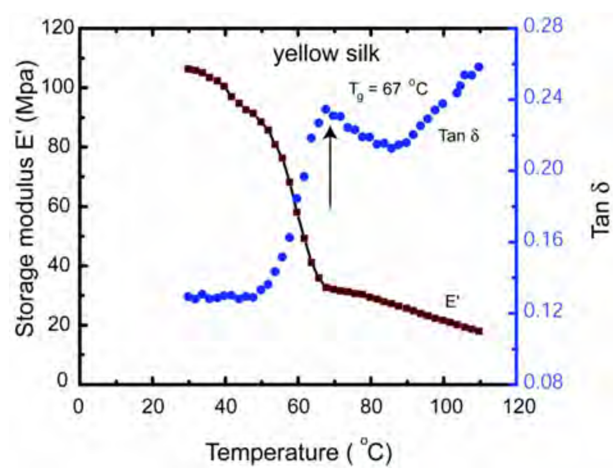

Fig . 7: DMTA Scan of Nistari Silk Fibre

4. Conclusion

The frequency downshift can be explained by the decreasing double bond character of the carbonyl group in the presence of bonding, i.e., increase in electro negative character of the oxygen atom. The shift of Amide-II band to higher frequencies suggests bonding at the N-H sites of the silk. XRD scan indicates that Nistari fibres are more amorphous compared to Bivoltine races. From DMTA ‘Visco elastic property of material’ and ‘glass transition temperature’ can be found. The thermal response of the Bivoltine silk fibres is interpreted in terms of glass transition temperature (T_g) (78°C) and similarly for Nistari T_g is 67°C. DMTA reflects the XRD results. The percentage change of storage modulus of Nistari silk is more compared to Bivoltine silk fibre.

References

1. Ramgopal G *et al*., *J Appl Poly Sci* **63** (1997) 395-400
2. Shimizu M *Sericultural J Sci Jpn* **20** (1951) 15
3. Kratky O and Schauenstein E *Disc Faradaysoc* **11** (1951) 171
4. Ranganathn SR and Quayyaum Z *New Horizons for Jute* National Information Centre for Textile and Allied Subjects, Ahmedabad (1993)
5. Chakravarty AC *Jute Bullatine* **33** (1970)
6. Liauw CM, Khunova V, Lees GC and Rothon RN *Macromol Symp* **194** (2003) 191
7. Morgan AB *Polym Adv Technol* **17** (2000) 206
8. Bueche F *Physical Properties of Polymers* Interscience Pub., NY, (1962)
9. Good I *Archeologicil Textile* A Review Research Annual Review of Antropology pp 209-226
10. OBV Parker “Polymer chemistry”, Applied Science Pub., London, (1974)
11. Encyclopedia of Polymer Sci. and Tech Plastics, Resins, Rubbers and Fibres, (Eds: Mark HF, Gaylord NG and Bikales NM) Interscience Pub., New York, **2** (1965)
12. “Rheology of Polymers”, (Eds : Vinogradov GV and Malkin AYA) Mir Publishers, Moscow (1980)
13. Gowariker VR, Viswanathan NV and Sreedar J *Polymer Sciences* Wiley Eastern Ltd., New Delhi, (1991)
14. Rippon JA *et al*., *The Structure of Wool* Chapter 1, *In*: Wool Dyeing Lewis, DM (1992)
15. Leeder ID *Wool-Nature Wonder Fibres*, Ocean Grove, Vic: Astralasian Textiles Publishers (1984)
16. Rippon JA *et al*., Wool, in Encyclopedia of Polymer Science and Technology, New York: Inter Science Publishers (2003)
17. Taeka Narumi, Masahiko Kobayashi and Tadasu Mori; *J Sericultural Sci Jpn* **62** (1993) 489
18. Shamachary and Gowramma *Indian Silk* **26** (1988) 52
19. Kim byung-HO *Raw Silk Reeling Associated Business Central Ltd*., Colombo, Srilanka (1989)
20. Renata Zemaitytye, Analysis and Identification of Fiber Constitution of Archaeological textile, ISSN1392-1320 **12**(3) (2006)
21. Peceliunaite-Baziene E *The Textiles from Gintarai Cemetery Archaeologia Lituana* **3** (2002)
22. Knudsen LR Analysis and Reconstruct Table Woven Bands from the Celtic B NESAT **V** textile symposium in Neumu
23. Farke H *Archaeological Fiber* Restaurierung and Museumstechnick
24. Smith BC *Fundamentals of Fourier Transformation Spectroscopy*, USA, CRC Press LLC
25. CN Banwell Fundamentals of Molecular Spectroscopy. **4th** ed., ISBN 0-07-707976-0.