Characterization and diffusion studies in bivoltin silk fibers

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Abstract- The structural, thermal and mechanical behavior of Bivoltin silk fiber are studied using,XRD , DMTA, FTIR and physical parameters like rate of diffusion of mass are determined using Diffusion behavior. An x-ray diffraction (XRD) measurement reveals that Bivoltin is not fully amorphous but it is semi crystalline in nature. The glass transition temperature of these fibers was found to be 78 ^{0}C using Dynamic mechanical thermal Analysis (DMTA). Visco elastic property of material and glass transition temperature concludes that bivoltine is more suitable for silk fabrication. The chemical constituents like C=O, C-N stretching and N-H sites of these fibres were identified using Fourier Transform Infrared (FTIR) Spectroscopy.

Key words - Bivoltine silk, Congo Red, Dimetyl Sulfoxide**.**

1.INTRODUCTION

Natural polymers like silk fibres and wool are a continuous high molecular weight fibrous protein consisting of many kinds of amino acids. These are produced by different species silkworm of which the principal species is bombyx mori or the mulberry silkworm[1,2,3].It has been shown that depending on the conditions of the sample preparation, silk fibre in solid state exist in different conformations[4,5,]. In its natural state raw silk from silkworm contains a number of constituents other than the fibre [6,7,8,9]. 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 [10,11,12]. 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, silk and wool does not have a homogeneous structure. silk and wool fibres have highly complex physical and chemical compositions that have evolved over millions of year to protect silk worm and sheep from extremes of heat and cold [13,14,15].

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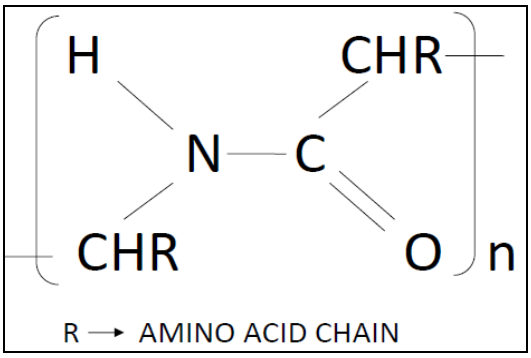
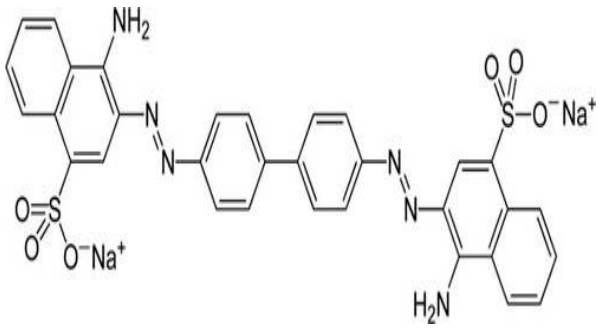
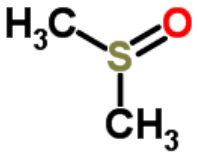
From the application point of view, these are excellent biomaterials for enzyme immobilized membranes used as biosensors. The most common use of silk are in manufacture of garments and in manufacture of decorative materials[16,17]. This property is due to the insolubility of the silk and immobilization of enzyme. Motivated by the interesting aspects of silk fibers mentioned above and to compare the diffusion of fluorescent dye molecules in wool [4,5] it is worthwhile to investigate the structural changes in the silk fibers. The structure of silk is depicted below [18,19,20]



CHEMICAL STRUCTURE OF POLYPEPTIDE CHAIN



Structural formula of CR



Structural formula of DMSO

2.EXPERIMENTAL

Popular Indian silk fiber strands like Bivoltine of required length and diameter has been reeled 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 races have higher tensile strength . The amount of sericin content in bivoltine is less compared to Nistari races [2,3]. Also, Bivoltine fibre shows significant improvement in crystalline size with annealing temperature by rearrangement of protein molecules while retaining its fiber features [2,3]. FTIR measurements were done using the FTIR spectrometer of model Alpha Of Bruker optocs make and DMTA measurements were done using a GABO Eplexor 150N DMTA at a measurement frequency of 10 Hz in the temperature range 0 to 120 ^{0}C. XRD measurement were done using a Jeol 8030 X-ray diffractrometer operated at an applied voltage of 40KV and 20mA, current using Cu Kα radiation.

Diffusion behavior of the polymer sample are studied with fluorescent dyes like Congo red [CR] and Dimethyl sulfoxide[DMSO] [31]. Structural formula of CR and DMSO as shown bellow.

Initially 1.5g of samples are taken, it is immersed in corresponding liquids about 10 minutes the liquids are taken with 100% concentration. Then the soaked samples are blotted with a blotting paper to remove excess dye and measured its weight using an electronic balance of WESNER make having an accuracy of 100 µg. The soaking process is continued with gradual increase in time up to 48 days.

3.RESULTS AND DISCUSSION:

XRD ANALYSIS:

A typical XRD scan of Bivoltine silk fiber is presented in figure 1. The XRD plot reveal that this fiber is not fully amorphous but it is semi crystalline in nature[3] .

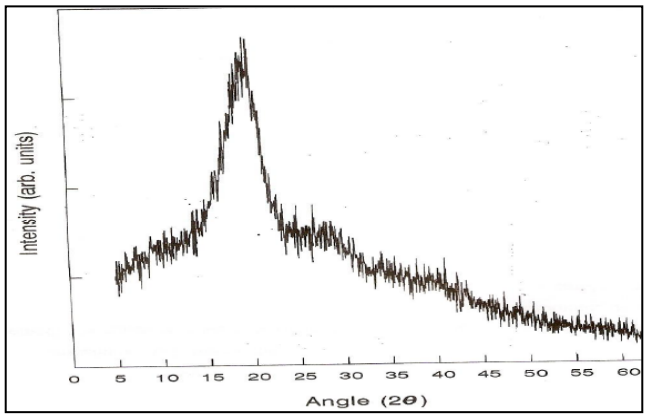


FIG 1: TYPICAL XRD SCAN OF BIVOLTIN SILK FIBER

DMTA RESULTS:

The DMTA plot of the silk fiber is presented in fig 2. The storage modulus of these fiber is 34 MPa. The storage modulus is almost constant upto 40^0 C beyond which it decreases. The tan δ peak for this fiber appears at 78 ^{0}C revealing its glass transition temperature at this temperature. DMTA reflects the XRD results of semi crystallanity in this polymer. [12,13,24]

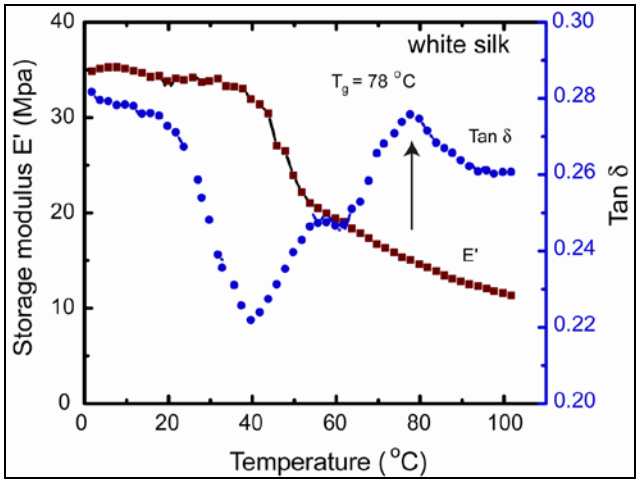


FIG 2: DMTA San of bivoltin fiber

FTIR RESULTS:

FTIR spectrums are taken for Bivoltine silk fiber is present in fig 3. The amide-I band at 1700-1600cm^{-1} is characteristic to the peptide C=O stretching reveals the information 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., a 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 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. [20,21,22,23,24]

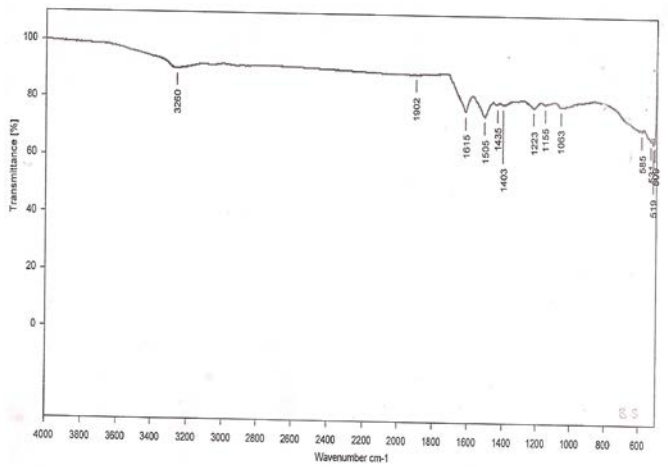


FIG 3;Typical FTIR graph of bivoltine silk fiber

4.CALCULATION OF DIFFUSION COEFFICIENT:

A typical graph showing the variation of Mass v/s Time of bivolti silk fibre in the dyes like CR and DMSO are presented in fig 4 and 5. In both the fluorescent dyes the Mass of sample increases initially and remains constant over a long period. To calculate the diffusion coefficient of sample in the above dyes a graph of [Wt-Wo/Ws-Wo] v/s √t is plotted in fig 6 and 7. The rate of mass diffusion coefficient for CR and DMSO is found to be $0.032X10^{-8}$ gms^{-1} and $0.012X10^{-7}gms^{-1}$.

We have used Fick's law of diffusion to understand the absorption mechanism. Stefan on modifying the theoretical equation of Fick's law of diffusion gives an approximate relation as

$$Mt/ Mm= 4(Dt/\pi l^2)^{1/2}$$

Where Mt and Mm are the masses of the penetrant taken up or lost at time t and m (time when the sample has reached the equilibrium weight). D is the diffusion coefficient and l is the thickness of the fiber. The fiber uptake at any time t (Mt) is calculated as

$$Mt = (Wt– Wo)/ Wo$$

Where Wo is the weight of the dry sample and Wt is the weight of the sample which has been soaked for a time t. Mm is calculated as

$$Mm = (Ws– Wo)/ Wo$$

Where Ws is the weight of the sample in the final stage of the absorption. A plot of Mt/ Mm vs √t is as shown in fig.8. It is evident from this figure that, throughout the period of absorption the ratio of Mt/ Mm varies linearly with √t [24,30]. The apparent diffusion coefficient is found to be $0.5543X10^{-7}cm^2s^{-1}$ for CR diffused in silk and $0.568X10^{-7}cm^2s^{-1}$ for DMSO diffused in silk. This is supported by the value reported by Mercer and Olofsson for diffusion constant ($Dk=1.61x10^{-7}$) compered with the present value. With this an order of magnitude greater than that of wool. It supports the semi crystalline behavior of compare to wool[4].

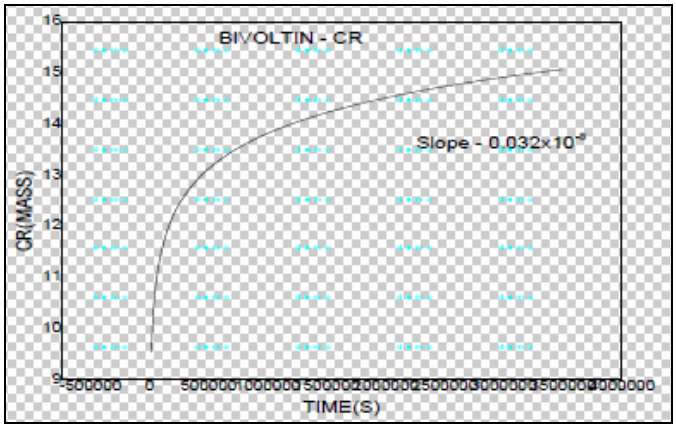


FIG 4:Mass v/s Time of bivoltin in CR

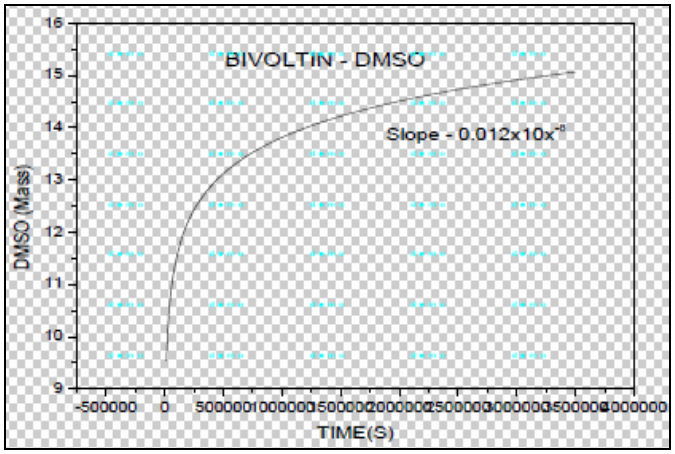


FIG 5: Mass v/s Time of bivoltin in DMSO

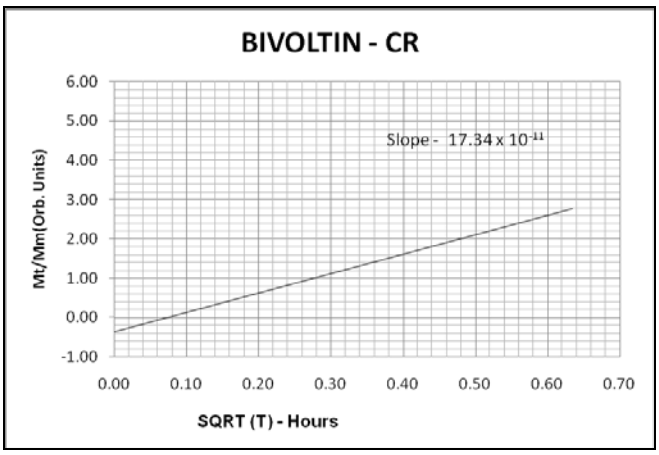


FIG 6: Variation of Mt/Mm as a function of the square root of absorption time in CR.

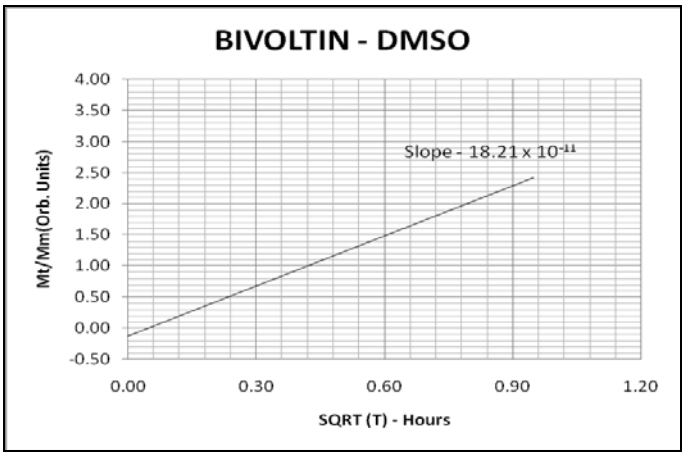


FIG 7: Variation of Mt/Mm as a function of the square root of absorption time in DMSO.

FTIR analysis of treated and untreated samples:

The bivoltin shows Amide I band at 1615cm^{-1}. Diffusion of CR and DMSO in bivoltin shows no IR changes.

In bivoltin, the amide II band occurs at 1505 cm^{-1}when there is bonding at N-H site in a peptide, there will be up shift in wave number. Amide II up shift by 11cm^{-1} and 10cm^{-1} after 48days of CR and DMSO treatment occurs at 1516cm^{-1} and 1516cm^{-1}. The shift of the amide II band to higher frequencies, after CR and DMSO uptake suggests banding at the N-H sites of the silk.

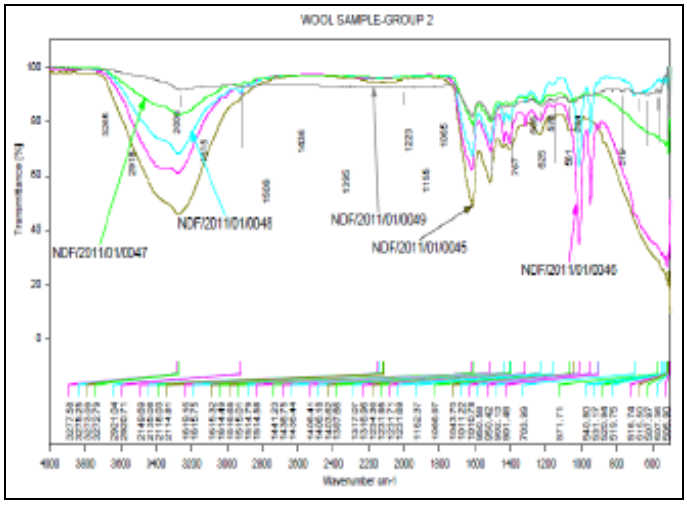


FIG 8: NDF/2011/01/0049-UNTREATED BIVOLTIN , 0048-ONE DAY DMSO TREATED BIVOLTIN, 0047- ONE DAY CR TREATED BIVOLTIN, 0046- 48 DAY DMSO TREATED BIVOLTIN, 0045- 48DAY CR TREATED BIVOLTIN

5.CONCLUSION:

We have made an attempt to understand the absorption behavior of a popular Indian variety bivoltin silk and the following conclusions are drawn: The XRD measurements reveal that the fiber is semi crystalline in nature and the DMTA measurements indicate the Tg of 78^{0}C. The possible reaction sites of the fluorescent dyes were identified using FTIR. The rate of mass diffusion coefficient of these dye molecules in wool fiber is found to be 0.032X10^{-8}gms^{-1} and 0.012X10^{-7} gms^{-1} . The apparent diffusion coefficient is found to be 0.5543X10^{-7}cm^{2}s^{-1} for CR diffused in silk and 0.568X10^{-7}cm^2 s^{-1} for DMSO diffused in silk.

6. REFERENCES

1. C.Rangnathaiah ,Chinese Journal of polymer Science Vol.21,No.3,(2003),325-332

2. G.Ramgopal & Et.al., Eur.Polym.J.Vol. 00, No.0,pp. 1-5,(1998)

3. G.Ramgopal & Et.al., Eur.Polym.J.Vol. 00, No.0,pp. 1-6,(1998)

4. Prasannakumar J.B., et al.,IJSER.,Vol 4,Issue 6(2013)

5. Prasannakumar J.B., et al., view of space.,Vol 1,Issue 2, 88-93(2013)

6. Cao, J.; Billows, C. A., Crystallinity Determination of Native and Stretched Wool by X-ray Diffraction, Polymer International, 1999, Vol. 48, pp1027.

7. Jinbo Yao and Yanbo Liu, Study on the Processing Technology of Stripping Wool Scales, Journal of Textile, Feb. 1994. pp
8. O. Kratky and E. Schauenstein,Disc.Faradaysoc., 11,171 (1951)

9. S.R Ranganathn and Z Quayyaum.'New Horizons for Jute. National Information Centre for Textile and Allied Subjects, Ahmedabad,1993,

10. A C Chakravarty. Jute Bullatine, Vol 33, 1970
11. Liauw C.M., Khunova V., Lees G.C.,Rothon R.N.:Macromol. Symp. 194,191(2003)

12. Morgan A.B: Polym. Adv. Technol. 17 ,206(2000)

13. F.Bueche; "Physical properties of Polymers" ,Interscience Pub.,NY, (1962)
14. Good ,I. Archeologicil textile;A Review Research Annual Review of Antropology pp.209-226. (2006)

15. "Polymer chemistry",O.B.V.Parker; Applied Science Pub.,London,(1974)

16. Encyclopedia of Polymer Sci. and Tech Plastics, Resins,Rubbers and Fibres,H.F.Mark, N.G.Gaylord, N.M.Bikales(eds.); Interscience Pub., New York,2,(1965)

17. "Rheology of Polymers",G.V.Vinogradov and A.YA.Malkin(eds.); Mir Publishers,Moscow,(1980).
18. V.R.Gowariker, N.V.Viswanathan and J.Sreedar;

19. "Polymer Sciences", Wiley Eastern Ltd., New Delhi,(1991).

20. Rippon, J.A.et al,(1992) The Structure of wool; Chapter 1,In;Wool Dyeing Lewis,DM

21. Leeder,I.D.(1984) Wool-nature wonder fibres, Ocean Grove, Vic:Astralasian Textiles Publishers,

22. Rippon, J.A. et al,(2003) Wool, in Encyclopedia of polymer Science and Technology,New York: Interscience Publishers.

23. Jinbo Yao and Yanbo Liu, Development of the Products of Cool Wool, Journal of Textiles, Nov., 1994. pp

24. Jinbo Yao, Journal of Engineered Fibers and Fabrics Volume 3, Issue 2—2008

25. Qinqian Zhou, Properties of Stretched Wool and Spinning Technology of Swelled Wool, Wool Textile Journal, Vol. 3, 2004, pp33-37.

26. Suoting Yang, Jianzhong Liu, Jinbo Yao et al. Researches on the Properties of Drawing Modified Wool, Journal of Textile Research, Vol. 23, No. 3, 2002, pp32-33.

27. R.Ramani, Eur.Polym. J. Vol.33, No.10-12, pp. 1753-1758,1997
28. Peceliunaite-Baziene,E.The Textiles from Gintarai Cemetery Archaeologia Lituana 3 2002 pp.75-78

29. Knudsen,L.R.Analysis and Reconstruct Table Woven Bands from the Celtic B NESAT V textile symposium in Neumu (2006)
30. Farke,H. Archaeological Fiber, Restaurierung and Museumstechnick.(in German) (2006)
31. Smith, B.C. Fundamentals of Fourier Trasformation Spectroscopy,USA,CRC Press LLC

32. Fundamentals of Molecular Spectroscopy.,C.N.Banwell 4th ed.,ISBN 0-07-707976-0
33. Mercer,E.H., and OlofssonN.B.–J.Polym.sci.6:671(1951)