Diffusion of fluorescent dye molecules in white wool fibers

Prasanna kumar J.B.1,3*, S.C.Nagaraju 2,3, A.Joseph Arul Pragasam 3 and G.Ramgopal 4.,

Abstract -The structural, thermal and mechanical behavior of white wool fibers are studied using FTIR, XRD, DMTA. and physical parameters like rate of Diffusion of mass are determined using Diffusion behavior. The chemical constituents like C=O, C-N stretching and N-H sites of these fibers were identified using Fourier Transform Infrared (FTIR) Spectroscopy. The X-ray diffraction (XRD) measurement reveals that the white wool is amorphous in nature. The glass transition temperature of these fibers was found to be 38 ^{o}C using Dynamic mechanical thermal Analysis (DMTA). Visco elastic property of material and glass transition temperature concludes that white wool is more suitable for wool fabrication.

Key words - White wool, Congo Red, Dimetyl Sulfoxide.

1.INTRODUCTION

Natural polymers like wool and silk fibers are a continuous high molecular weight fibrous protein consisting of many kinds of amino acids. Natural polymer like wool are produced by animal Sheep's outermost protective layer [1,2,3].It has been shown that depending on the region and conditions of the sample preparation, wool fiber in solid state exist in different conformations[4,5]. In its natural state raw wool from Sheep contains a number of constituents other than the fiber [6,7,8,9]. The main ones are wool grease, water soluble material derived from perspiration and contaminants such as dirt and vegetable matter that it picks up from the pastures [10,11,12].

These contaminants are removed during processing .Clean wool belongs to a group of proteins known as keratins. Unlike cotton and the majority of synthetic fibers, wool and silk does not have a homogeneous structure. The wool and silk fibers 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 [13,14,15].

1. Prasanna Kumar JB - Dept., of Physics, GFGC Tumkur , Tumkur Dist., Karnataka State., 09964521358.,prasannakumarjb@hotmail.com

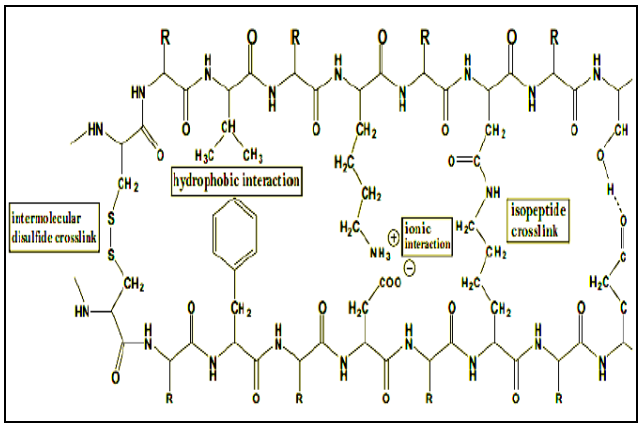
2. S.C.Nagaraju Dept., of Physics., Vidyavahini College., SIT Extn., Tumkur-572 103

3. , A.Joseph Arul Pragasam Dept., of Physics., Sathyabama University., Jeppiaar Nagar., chennai-119

4. G.Ramgopal Dept., of Physics., Maharani's science college., Palace Road., Bangalore-001

From the application point of view, these are excellent thermal and acoustic insulators used in construction of home, as well pads for soaking up oil spills. The most common use of wool are in manufacture of garments and in manufacture of blankets anti-static and noise-absorbing carpets [16,17].

Also diffusion of fluorescent dyes like Congo Red [CR] and Dimethyl Sulfoxide [DMSO] brings the structure changes in the polymers and helps to find the animal in the dark. Motivated by the interesting aspects of wool fibers mentioned above and their potential application it is worthwhile to investigate the structural changes in the wool fibers. The structure of wool is depicted below [18,19,20]

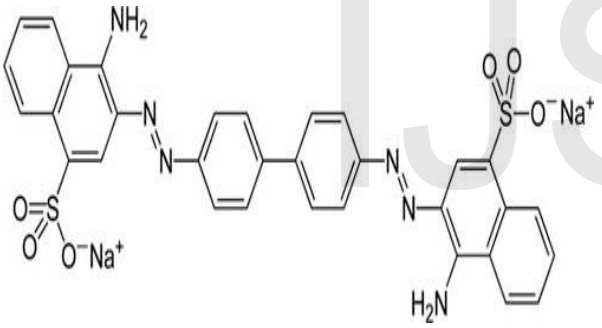


BONDS IN WOOL

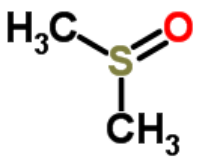
2.EXPERIMENTAL

Fibers of required length and diameter from white wool, a popular Indian wool has been reeled out by mechanical method. Generally, the white wool filament is milky white in colour and possesses higher lusture property [21]. The races have higher tensile strength compared to black wool [22]. The amount of sericin content is more, small in size and its characters are not as good for reeling compared to black wool [23]. 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 diffractometer 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.



Structural formula of CR



Structural formula of DMSO

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 results:

A typical XRD scan of white wool fiber is presented in figure 1. The XRD plot reveal that this fibre is amorphous in nature [3] .

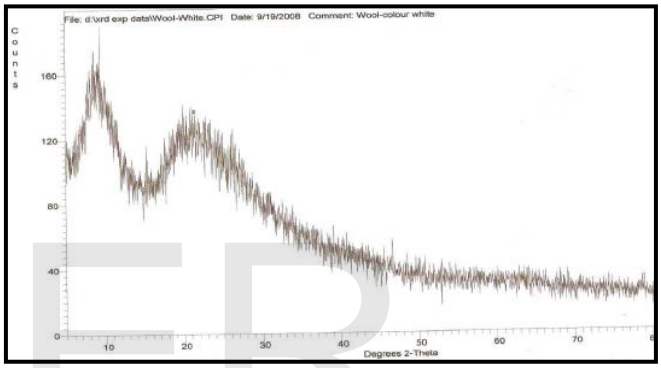


FIG 1: TYPICAL XRD SCAN OF WHITE WOOL FIBRE

DMTA results:

The DMTA plot of the wool fibers is presented in fig 2. The storage modulus of these fibres is around 38 MPa. The storage modulus shows a gradual decrease up to 60 ^{0}C and thereafter exhibits only a mild decrease. The tan δ peak for this fiber appears at 38 ^{0}C revealing its glass transition temperature at this temperature. DMTA reflects the XRD results of amorphosity in this polymer. [12,13,24]

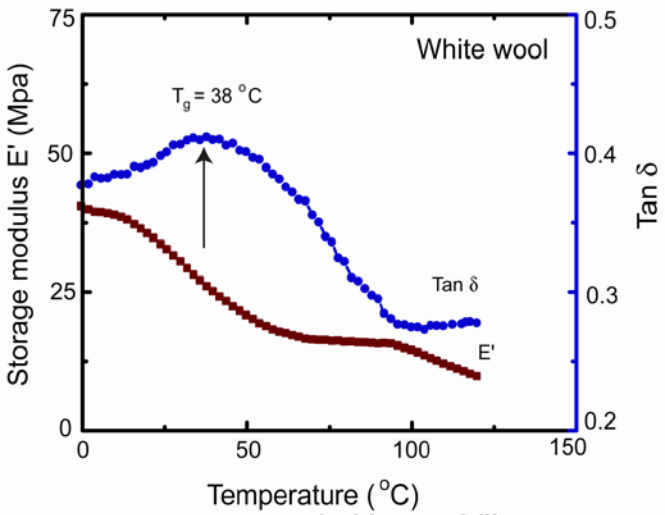


FIG 2: DMTA Scan of white wool fiber

FTIR results:

FTIR spectrum for the white wool fibre is presented 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. White wool shows Amide-I band at 1623cm^{-1}. The amide-II band occurs at 1515cm^{-1}, when there is bonding at N-H site in a peptide. There will be upshift in wavenumber. [25,26,27,28,29]

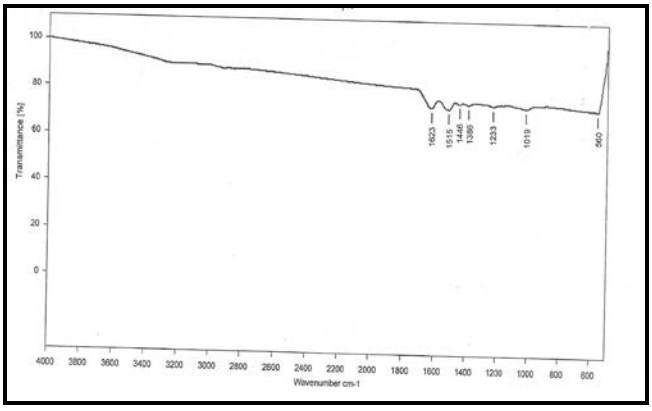


FIG.3: Typical FTIR graph of white wool fibre

Calculation of Diffusion coefficient:

A typical graph showing the variation of Mass v/s Time of White wool 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 6.48X10^{-8} gms^{-1} and 1.479X10^{-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 5.379X10^{-7}cm^{2}s^{-1} for CR diffused in wool and 5.33X10^{-7}cm^{2}s^{-1} for DMSO diffused in wool. This is supported by the value reported by Mercer and Olofsson for diffusion constant (Dk=1.61x10^{-7}) compared with the present value.

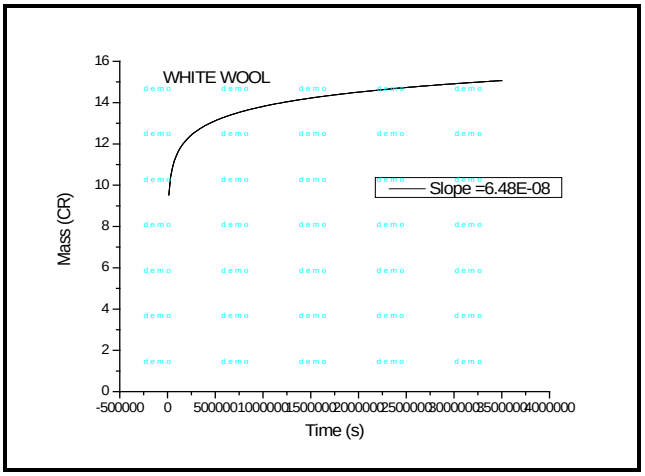


FIG 4: Mass v/s Time of white wool in CR

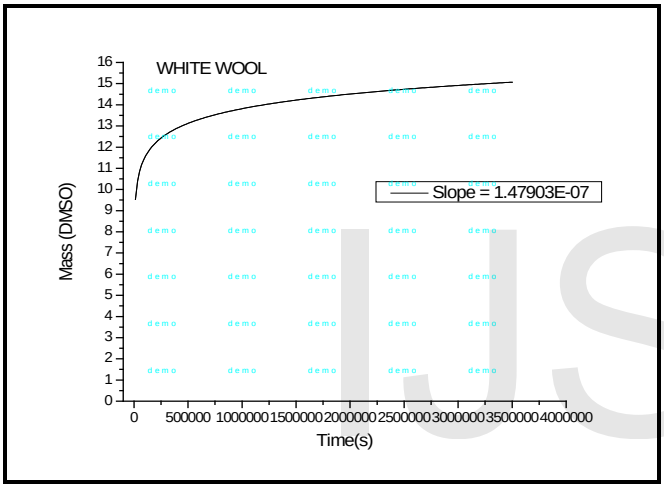


FIG 5: Mass v/s Time of white wool in DMSO

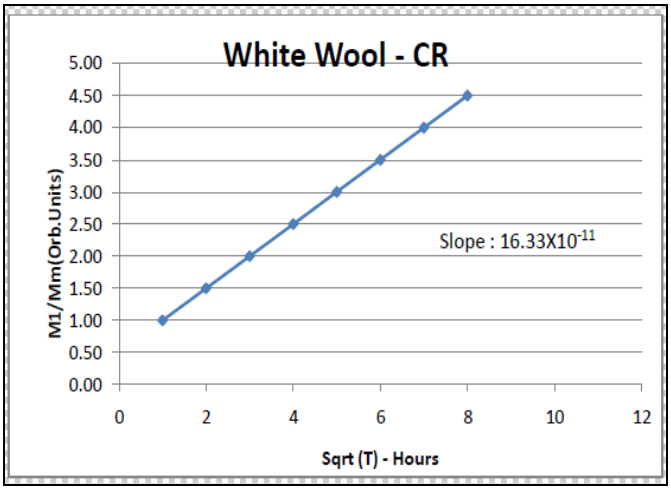


FIG 6: Variation of Mt/Mm as a function of the Square root of absorption time in CR.

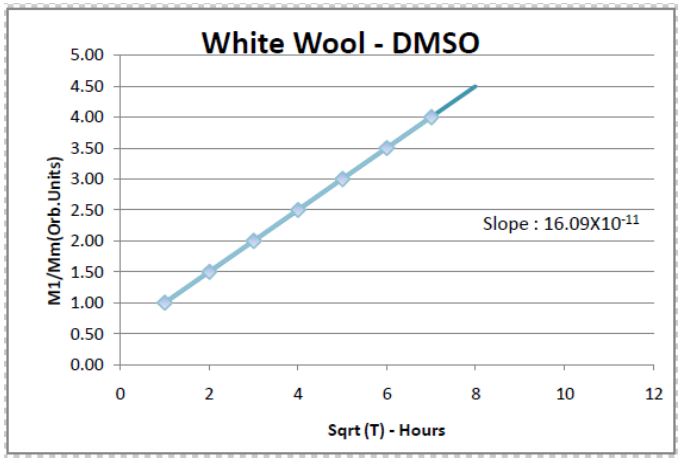


FIG 7: Variation of Mt/Mm as a function of the square root of absorption time in DMSO.

FTIR analysis of treated and untreated samples:

The white wool shows Amide I band at 1623cm^{-1} comparing diffusion of CR & DMSO in white wool, CR shows very small IR changes. The bonding at C=O site in a peptide is reflected by a up shift in wave number. Amide I up shift by 10.82cm^{-1} after 1day DMSO treatment occurs at 1633.82cm^{-1} and remains almost constant up to 48 days DMSO treatment occurs at1634.68cm^{-1} .

The frequency up shift can be explained by increase in double band character of the carbonyl group in the presence of bonding i.e., a decreased electronegative character of the oxygen atom.

In white wool, the amide II band occurs at 1516cm^{-1}. Amide II up shift by 21.88cm^{-1} after 1day of DMSO treatment occurs at 1537.88cm^{-1} and remains almost constant up to 48 days DMSO treatment occurs at 1538cm^{-1}.The shift of the amide II band to higher frequencies, after DMSO uptake suggests banding at the N-H sites of the wool. Almost disappearance of this band, after 48 days of CR treatment indicates a strong reaction at the N-H site.

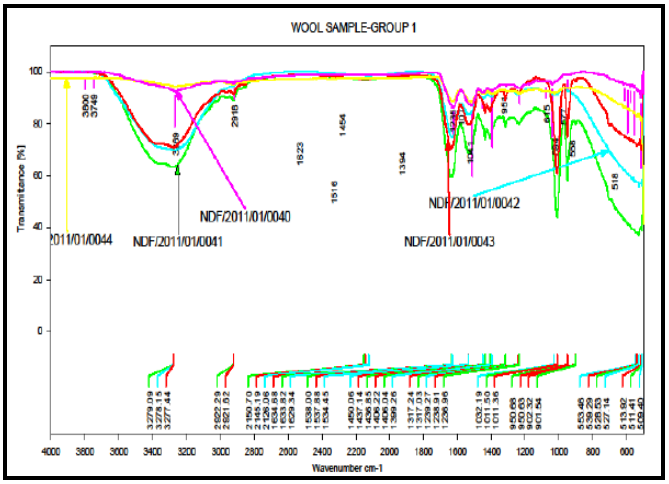


FIG10:NDF/2011/01/0044-UNTREATED WHITE WOOL, 0043-ONE DAY DMSO TREATED WHITE WOOL, 0042- ONE DAY CR TREATED WHITE WOOL, 0041- 48 DAY DMSO TREATED WHITE WOOL,0040- 48DAY CR TREATED WHITE WOOL.

4. CONCLUSION

We have made an attempt to understand the sorption behavior of a popular Indian variety white wool and the following conclusions are drawn: The XRD measurements reveal that the fibre is amorphous in nature and the DMTA measurements indicate the Tg of 38 ^{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 $6.48X10^{-8}$ gms^{-1} and $1.479X10^{-7}$ gms^{-1} . The apparent diffusion coefficient is found to be $5.379X10^{-7}cm^2s^{-1}$ for CR diffused in wool and $5.33X10^{-7}cm^2$ s^{-1} for DMSO diffused in wool.

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

5. Jinbo Yao and Yanbo Liu, Study on the Processing Technology of Stripping Wool Scales, Journal of Textile, Feb. 1994. pp

6. O.Kratky and E. Schauenstein,Disc.Faradaysoc., 11,171 (1951)

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

8. A C Chakravarty. Jute Bullatine, Vol **33**, 1970

9. Liauw C.M., Khunova V., Lees G.C.,Rothon R.N.:Macromol. Symp. 194,191(2003)

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

11. F.Bueche; "Physical properties of Polymers" ,Interscience Pub.,NY, (1962)

12. Good ,I. Archeologicil textile;A Review Research Annual Review of Antropology pp.209-226. (2006)

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

14. 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)

15. "Rheology of Polymers",G.V.Vinogradov and A.YA.Malkin(eds.); Mir Publishers,Moscow,(1980).

16. V.R.Gowariker, N.V.Viswanathan and J.Sreedar;

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

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

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

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

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

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

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

24. 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.

25. R.Ramani, Eur.Polym. J. Vol.33, No.10-12, pp. 1753-1758,1997

26. Peceliunaite-Baziene,E.The Textiles from Gintarai Cemetery Archaeologia Lituana 3 2002 pp.75-78

27. Knudsen,L.R.Analysis and Reconstruct Table Woven Bands from the Celtic B NESAT V textile symposium in Neumu (2006)

28. Farke,H. Archaeological Fiber, Restaurierung and Museumstechnick.(in German) (2006)

29. Smith, B.C. Fundamentals of Fourier Trasformation Spectroscopy,USA,CRC Press LLC

30. Fundamentals of Molecular Spectroscopy., C.N.Banwell 4th ed.,ISBN 0-07-707976-0

31. Mercer,E.H., and Olofsson N.B.– J.Polym.sci.6:671(1951)