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Study of Thermal Behavior of Silk Fibers Induced Heat Treatment

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ABSTRACT
The internal changes of raw and degummed muga (Antheraea assama) and eri (Samia Cynthia riciny) fibers induced by heat treatment at constant temperatures (313, 353, 393, 433 and 473K) are studied with a X-ray powder diffracto meter (Philips X'pert Pro) with high temperature attachment (Anton Paar, HTK-16). The peak intensity is found to increase with the rise in temperature as more and more tiny crystals of fibers aligned themselves linearly along the fibers. The degree of crystallinity (DC%) are found to be maximum at 353K for all the samples. At this temperature the DC% of muga raw, degummed by 0.3% Na_2CO_3 and degummed by formaldehyde are 71.65, 86.34 are 85.02 respectively; while those for eri raw, degummed by 0.3% Na_2CO_3 and formaldehyde are 64.62, 79.34 and 79.37 respectively. To provide further information on the thermal behaviours of the muga and eri fibers (raw and degummed), the expansion and contraction behaviour (Dry heat shrinkage) are investigated by thermo-mechanical analysis. The fibers show a measurable contraction at temperature 373K and 493K. At 373K, the shrinkage% are 2.3%, 29.1% and 1.9% respectively for muga raw, degummed by Na_2CO_3 and by formaldehyde. At 493K these values are 17.8%, 16.7% and 1.2% respectively. Also the thermo gravimetric (TG) study showed that there 9.1%, 8.1% and 9.2% weight loss of muga fiber during dehydration in three media viz. air, nitrogen and oxygen respectively. The weight losses are 35.2%, 27.7% and 38.5% during decomposition reaction. For eri, these values are 10%, 5.2%, 8.4% and 37.6%, 33.4%, 44.7% respectively.
Keywords: Antheraea assama, Samia Cynthia riciny, degree of crystallinity, dry heat shrinkage, thermo gravimetric.

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I. INTRODUCTION

Silk is one of the most important type of fibrous proteins, having potential application in textile and electrical industries [1]. Their possible use as biocompatible materials has been observed by the recent research[2]. Tsukada et al [3] observed that the wild silk fibroins contain a larger amount of amino acids with polar and ionizable side groups; these are reactive sites potentially exploitable for chemical reaction. The attempts towards correlating the fine structure with the properties should be aimed at elucidating the structure and properties at all levels. The correlation of property with respect to degree of crystallinity forms another important basis of understanding the mechanism of interaction of various structural units.

Studies on the physical, structural and chemical properties of silk fibers have been carried out since long back. The presence of peptide bonds in a protein was first demonstrated by Fisher[4]. The first X-ray diffraction pattern was obtained using silk fibers by Herzog and Jancke [5]. The muga and eri silk fibers are hygroscopic and semicrystalline in nature. They have great utility in textile industries, due to their essential characteristics of external forms and physico-chemical behaviour. It is evident that the reaction kinetics and enthalpy etc. of a material are based on their physico-chemical properties[6]. Thus the study of thermal behaviour of the natural silk fibers has great importance in textile industries.

Various investigators studied the thermo-physical properties of different natural fibers[7-9]. The XRD studies of annealed and quenched fibers were done by some researchers [10-11]. Besides, it is osversed that the expansion and contraction behaviours due to change of temperatures of some silk fibers are investigated by some workers [12-14]. Of course, no such change in behaviour due to change of temperature and due to XRD studies with continuous variation of temperature of raw and degummed muga and eri fibers endemic to north-east India have been noticed.

II. MATERIALS AND METHODS

Sample preparation:

Cocoons of muga and eri fibers were collected from different parts of north-east region of India The fibers were extracted from them; each of the fibers extracted from the cocoons were divided into three parts. Each of the first part was without any treatment, so used as raw samples. Each of the second parts of the fibers was boiled with 0.3% Na_2CO_3 solution for about an hour. After cooling, the fibers were washed with distilled water to remove alkaline substance and allowed to dry normally. Each of the third part was immerged into formaldehyde solution for about 24 hours at room temperature. Then they were washed with distilled water and allowed to dry normally.

Experimental arrangement:

For X-ray diffraction, the very finely cut fiber samples were glued (with Japan lacquer) to the groove of the sample holder of high temperature camera (Anton Paar, HTK-16) with temperature controller TCU 2000, mounted in the X-ray powder diffractometer. Software program were made for high temperature measurement of the fiber samples with the help of X'Pert software.To detect the expansion and contraction properties of raw and degummed silk fibers an 'Innovative DTC-96' manufactured by 'Tempo instruments and equipments (1) Pvt. Ltd., Bombay was used. The thermogravimetric (TG) analysis were performed to investigate change in weight of the samples and the thermal stability of them.

Measurements:

The XRD high temperature measurements were done in X-ray powder diffractometer of (Philips X'Pert Pro). The fiber samples were scanned at different constant temperatures 313 K, 353 K, 393 K, 433 K and 473 K respectively with step size 0.04^0 and time per step 0.5 s. The samples were heated @ 20^0/min. The fiber samples were subjected to X-radiation (Cu Kα λ=1.54 Å). The voltage applied to the x-ray tube was 40 KV and the current were 20 mA. Programmable divergence slit with irradiated length of 8 mm were used during the measurement with programmable receiving slit being used at the other end with slit height of 0.1 mm. the incident beam mask was fixed at 10 mm. The diffracted beam soller slit was fixed at 0.04 rad. Diffracted beam mask was not used. The pulse height distribution for the detector at upper and lower levels was fixed at 80% and 35% respectively. The scanning range was taken from 10^0 to 30^0.

To measure the thermal expansion and contraction of the fibers, single filament of it is taken. During the heat treatment, a load of 5 mg was applied. The measurements were taken at the room temperature (301K). These measurements were repeated for reproducibility.

For thermo gravimetric study, 5 mg of the fibrous sample was taken on the porcelain crucible specially designed for this purpose. After inserting the sample holder with the crucible into the centre of the furnace carefully, the temperature control unit and other related recording switches were made on so as to heat the sample at the heating rate of 10K/min- The air was allowed to pass through at constant rate around the opening space of the sample holder inside the furnace- The TG recorder was allowed to scan the sample continuously fiom room temperature 295K upto temperature specified 673K for fibres. Similar records of TG were made for nitrogen and oxygen atmosphere also.

III. RESULTS AND DISCUSSION:

In fig.1, the XRD of raw and degummed muga fiber at different temperatures are shown. The three diffraction peaks of the samples corresponding to the 2θ values, attributed to the β crystalline structure[19]. The peaks corresponding to 2θ values shifted slightly with the change of temperatures. This shift of the peaks could be attributed to the slight change of the interplaner

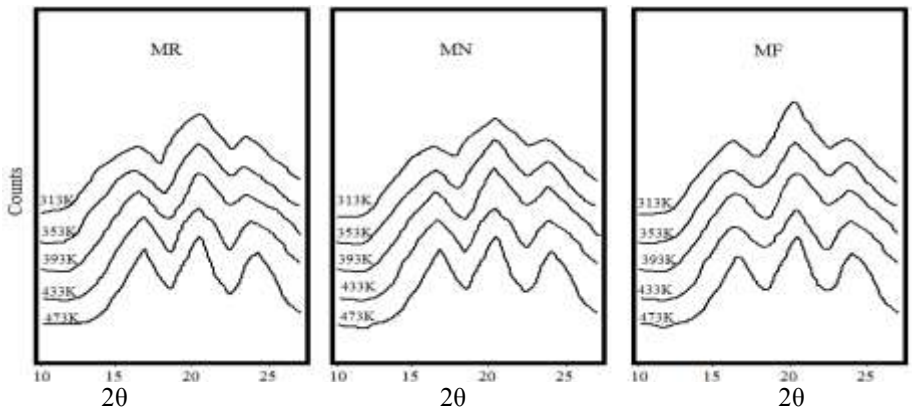

Fig.1- .XRD of raw and degummed muga fiber at different temperatures.
(MR- muga raw, MN- muga degummed by 0.3% Na_2CO_3, MF- muga degummed by formaldehyde)

spacing of the β crystals. It is observed from the fig.3, that there is no significant change of the crystalline structure of the fibers, due to the heat treatment from temperature 313K to 473K for all the fiber samples.The change of peak height with corresponding intensity and degree of crystallinity for raw and degummed muga and eri fibers are displayed in table 1 and table 2 respectively. The values of percentage degree of crystallinity were calculated on the basis of the formula used by Teh and

Table 1: Parameters obtained from XRD spectrum of raw and degummed muga fibers.

Samples	Temp. (K)	2θ (degree)	d_{hkl} (Å)	I_{max}	I_{min}	DC (%)
Muga Raw	313	20.87	4.34	61.09	21.33	64.08
	352	20.91	4.30	69.78	19.78	71.65
	393	20.12	4.44	69.23	21.55	68.87
	433	20.57	4.35	66.11	19.15	71.03
	473	20.39	4.36	67.21	21.43	68.12
Muga Degummed by 0.3% Na_2CO_3	313	20.84	4.28	47.63	12.49	73.78
	352	20.97	4.19	61.34	8.38	86.34
	393	20.67	4.25	53.12	13.69	74.23
	433	20.23	4.39	57.04	12.80	77.56
	473	20.38	4.35	54.08	12.74	76.45
Muga Degummed by formaldehyde	313	20.85	4.28	90.37	19.69	78.21
	352	20.91	4.24	120.45	18.04	85.02
	393	19.96	4.45	103.06	25.74	75.02
	433	20.37	4.34	100.21	20.37	79.67
	473	20.59.	4.31	92.67	21.01	77.34

Table 2: Parameters obtained from XRD spectrum of raw and degummed eri fibers.

Samples	Temp. (K)	2θ (degree)	d_{hkl} (Å)	I_{max}	I_{min}	DC (%)
Eri Raw	313	20.87	4.12	58.12	24.92	57.12
	352	20.91	4.04	65.89	23.28	64.62
	393	20.12	4.34	65.07	25.13	61.38
	433	20.57	4.21	62.42	22.60	63.78
	473	20.39	4.19	61.76	24.20	60.81
Eri Degummed by 0.3% Na_2CO_3	313	20.84	4.14	45.45	14.80	67.43
	352	20.97	4.07	59.23	12.24	79.34
	393	20.67	4.10	51.56	17.92	65.23
	433	20.23	4.19	55.78	17.77	68.15
	473	20.38	4.12	52.41	18.41	64.87
Eri Degummed by formaldehyde	313	20.85	4.09	88.05	22.06	72.67
	352	20.91	4.07	117.67	24.27	79.37
	393	19.96	4.23	100.48	30.89	69.25
	433	20.37	4.16	97.39	29.10	70.12
	473	20.59.	4.33	89.36	28.99	67.56

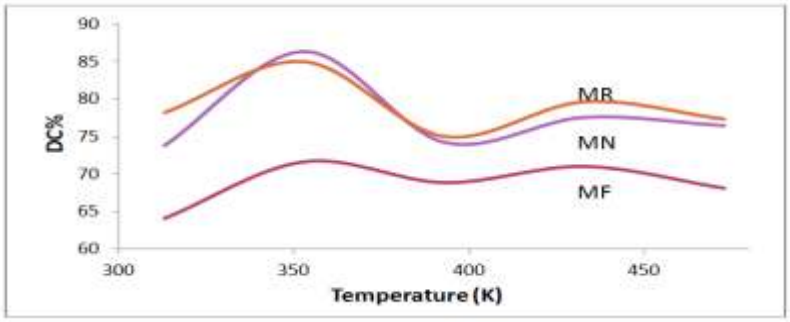

Fig . 2 – Variation of degree of crystallinity of muga fiber with temperature.
(MR- Muga raw, MN- Muga degummed by Na_2CO_3, MF- Muga degummed by formaldehyde)

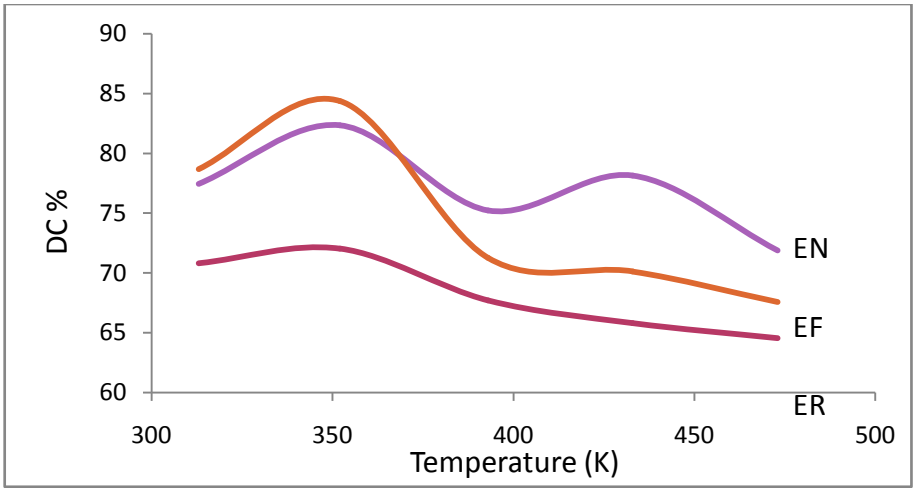

Fig. 3- Variation of degree of crystallinity of eri fiber with temperature.
(ER- Eri raw, EN- Eri degummed by Na_2CO_3, EF- Eri degummed by formaldehyde)

Ruddin[20]. The degree of crystallinity shows a specific trend in all the samples. For all the samples it increases from temperature 313K to 353K and then decreases at 393K. This may be attributed to the dissociation of water molecules embedded in the amorphous region of the fibers. This result agrees with the studies done by other researchers[21]. Again it shows a rising trend at 433K and decreasing trend at 473K. These are shown in fig.2 and in fig.3. This may be due to the interfacial polarization effect to decomposition state.

The shrinkage percentage of muga and eri fibers (raw and degummed) are shown in fig.2 and fig.3 respectively. It is seen that all the fibers exhibit considerable contraction, in the range from 353K to 373K. This may be attributed to the evaporation of water vapour absorbed by the samples. The quantity of contraction of muga raw, muga degummed by 0.3% Na_2CO_3 and muga degummed by formaldehyde at 373K are 2.3%, 29.1% and 1.9% respectively. The length of the fibers remained unchanged from temperature 395K to 470K; then again occurred contraction distinctly at temperature 495K. The quantity of contraction at this temperature for muga raw, degummed by 0.3% $NaCO_3$ and degummed by formaldehyde are 17.8%, 16.7% and 1.2% respectively. For eri raw, degummed by Na_2CO_3 and by formaldehyde the shrinkage% at 370K are 2.8, 25.3 and 2.2 respectively. At 490K, these values are 24.4, 22.3 and 3.2 respectively. This may be due to partial thermal decomposition by the samples. This may be resulted due to the breaking and reforming the inter-chain hydrogen bond and to the partial thermal decomposition. The temperature at the final extension may be the decomposition temperature of the fiber with β molecular configuration[15]This thermo-mechanical analysis thermograms shown by fig.1 is similar to the DTG thermogram of muga fiber[16] in this range. It is also observed that the thermal stability of muga fiber due to degumming by 0.3% Na_2CO_3 increases, while the fiber degumming by formaldehyde decreases.

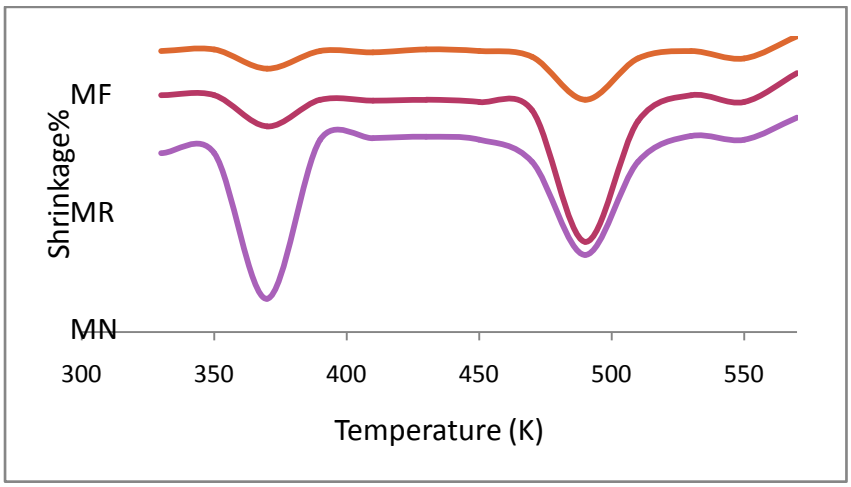

Fig.4- Dry heat shrinkage of raw and degummed muga fibers with temperature.
(MR- muga raw, MN- muga degummed by 0.3% Na_2CO_3, MF- muga degummed by formaldehyde)

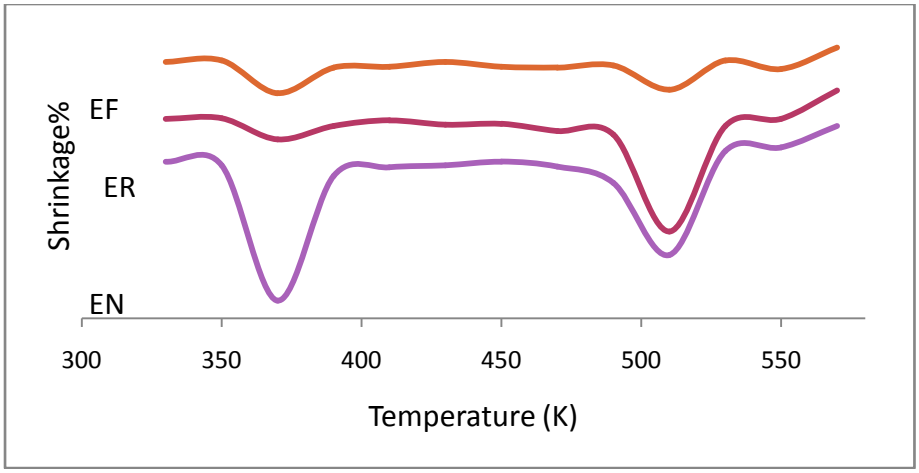

Fig.5- Dry heat shrinkage of raw and degummed eri fibers with temperature.
(ER- eri raw, EN- eri degummed by 0.3% Na_2CO_3, EF- eri degummed by formaldehyde)

The TG thermograms of muga and eri silk fibers are shown in fig.6. The TG curves show gradual beginning of weightloss at about 300K for the fibers in air atmosphere. It continues to 390K for muga and 400K for eri fibers. The weight losses, during this stage, are 9.1% and 10.0% for muga and eri fibers respectively. It may be inferred that the weight loss is occurred due to dehydration of absorbed water molecules associated with the silk fibers. The DTA study of these fibers by some investigators also agrees very close to this result[17].

The TG thermograms show the beginning of the second step weight loss at about 515K for muga and 505K for eri fibers. The process continues to 655K for muga and to 665K for eri fibers. It may be inferred that these weight losses occurred due to decomposition. It may be observed that the silk fibers under experiment show similar thermal behaviour in the three media, viz. air, oxygen and nitrogen. It is also noticed that the dehydration and decomposition are less in nitrogen and more in oxygen than in air, which may inferred that the medium has important role in thermo-chemical reactions to transfer the fibrous solids gradually into various gases during the process of irreversible decomposition. The gases thus evolved due to thermal degradation in the decomposition stage may be water vapour, carbon dioxide and carbon monoxide; which was observed earlier by some investigators by IR absorption spectroscopy technique[18].

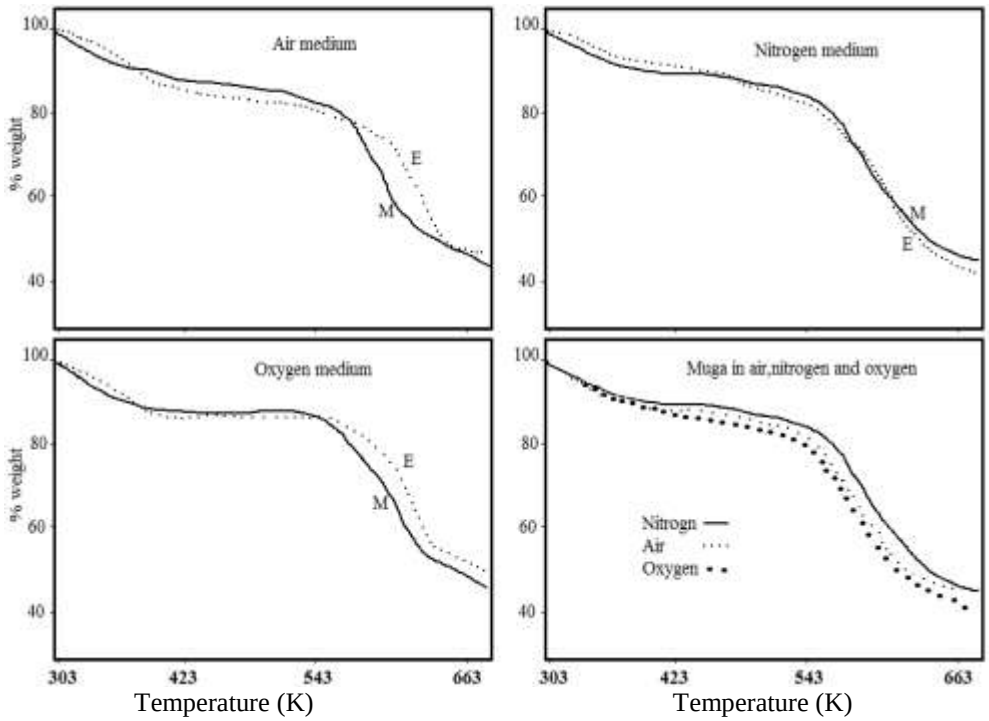

Fig.6. TG thermograms of raw muga fibers in air, oxygen and air medium.

The various TG parameters for the two fibers are shown in table 3.

Table 3. TG data of raw muga and eri silk fibers under different medium.
(Deh.-Dehydraion, Dec.-Decomposition)

Sample	Reaction step	Air medium		Nitrogen medium		Oxygen medium	
		Temp. range (K)	Wt. loss %	Temp. range (K)	Wt.loss %	Temp. range (K)	Wt. loss %
Muga	Deh.	300-390	9.1	300-365	8.1	300-390	9.2
	Dec.	515-655	35.2	505-665	27.7	495-640	38.5
Eri	Deh.	300-400	10.0	300-370	5.2	300-390	8.4
	Dec.	510-665	37.6	535-660	33.4	470-640	44.7

IV. CONCLUSION

The muga and eri silk fibers (raw and degummed) have found to retain original crystalline structure despite the heat treatment from temperature 313K to 473K. of course, during the heat treatment the shape of amorphous region changes to some extent. This may be attributed to the dissociation of water molecules embedded in the amorphous region of the semicrystalline fibers. It is inferred from the dry heat shrinkage observation that the thermal stability increases due to degumming both muga and eri fibers by 0.3% Na_2CO_3. The thermo gravimetric study indicates that both the silk fibers show two step variations in two distinct temperature ranges. The first step at lower temperature range represents their dehydration character and the second step at reasonably higher temperature range shows their decomposition reaction. During the decomposition stage the structural set up of the silk fibers is broken and fibrous molecules are transformed into gases.

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