Thermal analysis of eri and muga fibers

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Abstract:

The fibers were directly extracted by removing the floss from some eri (*Samia cynthia ricini*) and muga (*Antheraea assama*) cocoons collected from various places of north-east region of India. The fibers so extracted is washed with distilled water and then dried normally. These were used as raw samples. Some of the cocoons were boiled in 0.3% Sodium Carbonate for about one hour, and then cooled. The fibers were then extracted, washed with distilled water and the dried normally. These were used as degummed samples. The raw and degummed fibers were cut into tiny particle size; and sent to laboratory for experiments.

The thermodynamical properties of eri and muga silk fibers have been investigated in details by DTA, DSC and TG techniques. The experiments have been carried out in the temperature range 298K to 673K. The dehydration and rehydration phenomena, during thermal treatment, show the hydrophilic nature of the silk fibers. The dehydration and decomposition, the two step activities attributed in the fibers. The first step at lower temperature range shows dehydration while the second step at higher temperature range represents decomposition character. During DSC, the weight loss percentage of eri is 49.25 and of muga is 37.26 in decomposition stage. The thermal stability of muga fiber is found more than in the eri fiber, as the crystalline orientation of muga is better. It is also found that media (atmosphere) has important role for the variation of thermodynamical properties of the fibers.

Key words:

Samia cynthia ricini, Antheraea assama, Differential thermal analysis, Differential scaning calorimetry, Thermogravimetry analysis, Decomposition, Dehydration.

Introduction:

Natural silk fibers are basically protein fibers having potential applications in textile and electrical industries [1-5]. Muga, eri and pat silk fibers have attracted the scientists and technologists because of their commercial importance. Such fibers are composed of two brins of fibroins stretched from two glands of the silk worms. The thermal properties of various cellulose and protein fibers by Differential Scanning Calorimetry (DSC) technique have been reported by different workers [6-9]. The thermodynamic behaviours of silk fibers have been studied at room temperature as well as at different higher temperatures at which they are quenched and annealed [10]. In present investigation, eri and muga fibers are subjected to DTA, DSC and TG arrangements at different temperatures to study their behaviours with rise in temperatures.

Fibroin and sericin are the two main constituents of the silk protein. The fibroin is the structural center of the silk, while sericin is the sticky material around it. Fibroin composed of macromolecules with linear structure and oriented along the axis of fiber. Sericin composed of 18 amino acids. Studies of chemical and physical properties of the silk fibers have been performed since long back. Investigation on the reaction kinematics of organic protein complexes with the DSC technique has been done by many workers [11-16].

Sample preparation:

Eri and muga cocoons were collected from various places of north east region of India. The fibers were directly extracted by removing the floss from some of the cocoons. These were washed with distilled water and then dried normally. These are used as raw fibers. Some cocoons were boiled in 0.3% sodium carbonate solution for about one hour, and then cooled. The fibers were then extracted by removing the floss. These were then washed with distilled water to make free from any alkali and then dried normally. These are taken as degummed samples.

The raw and degummed fibers were cut into tiny particle size; thus the samples became ready to send to laboratory for experiments.

Methods:

For DTA, about 100 mg of each of the samples were mixed with 200 mg of calcinated alumina, which is the best proportion for obtaining good results. The records of DTA thermograms were made from room temperature 298K to 673K for all the fibers. The records of each of the samples were repeated thrice from room temperature to 673K to check the reproducibility of results.

For DSC, about 2.9 mg of each of the samples were kept in the aluminium sample pan of the DSC cell in air atmosphere purged at rate of 30 cm^3/min. The DSC thermograms were recorded very carefully. The maximum rate of scanning was maintained to get high temperature accuracy. The thermograms of scanning of flow of heat as a function of temperature were recorded in DSC with optimized the base line.

For TG, the sample of about 5 mg was taken on the porcelain container specially designed for this purpose. The sample holder with the container was inserted into the centre of the furnace carefully; the other related recording units were switched on to heat the sample at the heating rate of 10K/min. The TG recorder scans the sample continuously from room temperature 295K up to 673K. For nitrogen and oxygen atmosphere also similar records of TG were made, at the same rate as controlled for air atmosphere.

Results and discussion:

The differential thermal analysis (DTA) thermograms of eri and muga (raw and degummed) fibers at the heating rate 10K/min in air medium are shown in figures 1 and 2 respectively. The DTA thermograms of raw and degummed investigated fibers show nearly similar thermal behaviours.

Each of the thermograms shows one endothermic and one exothermic change within a certain temperature ranges. For raw samples, the endothermal change takes place in the temperature ranges 304K – 307K (ΔT_{min} = 343K) for eri and 305K – 398K (ΔT_{min} = 344K) for muga fibers in air medium. On the other hand, the exothermic change takes place in the temperature range 495K – 618K (ΔT_{max} = 595K) for eri and 501K – 620K (ΔT_{max} = 602K) in air medium.

Table 1 shows the different endothermic and exothermic behaviours in DTA thermograms of eri and muga fibers under various thermal treatments (raw, degummed, quenched and annealed).

At lower temperature range, a wide hump instead of the endothermic peak, attributed in the thermograms of each quenched fiber (heated to temperature 433K, cooled rapidly and records are noted immediately) indicates the dehydration process takes place due to thermal effect. The formation of endothermic peak in the thermograms of each annealed fibers (heated to temperature 433K, cooled slowly in air for 12 hours) shows the rehydration reaction attributed due to prolonged exposure of the heated fiber in air atmosphere. The dehydration and rehydration phenomena, under thermal treatments indicate that these silk fibers are hydrophilic in nature.

From the exothermic reactions occurred at 495K for degummed eri fiber and at 501K for degummed muga fiber, it can be inferred that the decomposition begins under the influence of thermal agitation at different temperature ranges. Both the silk fibers under study show nearly similar behaviours under different thermal conditions.

The DSC thermograms of eri and muga fibers in air atmosphere, at the heating rate 10K/min, are shown in figure 3. The results of the thermal analysis are given in table 2.

Fig. 1   Fig. 2
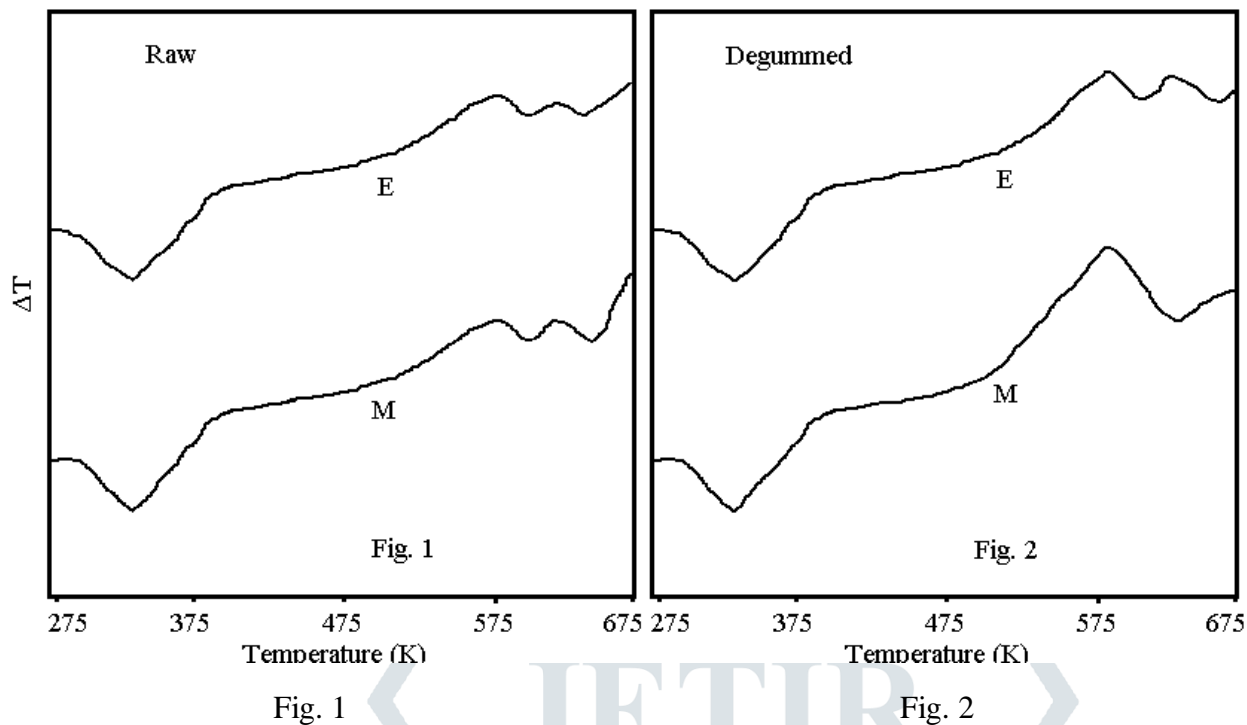
The shifting of DSC curves from the base line gives the heat capacity of the fiber samples. The traces of DSC show two distinct peaks as observed earlier for Bombyx mori fiber [18]. The thermograms indicate two distinct reactions in two stages. The first endothermic peaks for eri and muga fibers take place at the temperature ranges 344 – 405K (ΔT_{min} = 422K) and 425 – 445K (ΔT_{min} = 430K) respectively. The second endothermic peaks for eri at 644 – 688K (ΔT_{min} = 661K) and for muga at 634 – 695K (ΔT_{min} = 656K) are shown.

The second endothermic peaks, for eri with maxima at 661K and for muga at 656K may take place due to degradation of crystallinity caused by decomposition of the fibrous molecules. The weight loss during the decomposition stage is more in eri than in muga fiber (table 2). Moreover, the kinetic reaction for decomposition in eri fiber takes place at lower temperature (about 644K). The kinetic reaction data such as activation energy, obtained from these results, it is confirmed that the thermal stability is less in eri fiber and more in muga fiber. From this, it may be inferred that the thermal stability is dependable on the crystalline property of the sample. This stability is more in muga fiber due to its well defined crystalline orientation. The x-ray diffraction analysis observed by some investigators also agrees with the results [19].

Table 1- DTA data for eri and muga fibers:

(A – raw fiber,   B – degummed fiber,   C – annealed fiber, D – quenched fiber   )

Sample	Reaction step	DTA data		Nature of Reaction
		Temp. range (K)	Peak temp. (K)	
Eri (A)	1	304 – 397	343	Dehydration
	2	495 – 618	595	Decomposition
(B)	1	304 – 400	344	Dehydration
	2	495 – 627	606	Decomposition
(C)	1	305 – 401	342	Dehydration
	2	514 – 636	602	Decomposition
(D)	1	---- ----	----	---------

	2	498 – 629	596	Decomposition
Muga (A)	1	305 – 398	344	Dehydration
	2	497 – 617	597	Decomposition
(B)	1	304 – 401	343	Dehydration
	2	504 – 634	605	Decomposition
(C)	1	304 – 399	347	Dehydration
	2	517 – 639	602	Decomposition
(D)	1	---- ----	----	---------
	2	504 – 634	597	Decomposition

Figure 4 shows the plot of α (fraction of the reaction completed) against time at three different temperatures for each transition. These results indicate that the cause of the reaction is increased exponentially at a regular rate with time for any transition temperature. From this DSC results it may be inferred that the first endothermic peaks shown by eri and muga fibers represent the absorption of heat by the samples for dehydration. This idea is also supported by the DTA study. From the DSC thermograms (figures 3 & 4) and the reaction kinetic data (table 2), it is evident that the absorption and desorption of surface water molecules from the samples is more
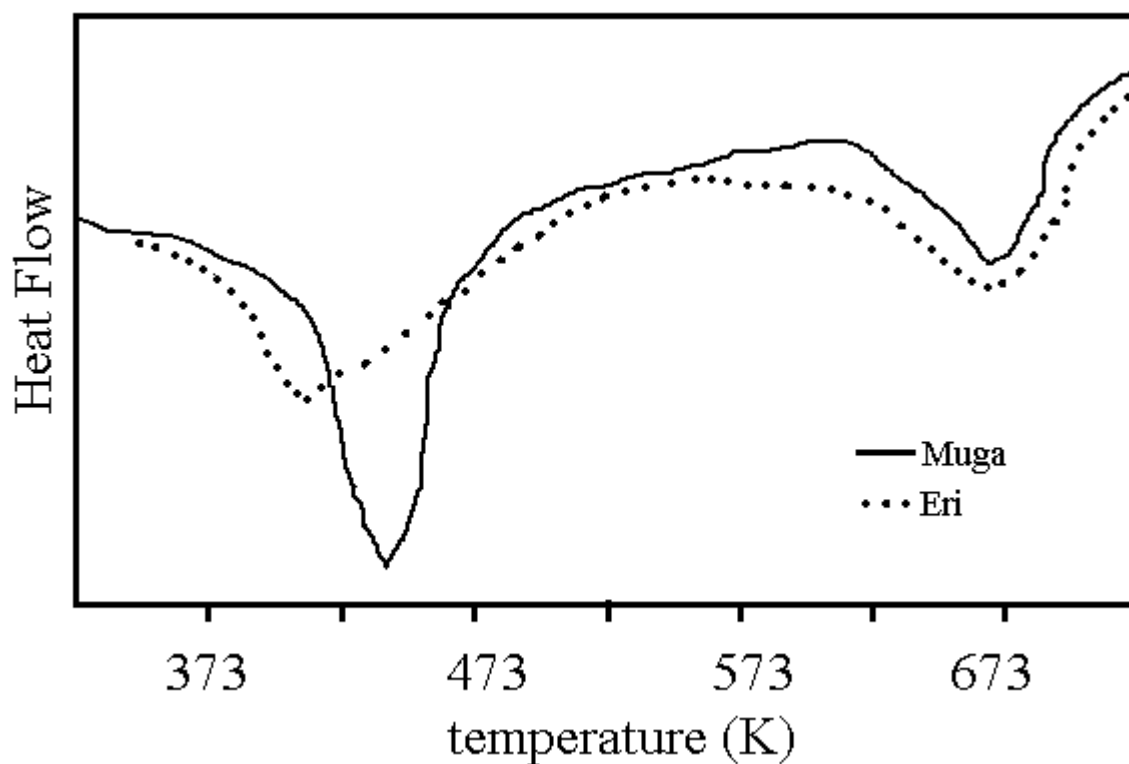

Fig 3- DSC thermograms of eri and muga fibers (in air), at heating rate 10K/min.

Table 2- Reaction kinetic data of DSC thermograms during transition period.

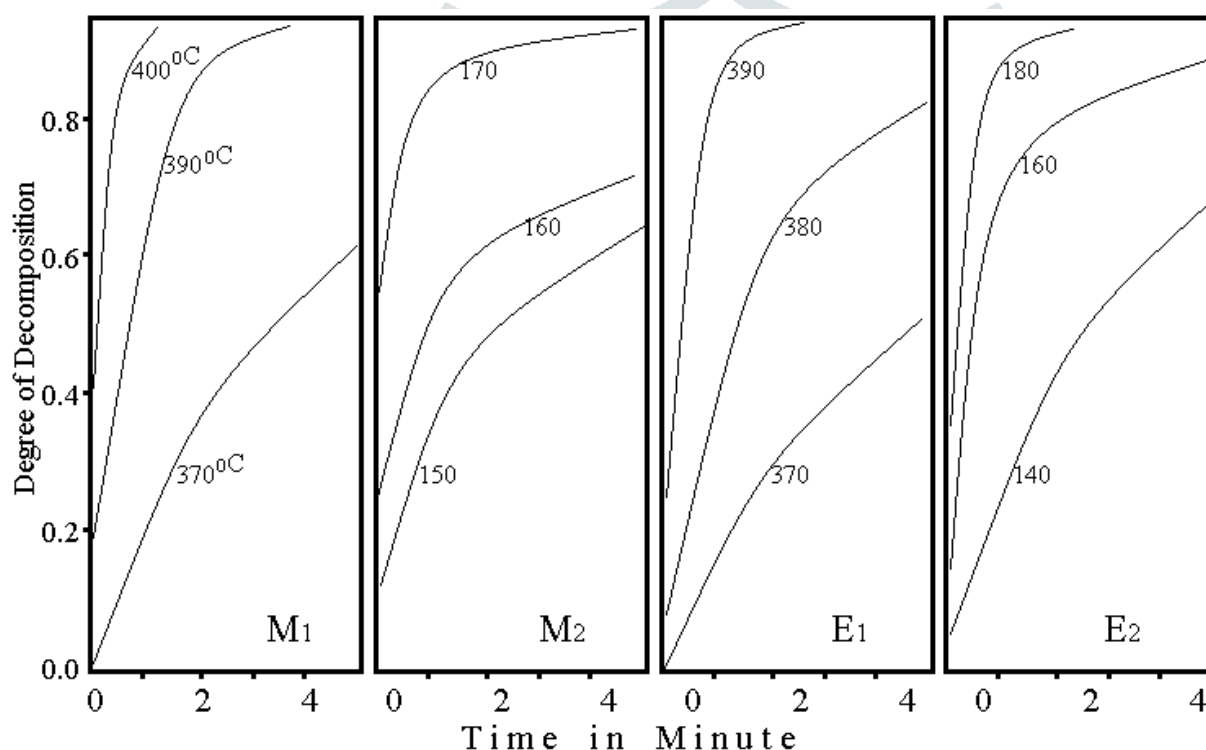| Sample	Step	Temp. range (K)	Peak temp. (K)	Wt. loss %	$L_n K_0$	Activation energy E_a	Enthalpy ΔH	Order of reaction	Nature of reaction
Eri	1	344 – 405	422	----	29.25	117.78	546.54	1.62	Dehydration
	2	644 – 688	661	49.25	67.39	392.57	393.42	1.03	Decomposition
Muga	1	425 – 445	430	----	40.48	128.02	453.11	1.71	Dehydration
	2	634 - 695	656	37.26	66.86	387.65	454.49	1.13	Decomposition

Fig. 4- graph of α (fraction of reaction completed) against time at three different temperatures (degree celcius) around the transition points. (M$_1$, M$_2$ – Muga, E$_1$, E$_2$ – Eri)

in muga than in eri fibers. The return of the thermograms of differential scanning calorimetry to the base line after the completion of dehydration reactions beyond 405K for eri and 445K for muga samples indicates that during the dehydration process, the initial crystalline arrangement of the semicrystalline fibers does not change. This is in close agreement with the report of XRD investigations earlier [20].

The TG records of silk fibers- muga and eri at the heating rate 10K/min in three different medium, viz. air, nitrogen and oxygen are shown in figure 5 (a,b and c). The various TG data of the fiber samples at different temperatures are displayed in table 3.

It is observed from the TG curves that there is a gradual beginning of weight loss at about 302K for both the fibers, under study, in air atmosphere. It continues to 400K for eri and 390K for muga fiber. The weight losses are 9.8% for eri and 9.2% for muga fiber. These results when compared with the DTA study, it can be inferred that the weight loss is taken place due to dehydration of the absorbed water molecules associated with the silk fibers. The fibrous complexes, at the end of this process, become anhydrous compounds by temperature arrest technique.

The TG curves show the beginning of the second step weight loss at temperature about 510K and 515K for eri and muga respectively in air medium. This process continues to 655K for muga and 665K for eri. Comparing these TG results with the DTA study, it may be inferred that these
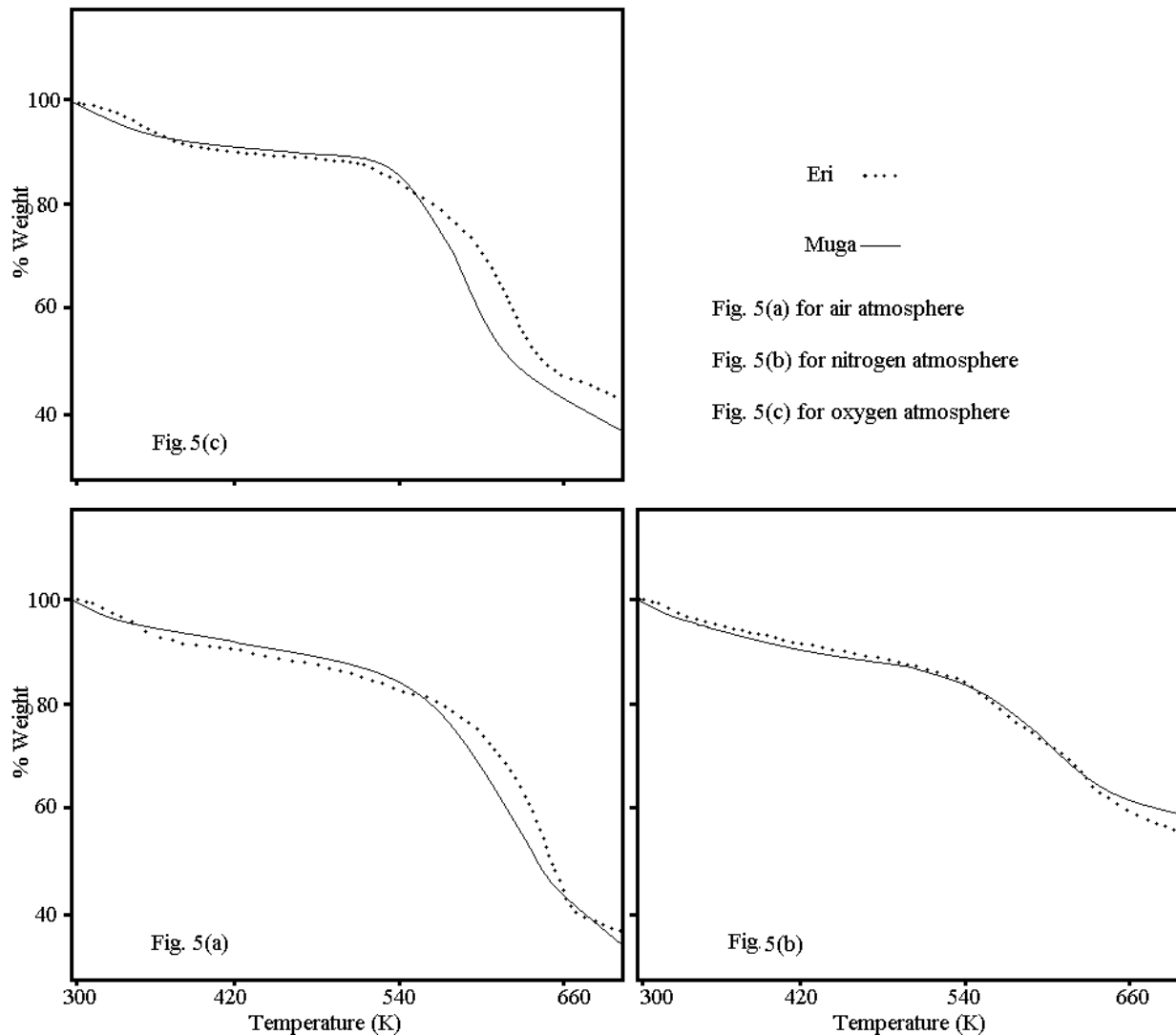

Fig. 5- TG thermograms of muga and eri fibers at heating rate 10K/min (in air, nitrogen and oxygen atmospheres)

weight losses are taken place due to decomposition. The Differential scanning calorimetry study also agrees with this result. The DSC observation performed by some earlier investigators gives strong support to it [21]. It is evident that thermal degradation is gradual at initial state and it increases due to rise of temperature.

For kinetic study of the samples in air, nitrogen and oxygen atmosphere, the relevant portions of the thermograms in the various stages are chosen. Both the silk fibers show nearly similar behaviour in the three media. From the figure 5(a,b,c) and table 3, it is seen that the dehydration and decomposition reactions are less in nitrogen and more in oxygen than that in air medium. It may be inferred, from these results, that the medium has an important role in the thermo-chemical reactions for transferring the fibrous solids gradually into various gases during the process of irreversible decomposition. Due to thermal degradation in this stage, some gases evolve in the form of water vapour, carbon-monoxide and carbon-dioxide; which is supported by some investigators [22] by IR absorption spectroscopic investigation of polymers.

Table 3- TG data of raw muga and eri silk fibers under different medium.

Sample	Reaction step	Air medium		Nitrogen medium		Oxygen medium	
		Temp. range (K)	Weight loss %	Temp. range (K)	Weight loss %	Temp. range (K)	Weight loss %
Eri	Dehydration	302-400	9.8	300-370	5.2	302-390	8.4
	Decomposition	510-665	37.8	535-660	33.4	470-640	44.7
Muga	Dehydration	302-390	9.2	300-365	8.1	302-390	9.2
	Decomposition	515-655	35.2	505-665	27.7	495-640	38.5

Conclusion:

From the investigations with different physical methods , it has been confirmed that the natural silk fibers are hydrophylic in nature. Both silk fibers under study show two step variations in two distinct temperature ranges represents their dehydration character and their decomposition. During decomposition stage the structural set up of the natural fibers is broken and fibrous molecules are transformed in to gases - carbon monoxide and carbon dioxide etc. The thermal stability depends on the crystalline structure of the sample. The stability is more in muga for its good crystalline orientation. Different kinds of thermodynamical parameters are found to vary significantly during dehydration and decomposition reactions attributed in the fibers in thermal conditions. Different media have also important roles for variation of thermodynamical properties of the fibers.

References:

[1]. Bora M N, Saikia D, Saikia R, Talukdar C, 1997, High themp- High pressure, vol. 29, p 683- 688.

[2]. Duswalt A A, 1974, Thermocimica, ACTA, vol 8, p 15.

[3]. Bora M N, Baruah G C, Talukdar C, 1995, Thermocimica ACTA, 218, 433-443.

[4]. Antal M J, Overend R P and Milne T; Combustion Sci. Technology, vol 21, p 141.

[5]. Bora M N, Bardoloi S, Talukdar D, Talukdar M and Talukdar C, proc. of ATPC, held in Japan,

Aug,21-24,2007.

[6]. Gregorski K S, 1982, proc. &th Int. Conf. on Anal.phys. 1,90.

[7]. Ray P K, 1967, Textile Res. Journal, 37, 434.

[8]. Goto M and Suyama K, 2000; J. of Applied Biochem - Biotechnol. 84, 1021-1038.

[9]. Ruan Q X and Zhou P, 2008; J. of Molecular structure, 883, 884; 85-90.

[10]. Bora M N, Talukdar C and Talukdar M; 1999, Indian J of Fiber & Text. Research, vol 24, p 172-

176.

[11]. Brown M E,Dollimore D and Galwey A K; Thermo chim., Acta, 21. 103 (1977).

[12]. Deb N, Gogoi P K and Dass N N; Thermo chim. Acta, 140, 145 (1989.

[13]. Venger A E, Tumysheva T V, Fraiman Y E and Kholopitsa V E; Dep. Doc. VINITI, 3293.

[14]. Morales J, Herman L, Flores LV and Orlega A; J of Thermal Anal. 24 (11), 23 (1982).

[15]. Dooren V, Adrianus A, Muller D & Berod W; Thermo chim. Acta, 65 (2-3),257-67,(1983).

[16]. Bhuyan K and Dass N N; J Macromol. Sci. Chem. A 25 (12), pp 1667 (1988).

[17]. Freeman E S and Carroll B; J Phys.Chem 62, 394 (1958).

[18]. Ishikawa H, Tsukada M, Teizume I, Konia A, Hirabayashi K; Semi Gakkaishi, 28 (4-5), 91, (1972).

[19]. Mc Cubbin W L, J. of Applied Polym. Sci., 17, 951-957 (1970).

[20]. Baruah G C and Bora M N; J. of Assam Sci. Soc., 32(3) 6, 1990.

[21]. Mann, J and Marrinan H J, J. of Polymer Sci. 32- 357 (1958).

[22]. Nakamoto K; IR Spectra of Inorganic & coordinated compounds, IInd Edn. Willey New York, pp. 83, 89, 245 (1969).