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INVESTIGATION ON THE THERMODYNAMICAL PROPERTIES OF SOME NATURAL SILK FIBRES WITH VARIOUS PHYSICAL METHODS

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KEYWORDS : enthalpy, entropy, activation energy, dehydration, decomposition, transition, heat capacity, reaction kinetics, silk fibres.

ABSTRACT

Thermodynamical properties : such as enthalpy, heat of reaction etc. causes for thermal reaction of natural silk fibres— Muga, Eri and Pat, endemic to North East India, have been investigated by Differential Scanning Calorimetry (DSC), Differential Thermal Analysis (DTA), Differential Thermogravimetry (DTG) and Thermogravimetry (TG) methods. The experiments have been carried out in the temperature range from 298K to 693K.

The thermograms of the samples have shown two thermal reaction steps on the temperature ranges 333—405K and 560—675K. The first transition peak has been revealed the dehydration of the water molecules from the semi-crystalline hosts. The second peak has confirmed the irreversible dissociation of the crystallites.

The heat of reaction, activation energy, reaction order, Arrhenious frequency factor at the dehydration and the decomposition steps for the samples have been computed. Significances of these observations for suitability of such fibres in the technological applications have been discussed.

INTRODUCTION

The silk fibres : Muga, Eri and Pat are semi-crystalline and hygroscopic in nature. Investigation on these properties of organic fibres have been made by various workers (Warwicker, 1954, Mahanta, et al., 1959 and Baruah et al., 1990). Due to essential characteristics of external forms and of physico-chemical properties, they have great utilities in various textile and other industries as well. It is evident that reaction kinetics of a material are based on its physico-chemical properties. Therefore, the study of the thermodynamical properties of these natural silk fibres certainly have great importance in textile and other technological fields.

Many attempts have been made to study the thermal behaviours of various polymeric materials. Studies of some thermophysical properties of silk fibres have been made by some investigators (Venger, et. al., 1982). But no such studies on these types of natural silk fibres, endemic to this region of India have been noticed.

It has become of interest to study the thermophysical and thermochemical behaviours of polymeric materials by the DSC, TGA, DTG and DTA analyses. Investigation on the reaction kinetics of organic complexes with the DSC and DTA techniques have been made by some workers (Green, et. al, 1970; Morales et al, 1982; Dooren, et al. 1983, Bhuyan and Das, 1988). The reaction kinetics of some silk fibres with the DSC method have been studied (Ishikawa, et al.,1972). Evaluation of kinetic data from TG and DTG techniques in some Polymers have been reviewed and widely used by many investigators (Mikroyannidis, 1988; Jazoszynska et al, 1980, Dev, et al. 1989 a). Further investigation on the thermal decomposition for some synthetic polimeric materials have been undertaken (Dev. et al., 1989 b). But no such studies on organic silk fibres— Muga, Eri and Pat have been yet noticed.

In recent years, interest has increased in the study of the structural and thermodynamical properties of polymeric insulators. Moreover, the blending of the Muga, Eri and Pat fibres readily available in this region of India with locally produced synthetic polyester and plant fibres may open a new scope in the various industrial fields.

In view of these facts, attempts have been made to study the thermodynamical properties, such as heat capacity, enthalpy, etc. cause for thermal transitions in silk fibres— Muga, Eri and Pat with the physical methods : DSC, DTA, TG amd DTG.

EXPERIMENTAL

Materials and sample Preparation

The silk fibres : Muga, Eri and Pat were taken out from the middle portion of fresh cocoons collected from different parts of North East India. Some of them were used for measurements without treatment (untreated or raw samples).

Some parts of fibres were degummed by delignification process described elsewhere (Baruah, et al. 1990).

Some portions of fibres were heated to 373 K, some at 423 K and some at 483 K for 8 hours and then cooled rapidly or slowly to room temperature (298 K). These were used to study the quenching and annealing effects.

Measurements

The DSC thermograms were recorded with a Mettler TA 3000 System coupled with TA Processor and Printer Plotter. Samples of silk fibres (2.9 mg) were kept in the aluminium sample pans of the DSC cell under air atmosphere purged at a rate of 30 cm^3/min. The maximum scanning rate of 5K/min and 10 K/min were maintained to get

high temperature accuracy. At the beginning, the calibration of the DSC sensor was checked using heat of fusion of known quantity of Indium. The thermograms of scanning of heat flow as a function of temperature were recorded in DSC with optimised the baseline.

The records of thermogravimetry (TG) and differential thermogravimetry (DTG) of the fibres were carried out with Perkin-Elmer Thermal Analyser, operating at heating rate of 5K/min and 10K/min in the dynamic air, nitrogen and oxygen atmospheres with a flow rate of 30 cm^3/min.The DTG thermograms had falicitated the effort to resolve the complex TG curves. Thermograms of the differential thermal analysis were recorded in the same Thermal Analyser in air atmosphere used for TG and DTG measurements. The calibrations of TG, DTG and DTA sensor were also checked with the inert sample to remove the baseline errors.

RESULTS AND DISCUSSION

The untreated silk fibres— Muga, Eri and Pat are golden yellow, pale brown and dull white respectively. After delignification, the fibres become slightly stiff and bright due to removal of the gum (sericin) embeded in the amorphous region of the fibres.

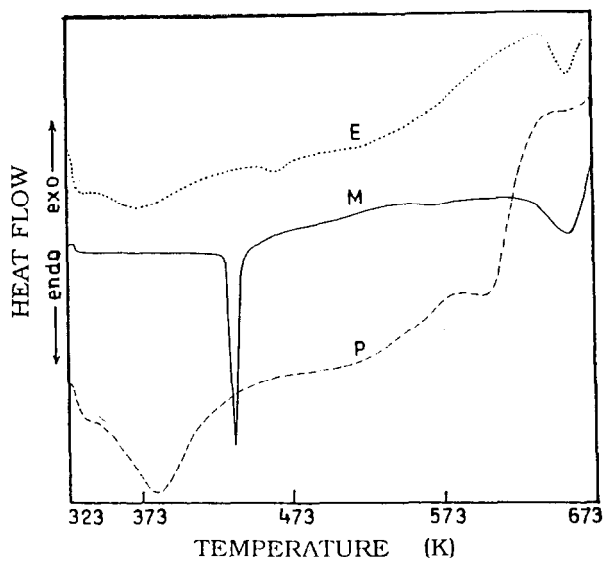

Fig.1. Plot of heat flow Vs temperature in air (heating rate10K/min)
Samples : M— Muga, E— Eri, P— Pat.

The DSC thermograms of Muga, Eri and Pat silk fibres at the heating rate 10K/min in the air atmosphere are displayed in the Figure 1. The thermal analysis results are summarised in the Table I.

Table I.

Reaction kinetic data of the DSC thermograms at the transition periods

Sample	Heating Rate (K/min)	Step	Peak Temp. (K)	Activation Energy (E) (KJ/mol)	Reaction Order	Arrhenious Equation $\ln k_0$	Weight Loss (%) at 693 K	Reaction
MUGA	5	1	429	12.801	1.72	40.41	37.00	Dehydration
		2	655	38.766	1.14	66.67		Decomposition
	10	1	425	12.907	1.62	40.82	39.30	Dehydration
		2	650	38.924	1.05	66.81		Decomposition
ERI	5	1	421	11.782	1.63	29.24	49.30	Dehydration
		2	660	30.205	1.02	67.38		Decomposition
	10	1	399	11.890	1.53	29.54	50.12	Dehydration
		2	653	39.032	1.12	68.00		Decomposition
PAT	5	1	381	10.108	1.87	27.60	52.00	Dehydration
		2	577	30.182	1.28	62.87		Decomposition
	10	1	378	10.218	1.78	28.00	52.87	Dehydration
		2	571	31.001	1.00	63.01		Decomposition

The shifting of DSC thermograms from the base line represents the heat capacity of the fibres. The DSC traces show two distinct reactions in two stages. The first endothermic peaks for Muga, Eri and Pat fibres occur at the temperature ranges 409—493 K, 386—438 K and 338—402 K respectively. They represent the absorption of heat by the samples for dehydration. The IR spectral studies of annealed and quenched fibres from 423 K in air and vacuum observed earlier (Baruah, et al, 1991) have supported this result. The presence of broad IR bands arround 3000- 3650 cm^{-1} in anhydrous fibrous complexes when exposed to a humid atmosphere proves the behaviour of absorption and desorption of surface water molecules from the fibres. It is evident from the DSC thermograms (Figure 1) and reaction kinetic data (Table I) that dehydration is more in Muga and less in Eri than that in Pat fibre. During this period, the initial crystalline setup of the semi-crystalline fibres remains unaltered. This is in agreement with the X-ray diffraction results reported earlier (Baruah, et al., 1990). From the computed results of degree of crystallinity (DC) of X-ray diffractograms of delignified, dried and humid Muga fibre, it is found that the crystallinity of these treated samples is slightly higher then that of raw Muga fibre. This may be inferred from the results that the absorbed water molecules are mostly embeded in the amorphous region of the fibres. These water molecules may probably restrict the alignment of the chain molecules and thus give rise to strains in the crystalline part. On removal of these water molecules, the restrictive force being withdrawn, the molecular chains are free to rearrange within the crystals. This is in agreement with the results obtained for some plant fibres also (Ray, 1969).

The second endothermic peaks at the temperature ranges arround 623—698 K for Muga and Eri, and 563—602 K for Pat fibre attributed to degradation of crystallinity caused by decomposition of the fibrous molecules. The weight loss at the decomposition stage (Table I) is more in Pat and less in Muga than that in Eri. Further, the kinetic reaction for decomposition in Pat fibre starts at lower temperature (about 563 K). From these results of kinetic reaction data, it is assumed that the thermal stability is less in Pat and more in Muga than that in Eri.

The reaction kinetic data revealed in the DSC thermograms of thermally and chemically treated fibres are shown in the Table II.

Table II.

Reaction kinetic data of the DSC thermograms of thermo-chemically treated Muga fibre at heating rate 10 K/min in air atmosphere: (Samples: (a)— raw, (b)— delignified, (c)— annealed from 423 K, (d)— quenched from 423 K).

Sample	Stage	Peak temp. (K)	Activation energy (E) (KJ/mol.)	Reaction order	Arrhenious equation $\ln K_0$	Reaction
(a)	1	430	12.80	1.72	40.41	Dehydration
	2	656	38.76	1.14	66.65	Decompositon
(b)	1	429	12.72	1.68	40.39	Dehydration
	2	648	38.64	1.11	66.48	Decomposition
(c)	1	418	12.80	1.73	40.52	Dehydration
	2	662	38.77	1.16	66.70	Decomposition
(d)	1	432	12.79	1.71	40.51	Dehydration
	2	659	38.78	1.17	66.78	Decomposition

From the DSC data of untreated, delignified, annealed and quenched Muga samples (Table II), it may be inferred that the complex fibrous molecules are not tempered to greater extent by the thermo-chemical treatments.

The records of thermogravimetry (TG) as the plot of weight loss(%) versus temperature are displayed in the Figures 2 and 3. The thermodynamical data summarised from the records of TG, DTG and DTA analyses are shown in the Table III.

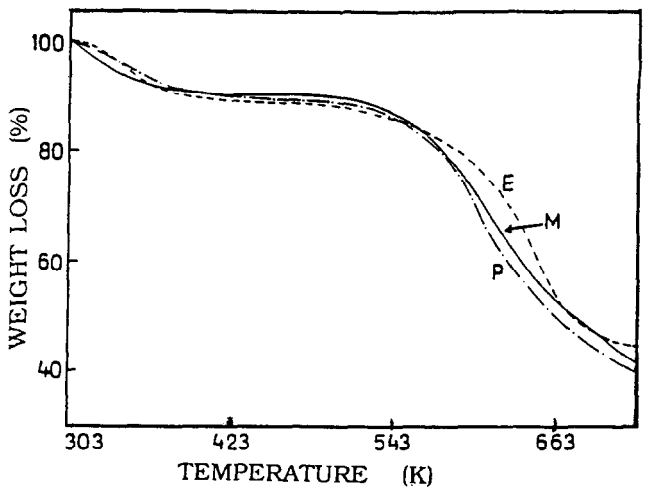

Fig.2 Weight loss (%) Vs temperature in air atmosphere.
Samples : M— Muga, E— Eri, P— Pat.

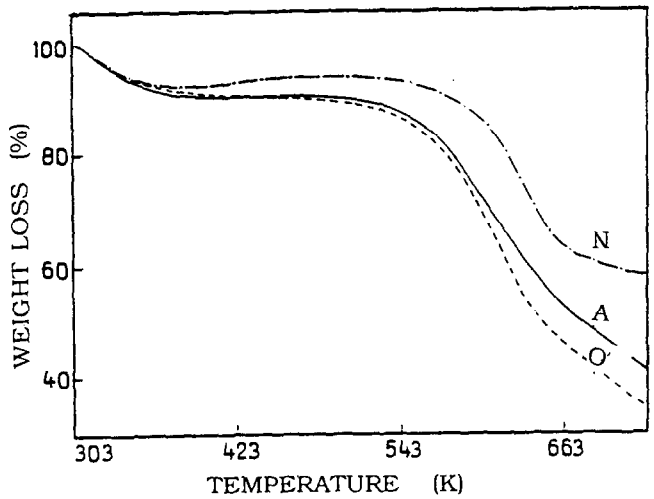

Fig 3 Weight loss (%) Vs temperature for Muga fibre in three atmospheres. (N—Nitrogen, A— Air, O— Oxygen)

TABLE III.

TG. DTG and DTA data under different atmospheres (Air, Oxygen and Nitrogen)

Sample	Medium	Step	TG data		DTG data		DTA data		Reaction
			Temp. range (K)	Weight loss (%)	Temp. range (K)	Peak temp. (K)	Temp. range (K)	Peak temp. (K)	
Muga	Air	1	313-390	8.80	313-403	343	305-403	348	Dehydration
		2	523-641	38.25	543-643	623	568-618	603	Decomposition
Eri	Air	1	313-384	10.31	312-403	348	309-393	305	Dehydration
		2	523-641	45.49	538-639	608	573-618	605	Decomposition
Pat	Air	1	312-380	8.82	303-394	334	312-403	342	Dehydration
		2	523-602	36.28	524-612	588	553-612	603	Decomposition
Muga	Oxygen	1	314-362	12.08	318-373	319	310-362	339	Dehydration
		2	524-658	49.03	453-654	612	562-609	601	Decomposition
Eri	Oxygen	1	312-374	10.98	312-361	316	319-399	355	Dehydration
		2	513-643	48.25	560-637	611	570-623	609	Decomposition
Pat	Oxygen	1	312-383	9.83	314-374	327	324-437	336	Dehydration
		2	533-658	49.03	533-632	573	545-634	623	Decomposition
Muga	Nitrogen	1	313-380	7.04	319-379	308	301-400	332	Dehydration
		2	523-656	32.89	553-653	647	560-609	601	Decomposition
Eri	Nitrogen	1	323-375	8.26	301-401	438	300-391	336	Dehydration
		2	503-639	35.28	562-680	647	582-621	612	Decomposition
Pat	Nitrogen	1	311-380	7.90	323-362	317	310-399	321	Dehydration
		2	533-629	34.32	534-643	601	550-601	602	Decomposition

It is seen from the data that both endotherms attributed in the DSC records are accompanied by the weight loss curves in TG. Corresponding to two stages displayed in TG thermograms (Figure 2), the DTG results (Table III) show two endothermic

peaks in the temperature range about 303—403 K and 543—643 K. The occurance of the former is due to dehydration and the later is due to decomposition stage as stated earlier from the DSC results. Similarly, the DTA results (Table III) show one endothermic peak at 348 K for Muga, 345K for Eri, 342K for Pat fibre and one exothermic peak at 603K for Muga, 605K for Eri and 603K for Pat. The endothermic peak corresponds to dehydration and the exothermic peak represents the decomposition stage. It is evident that the TG and DTG results are in agreement with DTA data within the limitation of the instrumental errors. Further, the results indicate that the thermal reactions—dehydration and decomposition occured in TG, DTG and DTA records correspond to the two-stage thermal reactions of DSC themograms.

The TG curves in air show the gradual beginning of weight loss at about 312 K in all fibres which continue upto 390 K. During this stage the weight losses are 8.8%, 10.3% and 8.82% for Muga, Eri and Pat respectively. The weight loss is occured due to dehydration of absorbed water molecules associated in the fibres. At the end of this process the fibrous complexes become anhydrous compounds by temperature arrest technique.

The TG thermograms show the beginning of weight loss at about 523 K for the fibres, which continue upto 641 K for Muga and Eri, and 602 K for Pat fibre. From the results of the TG, DTG and DTA thermograms in decomposition stage, (TAble III) it is evident that the thermal degradation is gradual at initial state, which increases with rise in temperature due to formation of defects as observed earlier in the DSC results.

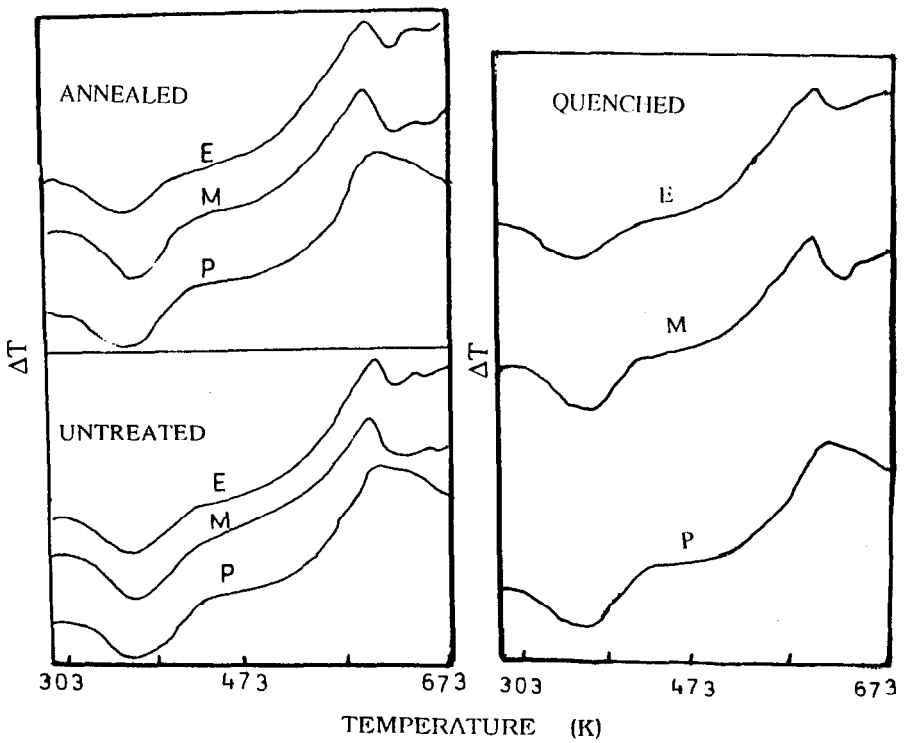

Fig. 4. DTA thermograms Vs temperature in air. (heating rate 10 km/min.)
Samples : M— Muga, E— Eri, P— Pat.

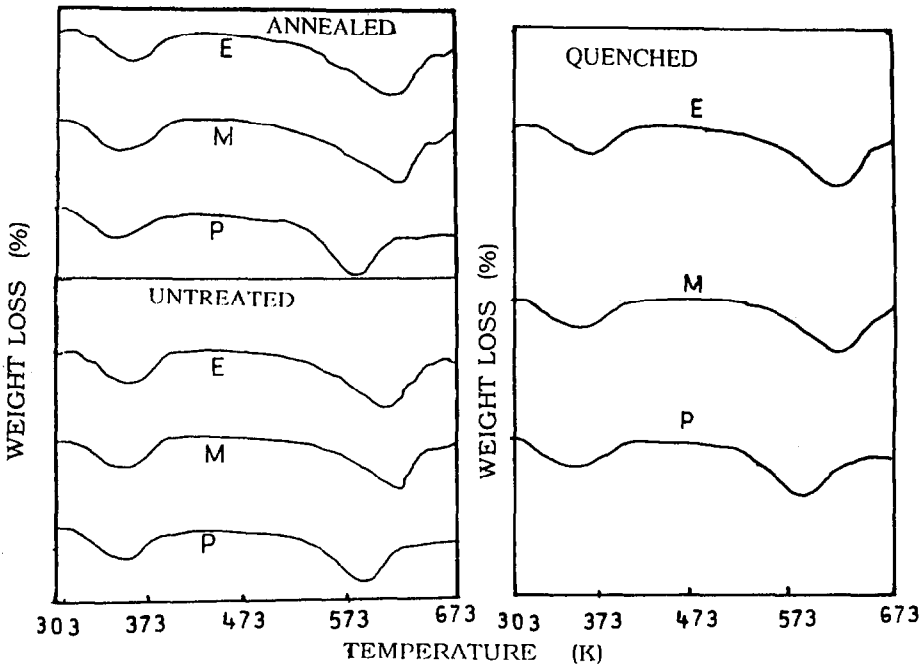

Fig.5. DTG thermograms Vs temperature in air (heating rate 10 K/min.)
Samples : M— Muga, E— Eri, P— Pat.

Figures 4 and 5 represent the thermograms of DTA and DTG for the fibres untreated, and annealed and quenched from 423 K. The annealed and quenched samples kept in a humid atmosphere for 6 hours show almost identical TG, DTG and DTA thermograms in dehydration and decomposition stages at the same temperature ranges. From these similar thermodynamical behaviours shown by untreated (raw) and treated (annealed and quenched) samples, it is inferred that the silk fibres may regain their original physical properties more or less under thermal treatments at moderate temperature. Further, it is evident that they absorb water in a humid atmosphere.

The relevant portions of the TG thermograms in the two stages are chosen for kinetic study in air, nitrogen and oxygen atmospheres. All fibres show almost similar thermal behaviour in three media. From the results (Figure 3 and Table III), it is evident that the dehydration and decomposition reactions are less in nitrogen and more in oxygen than that in air atmospher. The influence of these media in thermo-chemical reaction to transfer gadually the solids into gases during irreversible decomposition stage has been proved by the DTA records. The gases thus evolved due to thermal degradation in decomposition stage are traced out as water vapour, carbon mono-oxide and carbon dioxide by IR absorption spectroscopic investigation as described elsewhere (Nakamoto, 1969).

Table IV

Activation Energy (E) and Change of Entropy (ΔS) evaluated from TG and DTG data (a) Freeman and Carrol and (b) Modified Freeman and Carrol Methods.

Sample	Step	Air medium E (KJ/ mol) (a)	(b)	Air medium ΔS (e.u.)	Oxygen medium E (KJ/ mol) (a)	(b)	Oxygen medium ΔS (e.u.)	Nitrogen medium E (KJ/ mol) (a)	(b)	Nitrogen medium ΔS (e.u.)	Reaction
Muga	1	12.35	12.11	-158.71	12.48	12.39	-160.23	11.34	11.23	-147.21	Dehy.
	2	36.60	36.22	-164.68	36.23	35.52	-169.45	34.56	34.72	-160.21	Deco.
Eri	1	12.12	12.01	-164.22	12.51	12.34	-170.18	12.01	12.00	-159.12	Dehy.
	2	23.88	23.59	-168.32	23.91	23.99	-169.87	23.62	23.47	-160.23	Deco.
Pat	1	10.63	10.33	-155.11	10.91	10.82	-169.34	10.01	10.34	-158.92	Dehy.
	2	16.44	16.32	-169.21	16.98	16.89	-180.57	26.21	16.19	-160.16	Deco.

The activation energy (E) required to activate the thermal reactions in dehydration and decomposition stages, is computed using TG data on the basis of the differential equation of Freeman and Carrol, used earlier (Dev, et al. 1989 b). With the use of peak temperature of DTG data, the activation energy and hence the change of entropy (ΔS) is computed on the basis of modified Freeman and Carrol equation used by some workers for study of the thermal decomposition of some polymeric compounds (Dev, et al., 1989 b). The results are displayed in the Table IV. Both methods yeild almost similar values of activation energy. These values are slightly higher in oxygen medium and smaller in nitrogen medium than that in air medium. The negative values of change of entropy (ΔS) are obtained for both dehydration and decomposition stages. This indicates that thermal reaction in two stages are lower than that of the thermal reaction occured in the normal state for all fibres.

CONCLUSION

Delignification makes the silk fibres more tempered and rigid without effecting their crystal structures. Muga, Eri and Pat fibres possess identical thermodynamical properties. The fibres under study have absorption and desorption behaviours. Thermal stability is more in Muga than those of Eri or Pat fibre. The abosrption and desorption of atmospheric moisture with the consequent evolutin and absorption of heat add to the comfort of clothing of these fibres. Moreover, the thermal resistance possessed by these fibres make them convenient to use as fibre-insulators upto their decomposition limits.

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