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Investigations on Structural Characteristics, Thermal Stability, and Hygroscopicity of Sisal Fibers at Elevated Temperatures

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Abstract An effort has been made to study the thermophysical properties of sisal plant fiber available in North-East India in the temperature range from 310 K to 760 K. The effect of heat on the structural characteristics of the fiber using X-ray diffraction and the chemical behavior by the infrared (IR) technique has been examined. Thermodynamic studies of the fiber have been carried out using thermogravimetric (TG), derivative TG (DTG), and differential scanning calorimetric methods. The hygroscopic properties of the fiber have been investigated in the temperature range from 310 K to 430 K at different relative air humidities using an ordinary gravimetric analysis. The interplanar spacings of the sample heated to 370 K remained same with respect to their normal values, but the degree of crystallinity and crystallite sizes increased slightly. The degree of crystallinity of the sample heated to 450 K is decreased by 10.32 % from its normal value, and the corresponding interplanar spacings and crystallite sizes are decreased by a small amount. A sample heated to 530 K shows transformation of the fiber's crystalline structure to an amorphous state. The fiber shows thermal stability up to 500 K and follows two different closely related thermal decomposition processes in the temperature range of approximately 500 K to 630 K. Tests performed in oxygen can lead to combustion of the fibers in the temperature range of approximately 710 K to 720 K. The IR study of the sample heated at temperatures from 370 K to 600 K provides meaningful data to ascertain decomposition of the native structure of the fibers. The hygroscopicity of the fiber under heated conditions is less with respect to the value under ambient conditions. The saturation limit of moisture absorption of the fiber per gram varies and depends on the source as well as pretreatment of the sample.

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1 Introduction

Interest in the thermophysical properties of plant fibers and their composites has increased due to their important aspects of biocompatibility, possible biodegradation, non-toxicity, and abundance [1,2]. For a fiber to find its use for industrial applications, its physical properties must match the need of the applications. Hygroscopic properties play a crucial role in making fibers commercial and versatile. Crystallographic, thermodynamic, and hygroscopic studies of some major plant fibers such as cotton, flax, jute, ramie, etc. have been carried out by several investigators [3]. But investigations on thermophysical properties of plant fibers that are available in North-East India have not yet been carried out. Attempts have been made here to study the thermophysical properties of sisal (*Agave sisalana*), the minor plant fiber that is available in North-East India. In our studies, we examined the effect of heat on the structural characteristics of the fiber using the X-ray powder diffraction method and we studied the chemical behavior of the fiber using the infrared (IR) technique. The studies of thermal stabilities of sisal have been carried out using thermogravimetric (TG), derivative TG (DTG), and differential scanning calorimetric (DSC) methods. We have taken sisal fibers under ambient and annealed conditions to study their hygroscopic properties at constant relative humidity as well as at different relative humidities using ordinary gravimetric analysis.

2 Measurements

2.1 Materials

The sisal fibers were collected from different localities of North-East India. They were processed, and various samples needed for the present investigation were prepared by the methods described elsewhere [4]. The sisal fibers had a cellulosic content of 72 % to 75 % and a lignin content of 6 % to 8 %. The average diameter and density of the fiber were 0.18 mm and $1.57\,\mathrm{g \cdot cm^{-3}}$, respectively. Some parts of fibers were used for measurements without treatment and some of them were heated in a convection oven in an air atmosphere at different temperatures, namely 330 K, 370 K, 410 K, 450 K, 500 K, 530 K, and 600 K for 3 h separately by the processes adopted in other studies [5].

2.2 Crystallographic and Thermodynamic Measurements

X-ray diffraction (XRD) studies of sisal fibers under ambient and heated conditions were performed and scanned in a reflectance mode from 4° to 40° on an automatic powder diffractometer using Cu-K_α at 40 kV and 20 mA. Very finely cut (almost powdered) sisal fibers of 5 mg were used for each XRD scan. The XRD curves were analyzed using an SAS non-linear curve fitting program. The crystallite size was determined using the Scherrer equation, the degree of crystallinity was computed using the Harmans and Weidinger equation, and the interplanar spacing was calculated using the Bragg equation. IR spectra of the fibers were recorded in an air atmosphere on an FTIR spectrometer in the frequency range from $4000\,\mathrm{cm}^{-1}$ to $500\,\mathrm{cm}^{-1}$. The pallet used for each IR study was prepared by mixing 1 mg of finely cut (almost powdered) sisal fiber with 100 mg of KBr. Very finely cut fibers of 5 mg were taken on the specially designed porcelain crucible for each scan of TG, DTG, and DSC. The TG and DTG profiles were recorded at a heating rate of $10\,\mathrm{K \cdot min^{-1}}$ in air, oxygen, and nitrogen atmosphere in the temperature range from 310 K to 760 K on a Mettler-Toledo TGA/SDTA 851. The activation energies of fibers at different reaction steps were evaluated from the slope of the TG curve using the Freeman and Carroll equation. DSC scans of the fibers were taken at a heating rate of $10\,\mathrm{K \cdot min^{-1}}$ in an air atmosphere in the temperature range from 310 K to 760 K using the Mettler Toledo DSC 821 coupled with thermal analysis. Kinetic parameters such as activation energy, change of enthalpy, and change of entropy were evaluated using the DSC Analytical STAR Base software.

2.3 Gravimetric Moisture Absorption

The fibers were cut into pieces of 40 mm in length. Then the cut fiber-strips with a mass of 1 g were placed in a 25-ml weighing bottle (mass of 8.5 g). The open weighing bottle was placed at room temperature in a humidity chamber in which a relative air humidity of (98 ± 1) % is initially maintained. In this condition, the sample was left for a specified period as per requirements. Then the weighing bottle was closed; the sample was removed from the humidity chamber and weighed using an analytical balance (uncertainty = ±0.0001 g). The sample after weighing was dried in a convection oven at a temperature of (337 ± 2) K for 1 h to achieve a constant mass. The sample was cooled and reweighed on the analytical balance. A similar procedure was used to determine the saturation limits of each sample at different humidities. Humidity chambers of 75 %, 68 %, 58 %, 33 %, and 20 % were prepared using sodium chloride, cupric chloride, sodium bromide, magnesium chloride, and potassium acetate, respectively [6]. The hygroscopicity (H in %) of the sample was calculated using the following formula [7]:

$$H = \left[\frac{M_\mathrm{h} - M_\mathrm{d}}{M_\mathrm{d}} \times 100 \right] \%$$

where M_h and M_d are, respectively, the mass of the humidified sample (in g) and the mass of the sample after drying to a constant mass (in g). In all cases, the mean ± SD data from three repeated experiments were taken to ensure reliability of the results.

3 Results

The X-ray powder diffractograms of sisal fibers under unheated and different annealed conditions (at 370 K, 450 K, and 530 K) are shown in Fig. 1. The interplanar spacings,

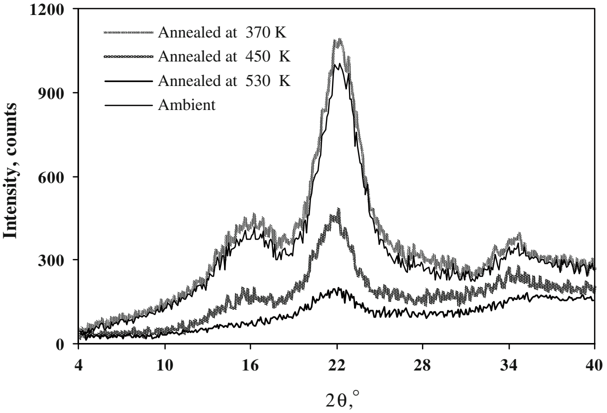

Fig. 1 X-ray powder diffractometer scans of sisal under unheated and annealed conditions

Table 1 Interplanar spacing, crystallite length, and degree of crystallinity of unheated and heated sisal fibers

Condition of the sample	Interplanar Spacing (Å)			Crystallite size (Å)			Degree of crystallinity (%)
	Peak-I	Peak-II	Peak-III	Peak-I	Peak-II	Peak-III	
Unheated	5.427	4.015	2.583	32.46	31.56	33.46	51.23
Annealed at 370 K	5.426	4.014	2.575	31.03	32.06	33.42	52.45
Annealed at 450 K	5.424	4.007	2.560	27.68	28.37	28.72	40.91
Annealed at 530 K	Unresolved low intensity peak						

crystallite size, and degree of crystallinity calculated from the corresponding diffractograms of the sample under both unheated and annealed conditions are listed in Table 1. Figure 1 shows that the X-ray diffractogram for the unheated sample consists of three sections of broad absorptions with different integral widths and heights, which is characteristic of cellulosic crystallographic structures. For the case of the sample annealed at 370 K, the general nature of X-ray powder diffraction patterns was almost similar to that under normal conditions. This indicates that the temperature of annealing on fibers under study is appreciably low to decompose the fiber [8]. Although overall crystalline structures of the sample annealed at 370 K did not change, a small change was observed in its structural parameters as reflected in the intensity pattern. The interplanar spacings of the sample annealed at 370 K corresponding to peaks I, II, and III decreased slightly from their normal values. The average crystallite size of the sample annealed at 370 K increases in the direction corresponding to peak II and decreases less significantly in the directions corresponding to peaks III and I. The degree of crystallinity of the sample annealed at 370 K increases by 1.22 % from its normal value. The decrease in crystallite sizes of the samples annealed at 370 K could be attributed to the change in dipole interactions, and the increase in crystallite size also can be assigned to the effect on weak bend interactions of the crystalline materials in the fibers. Similar results were found in some studies for other plant fibers [9].

The diffractogram of the fiber annealed at 450 K showed a significant decrease in basal reflections, and it was found that interplanar spacings and crystallite sizes corresponding to peaks I, II, and III were decreased by a small amount. The degree of crystallinity of the fiber annealed at 450 K was found to decrease by 10.32 %. This finding indicated that annealing results in a decrease in the crystallite length as well as the degree of crystallinity due to the prominent deterioration in crystalline orientation resulting from gradual degradation of crystalline regions in the fiber sample. Similar results were obtained for the case of muga, eri, and pat fibers by some investigators [10]. The diffractogram of the fiber annealed at 530 K showed the conversion of the patterns into a diffuse holo pattern on annealing at 530 K, indicating the transformation of the fiber crystalline structure to an amorphous state as a result of thermal decomposition [11].

The IR spectra of sisal under ambient and different annealed conditions are shown in Fig. 2. From comparisons with standard IR data of pure cellulose, the sample is concluded to be of cellulosic origin [12]. Figure 2 shows that no significant changes occurred in the IR spectra of the samples annealed at 370 K and 450 K. However, intensities of the peak resulting from OH in the 3600 cm^{-1} to 3125 cm^{-1} regions decreased very slightly for the sample annealed at 370 K, and this decrease is attributed to the loss of water molecules from the fibers during annealing [13]. However, a weak peak was found at 1730 cm^{-1} for the sample annealed at 450 K, which is assigned as C=O stretching that probably occurs from degradation of the cellulose and the subsequent opening of a sugar unit to generate a carboxyl functional group. A decrease in the intensity of the peak resulting from the OH stretching in the respective 3600 cm^{-1} to 3125 cm^{-1} regions was also observed for the sample annealed at 450 K.

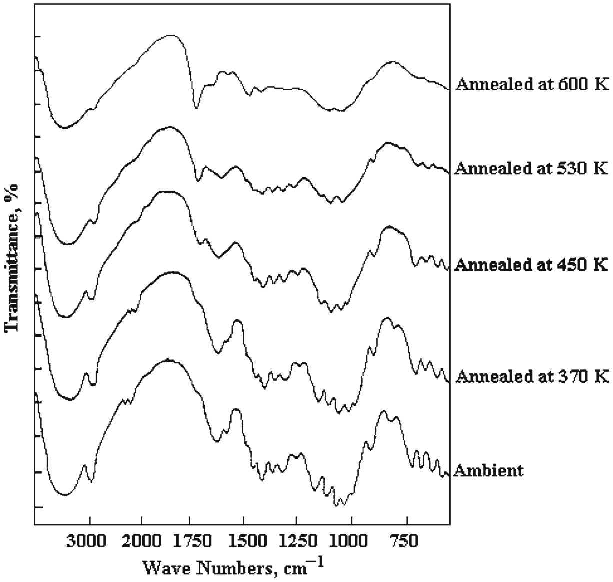

Fig. 2 The IR spectra of sisal fibers under unheated and annealed conditions

For the case of IR spectra of the sample annealed at a temperature of 530 K, it was observed that there was a rapid decline in the intensity of CH_2 deformation at $1430\,cm^{-1}$ and this result was attributed to the occurrence of decomposition processes in the fibers. The intensity of the peaks at $2940\,cm^{-1}$ due to CH_2 asymmetric stretching also decreased. There is a decline in the ring vibration at $1164\,cm^{-1}$. This decline of the C–O bond may be attributed to the cleavage of bridging the C–O–C bond in the cellulose, followed by the loss of crystallinity of the fibers. An XRD study of the sample at this temperature also revealed that crystallinity of the fiber is lost due to annealing at 530 K. The C=O stretching absorption at $1730\,cm^{-1}$ increased significantly for the sample on heating. This again supports the earlier discussion on the formation of the C=O functional group through thermal decomposition. A similar trend was also observed for the case of IR of the sample annealed at 600 K. This is consistent with the earlier results of Higgins [14].

The study of thermal stabilities of sisal fiber was carried out using TG, DTG, and DSC methods. The TG study was performed independently in air, oxygen, and nitrogen, and profiles are shown in Fig. 3a–c, respectively. The differential of each of the mass loss profiles is also shown in the respective figures. A DSC profile of the sample was taken in air and is shown in Fig. 4. The net mass loss of each sample in air, oxygen, and nitrogen atmospheres, and corresponding temperature ranges obtained from the

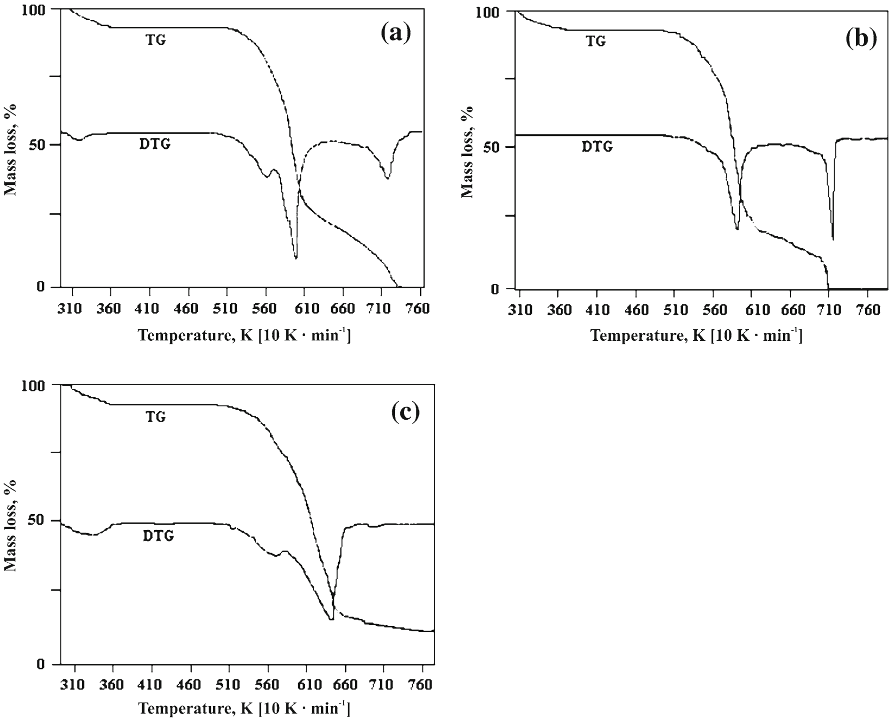

Fig. 3 (**a**) TG and DTG profiles of sisal in air atmosphere; (**b**) TG and DTG profiles of sisal in oxygen atmosphere; and (**c**) TG and DTG profiles of sisal in nitrogen atmosphere

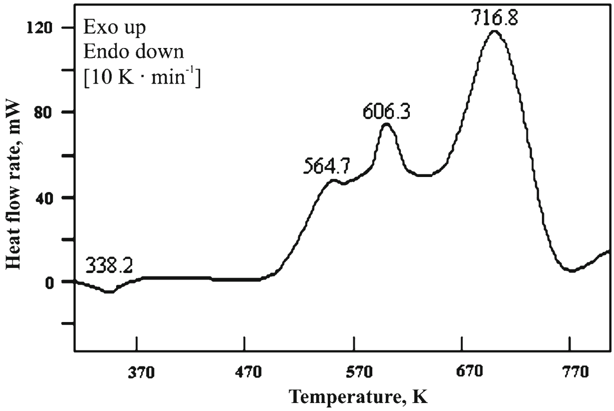

Fig. 4 DSC profile of sisal in air atmosphere

Table 2 Kinetic data from TG curves in air, oxygen, and nitrogen for sisal fiber

Atmosphere	Segment	Temperature (K)	Mass loss (%)	Activation energy (kJ · mol^{-1})	Reaction
Air	1	310–382	7.25	38.19	Dehydration
	2	506–580 580–613	29.16 32.64	64.23 89.71	Decomposition
	3	613–733	26.17	40.56	Decomposition
Oxygen	1	310–364	7.20	40.60	Dehydration
	2	503–580	30.56	30.11	Decomposition
		580–615	31.25	48.79	
	3	615–710 At 710	24.44 4.17	31.13 28.90	Decomposition
Nitrogen	1	310–361	7.25	90.50	Dehydration
	2	507–580	31.25	38.27	Decomposition
		589–640	42.35	97.22	
	3	640–710	4.44	6.34	Decomposition

respective TG's are shown in Table 2. The activation energy corresponding to thermal decomposition at various stages of the fiber in air, oxygen, and nitrogen atmosphere was calculated from respective TG curves using the Freeman and Carroll equation [15], and is shown in Table 2.

TG and DTG profiles in Fig. 3a–c showed three distinct thermal processes occur in the sample, invariably in the temperature range from 310 K to 760 K. The first thermal process of the sample under heating in air occurred with a sharp mass loss in the temperature range from 310 K to 382 K and the corresponding mass loss is 7.25 %. Corresponding changes were observed in DTG profiles of the sample indicating a depression at 326 K. Similar mass loss patterns were also observed for the sample in this low-temperature range in oxygen and nitrogen atmospheres and the respective mass losses were 7.20 % and 7.25 %. The DTG of the sample in nitrogen shows a depression at 325 K (Fig. 3c), while no change is observed in the DTG in oxygen in this low-temperature range (Fig. 3b). In the temperature range of approximately 310 K to 385 K, the mass losses are also well reflected in DSC profiles of sisal in air (Fig. 4).

An endothermic peak occurred in the DSC thermogram of the sample in air in this low-temperature range. Usually the losses of weakly interacting molecules on heating are reflected in the endothermic process in such a low-temperature range [15]. On the basis of this, the endothermic peak may be assigned to losses of water molecules from the surface or interstitial spaces. Since in this temperature range (310 K to 382 K) the XRD pattern of the sample retained its identity of the XRD pattern of the unheated sample as discussed above, it is assumed that losses of water may not be from the interstitial region of the fibers. This result is supported by the findings obtained from the IR study.

The spectroscopic study of the fibers indicated that no changes occurred in the original spectra of fibers when they had been annealed at 370 K, except for a slight decrease noticed in bands due to OH (free and H bonded) and CH stretching. Thus, it may be concluded that on thermal treatment in the lower range of temperature (310 K to 382 K), heat is absorbed by the fibers to remove the absorbed water molecules, which are mostly embedded in the amorphous region of the fibers.

The mass loss occurring in all samples during the first step of the kinetic reaction may be attributed to the dehydration process [16]. This result indicates that the fiber under study is hygroscopic in nature. Furthermore, the fibers show thermal stability up to approximately 500 K. The decomposition processes of the fiber are found to occur at temperatures above 500 K.

The second step of the kinetic reaction of sisal fiber in air occurs in the temperature range from 506 K to 613 K (Fig. 3a). In this second thermal process, the mass loss occurred in two different ways: one from 506 K to 580 K with a mass loss of 29.16 % and another from 580 K to 613 K with a mass loss of 32.64 %, resulting in a total mass loss of 61.80 %. The corresponding DTG curve of the sample in air shows a shoulder at 559 K along with the main peak at about 606 K, which supports the presence of two sets of mass loss during the second step of thermal decomposition as well as indicating the possibility of the occurrence of thermal decomposition of the fibers through two individual paths within this step. In both the nitrogen and oxygen atmospheres, the TG of sisal also showed two distinct sets of mass loss during this second thermal process. For the case of nitrogen (Fig. 3b), the net mass loss is 73.60 % in the range from 507 K to 640 K, whereas in oxygen (Fig. 3c), the net mass loss is 61.81 % in the range from 503 K to 615 K. Corresponding DTG profiles of the sample in oxygen and nitrogen support the two distinct sets of mass loss. The presence of two distinct sets of mass loss was also reflected in the DSC profiles of the sample in air in the temperature range from 538 K to 628 K.

Two small exothermic peaks were observed within this high-temperature range. The above result reveals that due to heating in this high-temperature range, the sample is decomposed and its crystallinity is totally lost. The XRD data in this range of temperature confirmed the decomposition through crystallinity loss in the structure of the fibers. Furthermore, in the second part of the second step, the occurrence of the sharp decrease in mass in TG profiles for the samples in air, oxygen, and nitrogen atmospheres as shown indicates the formation of a stable decomposed part of the fiber. From Table 2, it is also observed that the decrease in mass for each sample during the second step is found to be more rapid in nitrogen and less for oxygen as compared with air. This differences of mass loss found in TG profiles in different atmospheres during the second step may be attributed to oxygenation of the fibers in the presence of air and oxygen, whereas such an oxygenation reaction cannot take place in a nitrogen atmosphere. Thus, for the case of nitrogen there is more mass loss than in the case of oxygen in this region, and it is also logical that a hydrocarbon present in sugar will gain mass on oxygenation. In summary, these two processes can be termed as thermal decomposition (under nitrogen) and a thermal oxidative reaction (under oxygen). The oxygenation of the fibers in air is well supported by IR studies of the fibers in this high-temperature range. The IR spectra of the sample annealed at 530 K and 600 K showed the development of C=O groups, which indicate the oxidative nature of the initial decomposition occurring in this temperature range.

The third step of the kinetic reaction occurs only when TG is performed in oxygen and air, but does not occur in an inert atmosphere. A sharp peak appeared in the corresponding DTG profile in oxygen at approximately 710 K. Based on the above results, the changes observed during this third stage of thermal decomposition are attributed to the formation of carbon dioxide and carbon monoxide gases from the carbonized material that is formed during this stage. The presence of oxygen results in a complete conversion to gaseous material and arial oxidation leads to some amount of residual [17]. The amount of residual at the end of the heating processes under different air, oxygen, and nitrogen atmospheres are 4.78 %, 2.38 %, and 14.71 %, respectively. The third step of the kinetic reaction and the corresponding changes are well reflected by the exothermic process occurring in the DSC in air. An exothermic peak is observed for the DTG profile of the sample in this high-temperature range as shown in Fig. 4. The kinetic parameters such as activation energy, change of enthalpy, and change of entropy of the sample were computed from the integrated peak areas of the DSC profile in air and are shown in Table 3.

In order to study the hygroscopicity of the plant fibers, the gain in water content in fibrous samples due to moisture absorption was measured as a function of exposure time. The results of the gravimetric determination of moisture absorption in sisal fiber under ambient and annealed conditions are shown in Fig. 5. The sample under ambient condition is found to be more hygroscopic and loses hygroscopicity to a smaller extent in the case of preheated samples. In order to determine the environmental factor of the utility of the fibers, the hygroscopicity of the fibers was determined at different

Table 3 DSC data of sisal fiber in air (heating rate of 10 K·min^{-1})

Segment	Temperature range (K)	Peak temperature (K)	Activation energy (kJ · mol^{-1})	Change of enthalpy (mJ · g^{-1})	Reaction
1	310–384 (endo.)	338.2	44.78	48.29	Dehydration
2	538–576 (exo.)	564.7	82.17	68.09	Decomposition
	582–628 (exo.)	606.3	108.43	152.77	
3	647–765 (exo.)	716.8	193.45	223.43	Decomposition

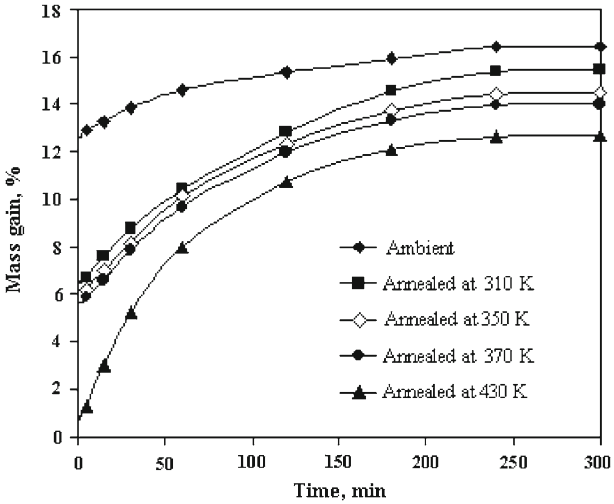

Fig. 5 Mass gain as a function of time for moisture absorption in sisal fiber under ambient and annealed conditions

Table 4 Hygroscopicity (H%) of sisal fibers at different relative air humidities

Relative air humidity (%)	Hygroscopicity (H%)
75	12.00
68	10.13
58	8.65
33	7.54
20	5.36

relative air humidities and the results are summarized in Table 4. From the results, it is evident that with an increase in the relative air humidity, the hygroscopicity of sisal increases. It is interesting to note that the samples have an approximately 5 % increase in mass due to absorption of water in a very low-humidity condition (∼20 %). The hygroscopicity of sisal fibers under an annealed condition is less with respect to its value under ambient conditions. This is attributed to the possible changes in the pore distribution and permeability of the fibers as a result of annealing. The variation of water absorption of the sample on heating may also be attributed to the greater number of interconnected hydroxyl groups contained in the native cellulose and in hydrated cellulose. This is consistent with the IR investigation of the sample.

4 Conclusion

XRD and IR studies under ambient conditions showed that sisal has a cellulosic structure in nature. The cellulosic structure of the plant fiber is unaffected on heating up to 450 K. However, the crystalline parameters of the sample such as the crystallinity and crystallite lengths of the fibers are slightly affected due to heating in this low-range of temperature. TG, DTG, and DSC studies showed that three distinct thermal processes occurred in the fiber under heating at temperature from 310 K to 760 K. The first step takes place in a temperature range from approximately 310 K to 380 K due to a dehydration process, and the crystallinity of the fiber remains intact in this range of temperature. No decomposition of the plant fiber takes place up to about 500 K. The second thermal process of the sample under heating in the high-temperature range (above 500 K) consisted of two different closely related processes, thermal decomposition leading to incomplete carbonization of the fibers. The original structural features of the cellulosic backbone are not completely lost in this high-temperature range. The third thermal process is representative of combustion of the fibers to carbonized material. An IR spectroscopic study of the sample annealed at different temperatures provides meaningful data to identify decomposition of the native structure of the fiber. For the case of moisture absorption, the saturation limit of sisal per unit gram varies and depends on the pretreatment of the fiber. With an increase in the relative air humidity, the water absorption of the fiber increases.

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