THERMAL PROPERTIES OF FLAX FIBER SCOURED BY DIFFERENT METHODS

by

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Thermal properties of flax roves untreated and treated were characterized by differential scanning calorimetry and thermal gravity analyzer in order to understand their thermal behavior in more detail and to evaluate the effect of scouring processing on the thermal behavior. Flax roves were treated with six kinds of methods including biological scouring, one bath, two bath, bleaching, alkali scouring, and industry chemical scouring as standards. Results showed that all treatments improved thermal stability of flax roves. The results indicated that glass transition temperature (T_g) decreased after scouring besides the sample by directly bleaching. It is more difficult to determine the endothermic peak of flax treated by chemical scouring in industry because it takes a very flat course. A distinct endothermic peak was observed for the untreated flax rove, while a distinct exothermic peak in different temperature interval was revealed for other four treated flax rove samples. For thermogravimetric analysis, thermal degradation of flax roves studied consists of three regions of the initial, main, and char decomposition, and the third stage consists of secondary weight loss and carbonization for flax roves with biological scouring, one-bath and two-bath. Besides, different residue left indicates that the bio-scoured flax roves are lost with volatile products and does not contribute to char formation. These results provide valuable preferences for mechanism and top value added application of bio-scouring in flax roves.

Key words: *flax, thermal properties, differential scanning calorimetry, thermal gravity analyzer*

Introduction

Flax fiber is a kind of natural bast fibers widely used for textiles (linen) and for technical applications, such as specialty papers, composites, and insulating material [1] due to its renewable nature, low cost, easy availability, environmental benefit (*i. e*. biodegradability), improved performance and ease of chemical and mechanical modifications [2]. In textiles the fiber eco-friendly extraction process like retting, scouring, and bleaching was accentuated to improve the fiber heterogeneity in strength, fineness, and color within the same variety, less attention is

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given on the thermal properties [1]. Usually the improvement in thermal properties inclusion of natural fibers about composites and insulating material is reported [3]. In the literature survey [3-8], the effect of different surface treatments on the thermal stability of natural fibers was discussed to improve lignocellulosic fiber/matrix adhesion in natural fiber composites. However, lack of studies concern the influence of fiber extraction methods on thermal properties. In addition to fiber refined process, some treatments such as enzymatic fiber extraction and cell treatments would be a promising alternative because of its beneficial effects on the environment, mechanical properties, and interfacial adhesion [9]. Therefore, thermal analysis study is necessary to determine the influence of different refined treatments on thermal stability of natural fibers and also to observe any degradation process during fibers production. The objective of this work was to report the thermal properties of the flax fibers untreated and treated with six kinds of scouring methods including biological scouring, one bath in which bleaching with H_2O_2 was conducted directly in the solution of bio-scouring without washing, two bath in which bleaching with H_2O_2 was carried out after washing for bio-scoured sample, only bleaching, alkali scouring, and standards in industry. On the other hand, the effect of different treatments on the thermal properties has also been discussed.

Experimental

Flax samples were successfully scoured with six kinds of treatments including biological scouring, one bath, two bath, bleaching, alkali scouring and standards and named as #1, #2, #3, #4, #5, and #6, respectively. In the investigation the untreated samples were named as #0 to compare with untreated samples. The process flow is shown in tab. 1.

Table 1. The process flow of flax samples treated with different methods

Samples	Treated methods	Process flow
#0	Untreated	Flax roves
#1	Biological scouring	Untreated sample – scouring with alkalophilic strains – inactivation-washing – air drying
#2	One bath	Untreated sample – scouring with alkalophilic strains – bleaching directly without changing solution-washing – air drying
#3	Two bath	Untreated sample – scouring with alkalophilic strains – washing – bleaching-washing – air drying
#4	Bleaching	Untreated sample – bleaching-washing – air drying
#5	Alkali scouring	Untreated sample – scouring with sodiun hydroxide – washing – air drying
#6	Standards	Alkali scouring and bleaching in industry – washing – air drying

For the process of the biological scouring, the flax roves were soaked in a 20 wt.% aqueous solution of DA8 strains screened for 12 h at temperature of 37 °C, initial pH value of 9, and shaking speed of 200 rpm. The additives of JFC (3 g/L), EDTA (4 g/L) and sodium tripolyphosphate (1%) were used in scouring solution. Afterwards, the treated roves were inactivated by boiling water and then washed for several times with deionised water up to neutral conditions, and air dried. The ratio of roves weight to solution volume corresponded to 1:15. For the process of the one bath, in the end of biological scouring, the scouring solution was heated to 90 °C. Afterwards, NaOH (0.8 g/L), Na_2CO_3(5.0 g/L), and Na_2SiO_3 (3.0 g/L) were added, re-

spectively, and mixed uniformly. Hydrogen peroxide (6.0 g/L) was then mixed to bleaching flax roves for 1 h and followed by washing for several times in distilled water and air drying. For the process of two-bath, the bleaching process was carried out after washing the samples of biological scouring. The samples of #3 were obtained after washing and air drying. The untreated samples were directly bleached, washed, and air-dried and obtained the sample of #4. The sample of #5 was obtained by alkali scouring, washing, and air drying. Alkalization consisted in soaking the untreated flax roves in a 8.0 wt.% aqueous solution of sodium hydroxid and Na_2CO_3 8.0% (o.w.f), respectively, for 3 h at the temperature of 95 °C. The sample of #6 as a standard came from industry and processed by alkali scouring, washing, bleaching, washing and dried in an oven. The ratio sample/solution was kept for all experiments 15 g of sample for 150 ml of solution.

Differential scanning calorimetry (DSC) analysis was performed by NETZSCH DSC 204F1 Phoenix under a nitrogen atmosphere. The samples were subjected to heating from 25 °C to 300 °C at a rate of 10 K/min. Temperature calibration and determination of the constant time of the instrument were performed by using standards of In and Zn, and the heat flow calibration with In. Isothermal and dynamic scans were carried out in nitrogen atmosphere. Thermogravimetric analysis (TGA) was executed by a thermoanalyzer of NETZSCH STA 409 PC/PG. Samples weighing between 1 and 5 mg were placed in ceramic crucibles and tests were carried out in N_2 atmosphere at the 40 ml/min of flow rate between 50 and 900 °C under the different scan rates of 10.0 K/min.

Results and discussion

DSC analysis

DSC is considered an excellent technique for understanding of thermal behavior and identifying phase transitions like glass transition of lignin for flax [10]. Figure 1 shows the DSC thermograms for flax rove samples, and thermal parameters were illustrated in tab. 2. Bleaching sample showed the highest glass transition temperature (T_g – 82.3 °C), compared to untreated sample (T_g – 71.9 °C), biological scouring (T_g – 68.1 °C), two bath (T_g – 56.3 °C), alkali scouring (T_g – 55.6 °C) and one bath (T_g – 55.5 °C). This suggested that the flexibility and irregularity of the molecular chains enhanced, and the free volume and amorphous regions of cellulose increased. Consequently, less energy was needed to make molecular chain segments moving. Generally, as T_g became lower, the sample was endowed better flexibility and soft handling. The higher glass transition temperature of bleaching sample can be possibly attributed to oxidation of gum from flax rove during directly bleaching using H_2O_2 which leads to higher molecular weight.

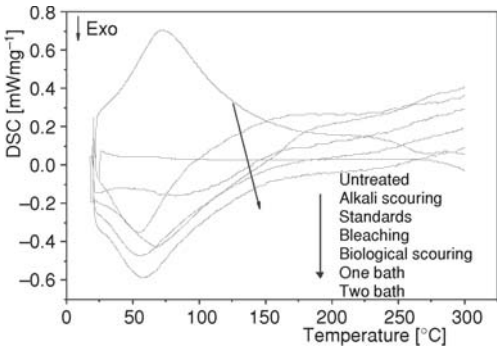

Figure 1. DSC thermograms for flax roves untreated and treated with different scouring methods

Thereby untreated flax rove reveals a distinct endothermic peak in the temperature interval between 42.9-121 °C. It is more difficult to determine the endothermic peak of flax treated by alkali scouring and bleaching in industry as a standard because it takes a very flat course. A possible explanation for the appearance is that the gum among flax fibers is lower. While it is

different that flax rove samples treated with other five kinds of methods reveals a distinct exothermic peak in different temperature interval, and they are 41.2-104.9 °C, 22-147 °C, 118.1 °C, 67.9-246 °C, and 33.1-95.2 °C, respectively. Except for the sample from bleaching and industry, for every sample the peak shifts to lower temperature and this effect is more evident when the scouring conditions are stronger. The shift can be explained assuming that the scoured flax is already degraded with a large fraction of oligomers and therefore less energy is necessary for their thermal decomposition [11].

Table 2. The first peak and other parameters for thermal degradation of untreated and treated flax roves

Samples	Area [Jg^{-1}]	Temperature [°C]				Height [$mWmg^{-1}$]
		Peak	Initial	Final	Broad	
#0	161.1	71.9	42.9	121	69.8	0.4527
#1	–114.8	68.1	41.2	104.9	80.9	0.3219
#2	–120.4	55.5	22	147	73.6	0.3218
#3	–117.9	56.3	–	118.1	67.5	0.3467
#4	–34.69	82.3	67.9	246	72.3	0.09484
#5	–108.5	55.6	33.1	95.2	54.3	0.3724
#6	–	–	–	–	–	–

On the other hand, different peak broads of samples were observed. The peak of samples treated with two-bath and alkali scouring is less broad than that the samples untreated, while the peak of samples treated with biological scouring, one bath and bleaching is more broad compared with untreated sample. This difference is likely to be due to the residual gum of flax roves after treating. The higher content of residual gum after scouring for flax rove samples, the broader peak of DSC curves can be observed. The peak area in the DSC curves of untreated and treated samples is different (shown in tab. 2). For every treated sample the peak area decreases compared with that of untreated samples. The peak height of DSC curves has the same trend.

TGA discussion

Thermogravimetry (TG) and differential thermogravimetry (DTG) curves for untreated and treated flax roves obtained in N_2 are shown in figs. 2 and 3. The thermal degradation temperatures and other thermal parameters were summarized in tab. 3. It could be seen that the TGA curves consisted of three weight loss stages and shifted to right side after scouring, which indicated that the thermal stability became better. It also can be seen in tab. 3 that the onset degradation temperatures tend to increase after scouring, compared with the untreated flax roves. It is partially due the fact that some fiber companions like hemicelluloses, pectin, lignin, and waxes, which degrade at a lower temperature, may be removed variously during scouring [5]. The TGA curves of all samples studied consists of three regions of 1, 2 and 3 as the initial,

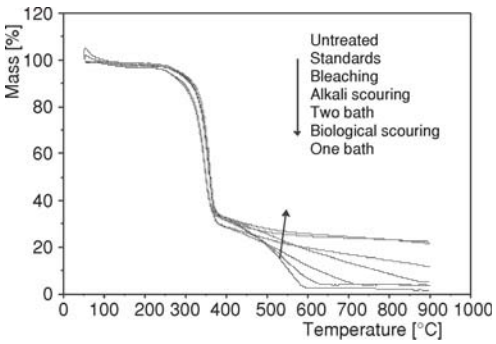

Figure 2. TGA curves of flax rove samples untreated and treated with different scouring methods

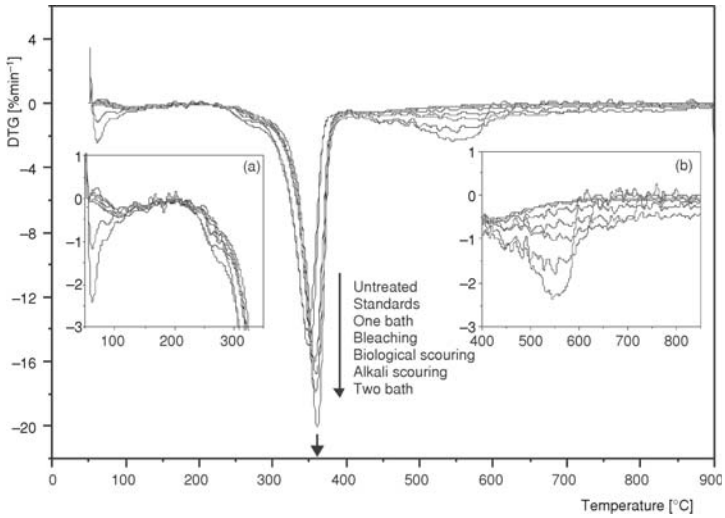

Figure 3. DTG thermograms of flax rove samples untreated and treated with different scouring methods. Magnified view in the temperature range: (a) 50-350 °C and (b) 400-850 °C

main, and char decomposition regions. In the first stage, the changes of the thermal properties and weight loss of fibers correspond to some physical damages (*e. g*. evaporation of water) occurring mostly in the amorphous region of the cellulose. The main thermal stage occurs in the second region, where weight loss is significant. Glucose together with all kinds of combustible gases generated in this region was deduced [12].

Moreover, thermal degradation in this region takes place in the crystalline region of the cellulose fibers. This decomposition peak at about 340-370 °C is due to the thermal depolymerization of hemicellulose and the glycosidic linkages of cellulose [2]. Production of char occurs at the third region at temperatures higher than 360 °C. This process continues by dewatering and charring reactions, releasing water and carbon dioxide and increasing the carbon and charred residues [12, 13]. In this process the significant difference is observed between flax roves untreated, treated by bleaching, alkali scouring, industry as standards and that of biological scouring, one-bath and two-bath. For the latter samples, the char decomposition region consists of secondary weight loss and carbonization. For flax rove treated with biological scouring, one-bath and two-bath the residue left at 624.8 °C (3.73%), 588.9 °C (1.45%), and 729.9 °C (3.81%), respectively, is less than that of untreated sample (21.51%), bleaching (5.2%), alkali

Table 3. The degradation temperatures of flax rove samples at different weight losses

Samples	Temperature [°C]				Residual mass [%]
	Initial	Peak	Final	Broad	
#0	319.6	347.1	365.2	–	21.51
#1	337.4	–	370.7	624.8	3.73
#2	331.7	–	368	588.9	1.45
#3	341.4	358.9	370.6	729.9	3.81
#4	333.7	–	368.7	–	5.2
#5	326.4	369.7	–	–	11.52
#6	321.9	349.3	366.5	–	22.27

scouring (11.52%) and standards (22.27%), which indicates that the bio-scoured flax roves are lost with volatile products and does not contribute to char formation.

DTG curves also give evidence for this as shown in fig. 3. Three peaks can be seen in fig. 3. For all samples studied, the first weight loss observed is attributed to the evaporation of water. The second peak is related to the degradation of cellulose, hemicelluloses, and pectins [9]. Except for untreated flax roves, all treated flax roves DTG curves do not show a significant shoulder between 250 and 350 °C, fig. 3(a), which corresponds with the lower pectins and hemicellulose content. Scouring treatment removes pectins and hemicelluloses which degrade at lower temperature, thereby the peak of DTG did not show a shoulder after rove scouring. For scouring treatment, the absence of shoulder could be explained by the thermal stability improvement of hemicelluloses and pectins. For flax roves treated with biological scouring, one-bath and two-bath, the third peak between 450 and 700 °C, fig. 3(b), might be due to the further breakage of decomposition products of fibers. At 360 °C, the formation of aromatic compounds starts, and between 450 and 700 °C, they constitute 88% of the ash. Ash produced by pure cellulose consists mainly of polycyclic aromatic compounds [6]. All fibers have a residual weight between 17 and 24 wt.% at 750 °C. The residual weight about 17% was observed for cellulose ash-less filter paper after heating from 20 to 900 °C [14]. In an inert atmosphere, the end-products of the degradation of cellulose are carbonaceous residues plus un-degraded fillers. As during flax plant growing, plant needs inorganic compounds as nutrients, these inorganic compounds will show up in the ash.

Conclusions

In this work, the thermal degradation of flax rove untreated and treated was investigated with DSC and TGA analyses. The flax rove used for these experiments underwent different stages and types of scouring or in one case. The flax rove came from industry was also chemically treated to obtain standard sample. The effects of flax rove scouring treatments using biological scouring, one-bath, two-bath, bleaching, alkalization, and chemical scouring on flax fiber thermal stability have been investigated. A clear difference in the various types of flax roves was observed through a comparison of these values, and an explanation for these differences was suggested. For DSC analysis, the results showed that scoured flax roves exhibit lower compared to untreated flax rove ones, accept for the sample by bleaching. It is more difficult to determine the endothermic peak of flax treated by chemical scouring in industry as a standard because it takes a very flat course. A distinct endothermic peak was observed for the untreated flax rove, while a distinct exothermic peak in different temperature interval was revealed for other four treated flax rove samples. For TGA and DTA analysis, results indicated that the thermal stability became better after scouring. The TGA curves of all samples studied consists of three regions of 1, 2, and 3 as the initial, main, and char decomposition regions. For flax roves with biological scouring, one-bath and two-bath, the char decomposition region consists of secondary weight loss and carbonization. Different residue left indicates that the bio-scoured flax roves are lost with volatile products and does not contribute to char formation. These results provide valuable preferences for mechanism and top value added application of bio-scouring in flax roves.

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