Thermal Degradation of Flax: The Determination of Kinetic Parameters with Thermogravimetric Analysis

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ABSTRACT: The thermal degradation of flax was investigated with thermogravimetric analysis. The flax used for these experiments underwent different stages of retting or, in one case, boiling. The most retted type of flax was also chemically treated to obtain elementary fibers. These samples were all tested in dynamic and isothermal runs after careful sample preparation. The resulting thermograms were analyzed and later used to calculate the kinetic parameters of cellulose degradation. These kinetic parameters included reaction constants and activation energies. A clear difference in the various tested types of flax was observed through a comparison of these values, and an explanation for these differences was suggested. © 2002 John Wiley & Sons, Inc. J Appl Polym Sci 83: 2634–2643, 2002

Key words: flax; thermal degradation; thermogravimetric analysis (TGA); kinetic parameters; cellulose; thermogravimetric analysis (TGA); fibers

INTRODUCTION

Flax fibers can be used as ecological alternatives to conventional reinforcing fibers (e.g., glass) in composites. Flax fibers are less dense than glass fibers, are renewable and combustible (for easy disposal of composites), and are relatively low in price.

A study of flax degradation at elevated temperatures is necessary because the production of composites often involves a temperature increase.

Because different retting degrees of flax have different compositions, they are likely to exhibit different degradation kinetics. Experiments with thermogravimetric analysis (TGA) should show which of the flax varieties is the most heat-resis-

tant and, therefore, the most suitable for use in composites.

THEORETICAL BACKGROUND

Because cellulose is the main component of flax, only the thermal degradation of cellulose is discussed. The thermal degradation of cellulose[1] depends on several test parameters, including the sample composition, time–temperature profile, type and pressure of gas surrounding the sample, and presence of inorganic impurities.

The literature on this subject is often rather complex and controversial. Therefore, only a short overview of possible reactions is given. This overview is based on the division of all possible reactions into three pathways (Fig. 1). These reaction pathways are as follows: at low temperatures, decomposition of the glycosyl units takes place; at higher temperatures, the glycosyl units are split by depolymerization, forming substances such as levoglucosan; and at even higher temper-
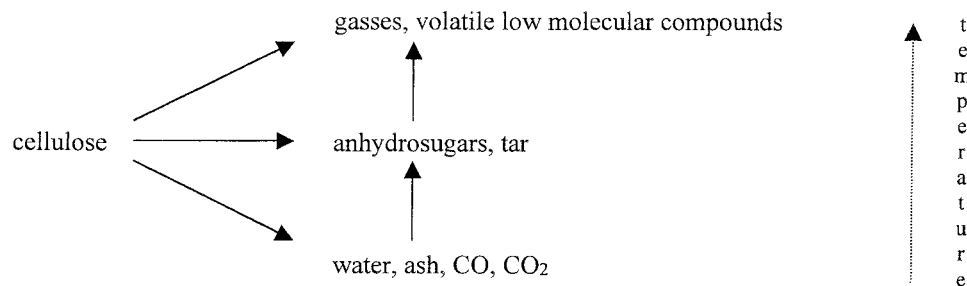
Figure 1 Possible pathways of cellulose degradation.

atures, the sample and all intermediary products immediately decompose into gases.

Reactions at Temperatures below 300°C

At relatively low temperatures such as the ambient temperature, it is hard to distinguish between the normal aging reactions and the actual thermal degradation. Degradation at such low temperatures is accelerated by the presence of water and autocatalyzed by CO_2 and carboxylic acids and consists of three phases, namely, the induction of the degradation, quick degradation, and slow degradation. The degradation processes mentioned previously are quicker in air than in an inert atmosphere (e.g., nitrogen).

However, at temperatures greater than 300°C, the degradation process is different. Thermal degradation at higher temperatures is caused by the destruction of hydrogen bridges; the loss of water; glass transitions; changes in crystallinity; and the formation of free radicals, carbonyl groups, and carboxyl groups (especially in air). Most of these causes are correlated.

The formation of free radicals in air has already been noticed[1] at temperatures between 100 and 160°C. This, in turn, can lead to the formation of hydroperoxide groups that contribute to a large extent to the depolymerization of cellulose (by bond scission). In nitrogen, this phenomenon hardly takes place at all. Actually, hydroperoxide groups tend to disappear.

Besides depolymerization, a variety of oxidation and decomposition reactions take place, leading to the formation of carbonyl, carboxyl, lactone, and aldehyde functional groups. These reactions are much less significant in an inert atmosphere than in air.

All the reactions below 300°C are very slow and sometimes take several days to be completed. For rapid heating (with the TGA technique), the dif-

ferences between the measurements in air and nitrogen can be very small.

Reactions between 300 and 600°C

Unlike the reactions below 300°C, these reactions proceed rapidly.

In an inert atmosphere, between 310 and 390°C, an endothermic reaction takes place,[1] producing approximately 12% ash (from pure cellulose). In this reaction, three hydrolysis products are formed: tar (or a heavy oil fraction that vaporizes at higher temperatures), ash, and condensable and noncondensable gases. These products are the result of a series of transglycosidation and dehydration reactions.

However, an initiation reaction first has to take place, converting cellulose into its active form (polymer) and also forming phenol. At approximately 340°C, this polymer undergoes ring scission, leading to the formation of anhydrosugars such as levoglucosan. These substances then further dehydrate, forming smaller molecules such as glucose and furan (part of the tar fraction).[1]

At 350°C, the formation of aromatic compounds starts, and between 400 and 500°C, they constitute 88% of the ash. The ash produced by pure cellulose consists mainly of polycylic aromatic compounds. No literature on the ash of flax could be found, but it is only logical that because the flax plant needs inorganic compounds as nutrients, these inorganic compounds will show up in the ash.

EXPERIMENTAL

Materials

The following codes were given to the samples: G1, G2, M, F, E, and B. G stands for green (not

retted) flax, M for medium retted flax, F for fully retted flax, E for elementary fibers extracted from F, and B for boiled flax. All fiber types (except B) were scutched but not hackled. G1, M, and F originated from the same field, were harvested in the same year (1996), were of the same variety (Arianne). These samples were supplied by Debruyne NV (Arobsie, Belgium). G2 was supplied by Eurolino BVBA (Wevelgem, Belgium), and B was supplied by Jos Vanneste NV (Harelbeke, Belgium).

The extraction of E from F was done as follows: 2 h of refluxing in a saturated solution of ammonium oxalate in methanol, followed by 2.5 h of refluxing in a 1% solution of Na_2–ethylenediaminetetraacetic acid in water/methanol (2/1) and 15' refluxing in a 6% solution of sodium carbonate in water. Afterward, the flax was dried for 2 h at 80°C and allowed to condition under a standard atmosphere of 21°C and 65% relative humidity. The presence of elementary fibers was confirmed by optical microscopy.

Before testing, the flax fibers were cut (with a microtome) into pieces shorter than 1 mm. This was necessary for optimal heat transfer and good mixing of the sample.[2] The average length of the fibers was estimated to be 0.5 mm.

Test Procedure

The apparatus used for the tests was a TGA 1000 from Stanton Redcroft (PL Thermal Sciences Ltd., Epsom, UK). The parameters were the sample mass (2–3.5 mg) and the heating rate (10°C/min), and runs were carried out between 25 and 800°C. Sometimes, runs were broken off earlier because the mass had stabilized. Runs were carried out in both air and nitrogen at 20 mm/min.

Kinetics

The literature cited indicates that the thermal degradation of flax or cellulose follows first-order kinetics. The reaction rate is then expressed as

$$dc/dt = -kc \qquad (1)$$

where c and t are the concentration and time, respectively, and k is the reaction constant. In this specific case, c can be replaced by the mass (m), which leads to

$$dm/m = -k \, dt \qquad (2)$$

Even though k is called the reaction constant, it is only constant when the temperature remains con-

stant (as in isothermal TGA). Equation (2) can then be integrated to

$$\ln(m) = -kt - C \qquad (3)$$

where C is an integration constant. With the introduction of α, the remaining mass fraction, eq. (3) can be rewritten as

$$\ln(\alpha) = -kt - C' \qquad (4)$$

where $\alpha = (m - m_e)/(m_0 - m_e)$, with m_e being the mass at the end and m_0 being the mass at the beginning. If $1/\alpha$ is replaced by x, this leads to the final expression

$$\ln(x) = kt + C' \qquad (5)$$

Plotting $\ln(x)$ as a function of t at one constant temperature results in a straight line with a slope of k.[1,3] Furthermore,

$$k = k_0 \exp[-E_a/RT] \qquad (6)$$

where E_a is the activation energy (J/mol), R is the gas constant (8.32 J/mol), T is the temperature (K), and k_0 is the reaction constant at $T = 0$ K. This can also be converted to

$$\ln(k) = -E_a/RT + C'' \qquad (7)$$

Therefore, after several isothermal experiments, each resulting in a value for k, $\ln(k)$ can be plotted as a function of $1/T$, resulting in a straight line with a slope of $-E_a/R$, from which E_a can be determined.

However, E_a values can also be obtained from nonisothermal experiments and with the use of the Broido formula,[4,5,9] as shown in eq. (8):

$$\ln[\ln(x)] = -E_a/RT + [RZ/E_a\beta]T_m^2 \qquad (8)$$

where Z is a frequency factor, β is the heating rate, and T_m is the temperature at the maximum reaction rate. The last term of eq. (8) is a constant.

Plotting $\ln[\ln(x)]$ as a function of $1/T$ results in a straight line with a slope of $-E_a/R$. For each reaction or reaction step within the flax, this can be done. Peak 2 from the differential thermogravimetry (DTG) curves was selected for further calculations because of its magnitude and refer-
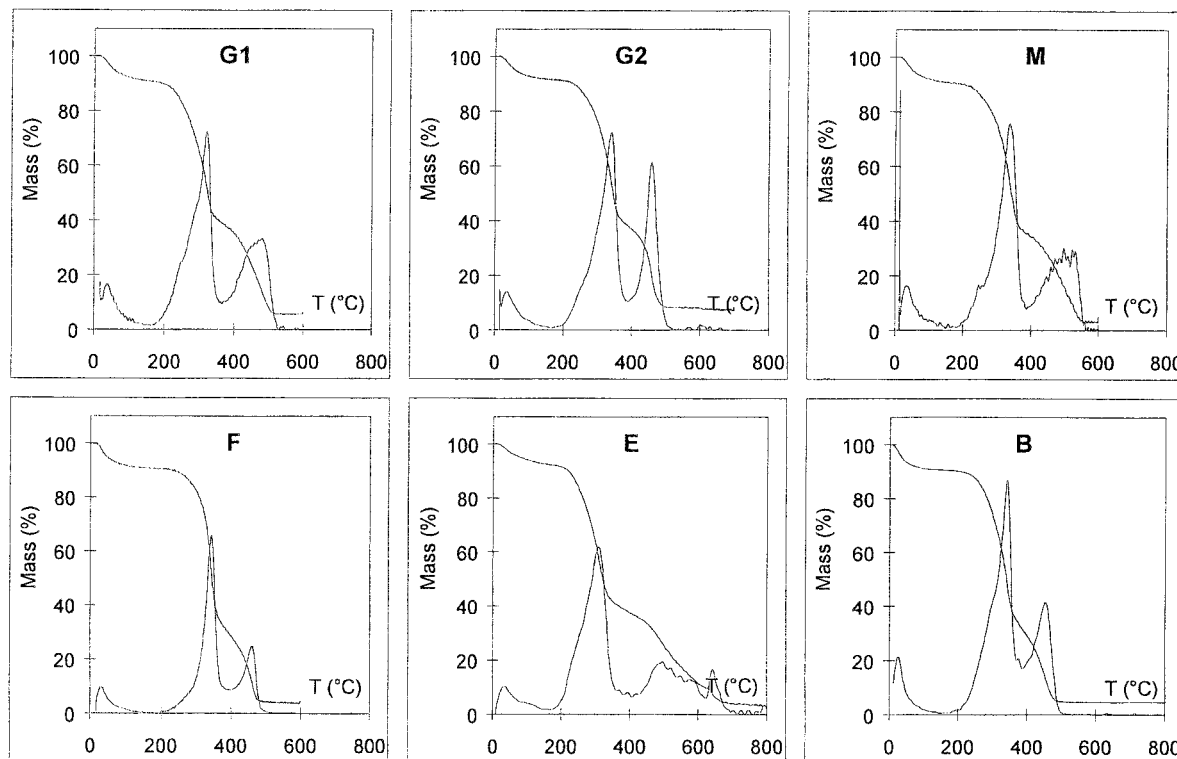
Figure 2   TGA curves of different types of flax in air.

ence values in the literature (shown later in Table VI).

RESULTS

Dynamic Test Runs

In Figures 2 and 3, one can see some examples of TGA curves in their original and differentiated state (DTG) on all tested types of flax in both air and nitrogen atmospheres. The average values resulting from these and other curves can be found in Tables I and II. The peaks reported are peaks in the DTG curves that correspond to points of maximum slope in the original TGA curves. For each of these peaks, the mass loss associated with it is calculated (between two DTG minima), and the corresponding peak temperature is reported.

When there was any doubt about the presence of a particular peak, additional tests were carried out. Values within parentheses are from peaks that could hardly be detected and are only indicative. The other values turned out to be reproducible.

Isothermal Test Runs

All the samples except B were tested at 60, 120, 180, and 230°C. The same apparatus and parameters as before were used, and only tests in air were carried out. The resulting curves (residual mass as a function of elapsed time) are shown in Figure 4. From these curves, the values in Table III were obtained. The residual masses after 300 min and after stabilization are given. Stabilization was only supposed to have taken place when the slope of the curves in Figure 4 reached a value between -0.005 and $0\%/\mathrm{min}$. The values within parentheses in Table III are only indicative because no stabilization could be reached within a reasonable time span.

Reaction Constants

On the basis of the isothermal experiments in air, only reaction constants could be determined.

The determination of E_a (of cellulose) could not be accomplished on the basis of these isothermal experiments because the four temperatures used were initially selected to reflect several composite production steps. These temperatures were gen-
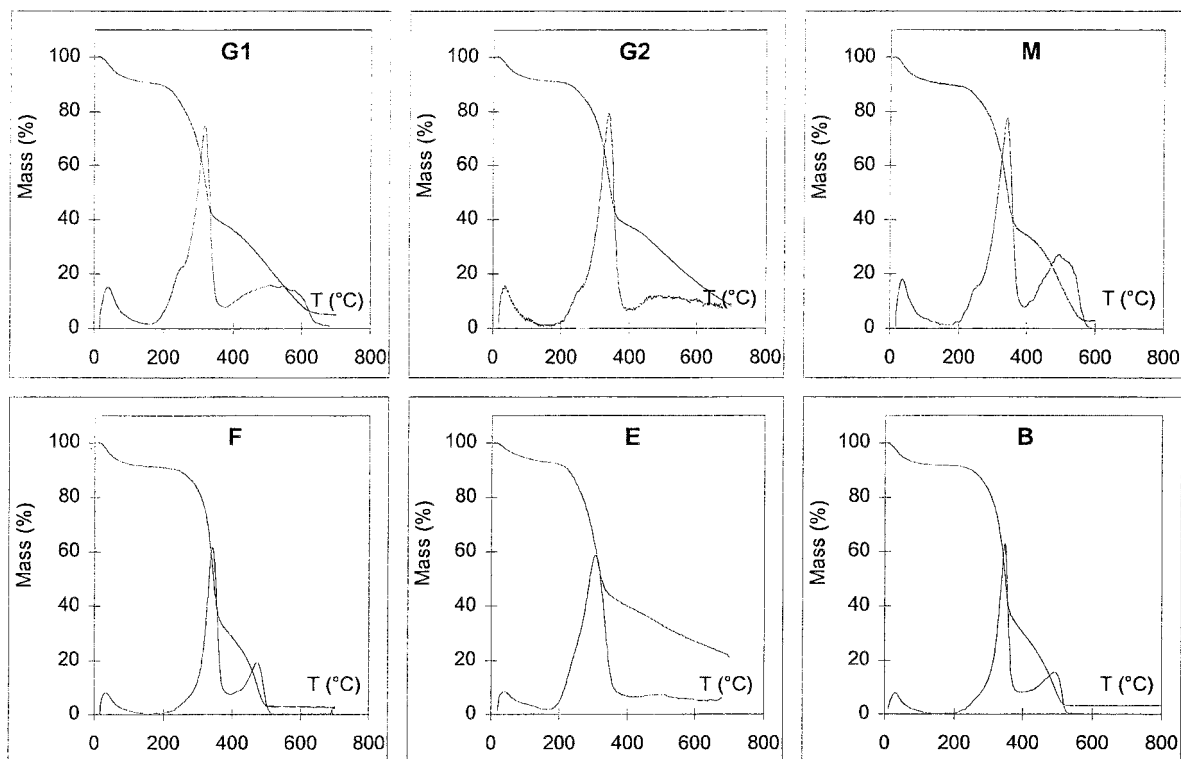
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Figure 3 TGA curves of different types of flax in nitrogen.

erally too low in comparison with the generally proposed[1] range of 275–315°C. However, the alternative method proposed by Broido can be used to determine E_a values, as discussed in the following paragraph.[9]

Figure 5 and Table IV show the determination of the reaction constants at 230°C. Reaction constants at lower temperatures were not determined because the mass loss due to physical phenomena (e.g., evaporation) tended to interfere with the pure chemical degradation of flax.

It is questionable whether actual reaction constants were of cellulose degradation alone. Hemicelluloses are generally thought to decompose first,[6] followed by cellulose and then lignin. Consequently, these reaction constants can partially be attributed to hemicellulose and lignin degradation. However, the reaction constants were determined over a time range in which severe mass loss was observed (Table III, Fig. 5). However, it is believed that much of the degradation that takes place is that of cellulose because it is the

Table I   DTG Peak Temperatures

Flax Type	Air				Nitrogen			
	Peak 1 T (°C)	Peak 2 T (°C)	Peak 3 T (°C)	Peak 4 T (°C)	Peak 1 T (°C)	Peak 2 T (°C)	Peak 3 T (°C)	Peak 4 T (°C)
G1	39.20	324.57	481.34	—	37.05	319.89	508.39	—
G2	32.84	339.39	459.31	—	35.84	338.79	(482.89)	—
M	33.96	335.50	497.90	—	37.39	339.64	494.84	—
F	30.67	344.13	459.93	—	34.92	348.99	473.23	—
E	34.55	306.91	491.35	641.57	34.88	307.29	486.11	—
B	26.19	341.67	453.90	—	30.65	346.55	491.41	—

Table II Mass Losses from TGA Curves

Flax Type	Air					Nitrogen				
	m_1 (%)	m_2 (%)	m_3 (%)	m_4 (%)	Ash (%)	m_1 (%)	m_2 (%)	m_3 (%)	m_4 (%)	Ash (%)
G1	9.37	51.69	32.90	—	6.04	9.40	52.35	33.19	—	5.06
G2	8.33	53.19	31.01	—	7.47	9.08	57.16	32.16	—	1.59
M	9.12	55.55	30.32	—	5.01	9.05	56.38	31.91	—	2.66
F	9.27	61.49	24.94	—	4.30	7.73	63.33	26.22	—	2.71
E	7.88	55.96	26.39	6.96	2.81	7.52	53.75	ND	—	ND
B	9.44	59.07	26.78	—	4.71	8.16	60.96	27.60	—	3.29

ND = not determined.

main component of flax. The reaction constants are, therefore, not of cellulose alone but a combination of cellulose, hemicellulose, and lignin.

E_a

Depending on the selected range in the $\ln[\ln(x)]$ − $1/T$ representation, slopes tended to vary drastically. Because there was no reference for which range to use, the range around the DTG peak maximum was chosen. These determinations of E_a are shown in Figure 6, and the resulting val-

ues are given in Table V. The E_a values of pure cellulose given in Table VI[3,4,6,7] can be used as a base of reference.

DISCUSSION

Nontreated Fibers

Several trends can be observed in the results for G1, G2, M, and F given in Tables I and II. For instance, increasing the degree of retting resulted
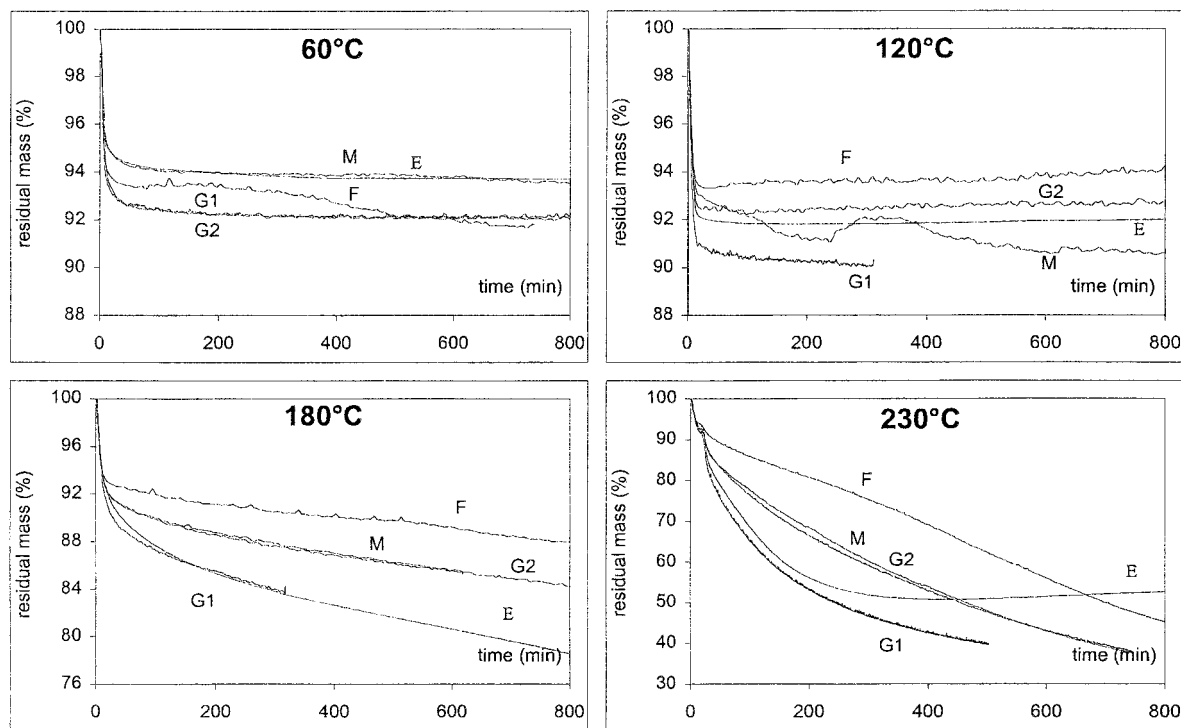

Figure 4 Isothermal TGA curves in air.

Table III   Residual Masses Resulting from Isothermal TGA

Flax Type	Mass (%) After 300 Min at				Mass (%) After Stabilization at			
	60°C	120°C	180°C	230°C	60°C	120°C	180°C	230°C
G1	92.2	90.0	84.0	46.7	92.0	90.1	(<83.8)	(<39.8)
G2	92.1	92.5	87.7	60.2	92.1	92.5	83.5	(<37.8)
M	93.9	92.1	87.9	59.1	93.5	90.3	85.5	(<38.2)
F	93.2	93.6	90.5	75.2	91.8	94.0	87.4	(<40.5)
E	93.8	91.8	83.8	51.8	93.7	92.0	(<77.3)	(<47.1)

in an increase in the mass loss around peak 2, whereas the opposite was the case for peak 3. Also, the degradation temperature indicated by peak 2 rose with an increasing degree of retting.

With respect to the literature findings given in Table VI, the presence of peak 3 in the DTG curves in nitrogen was somewhat strange. This led to the conclusion that this peak was (mainly) caused by the noncellulosic components of flax (also because this peak was not or hardly found in E). However, this peak was already reported for pure cellulose under air, so for measurements in air it looked as if it was caused by cellulose itself.

A possible explanation for this contradiction is that after peak 2 (attributed to cellulose), the degradation of cellulosic and noncellulosic compounds still continued. This process was much quicker in air than in nitrogen and so caused an extra peak (peak 3) in the DTG curve in air. In nitrogen, however, these reactions were much slower, which resulted in higher temperatures for peak 3 in nitrogen in comparison with air measurements. This, combined with an extra low content of noncellulosic compounds (e.g., in E), can lead to the partial or complete disappearance of peak 3. The original TGA curve, however, continued to descend. Extra proof for this theory is that the mass losses in peak 3 were always almost equal for measurements in air in comparison with the measurements in nitrogen. Therefore, the
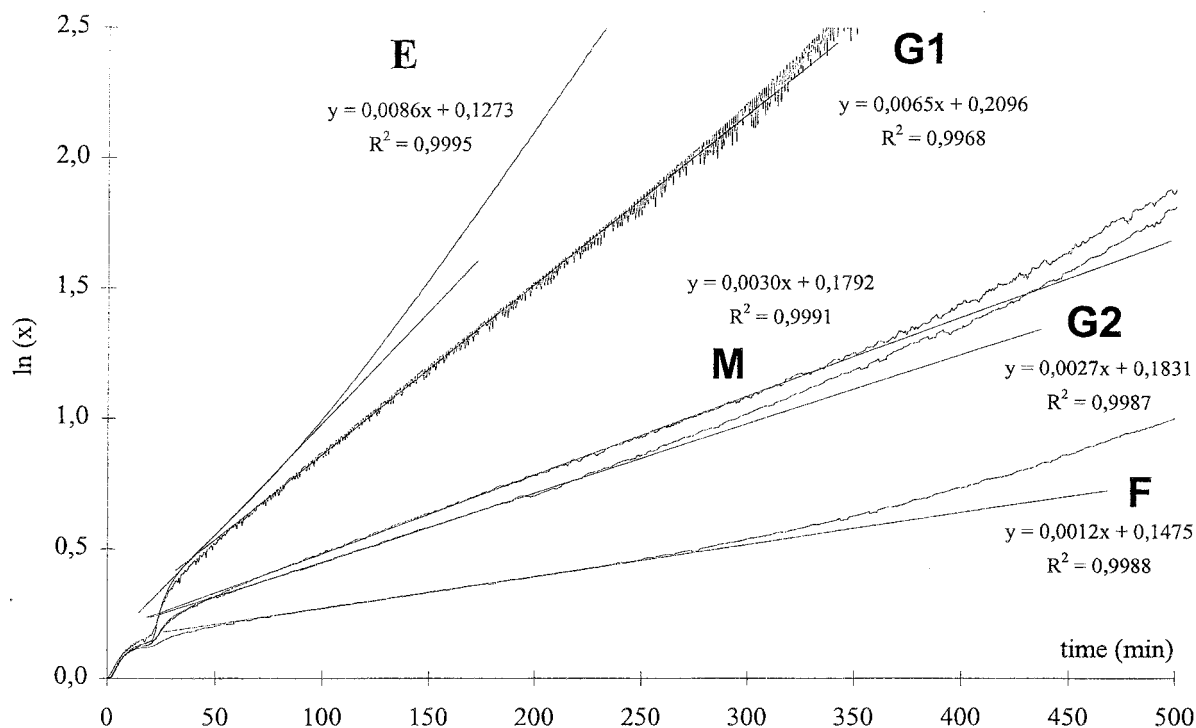

Figure 5   Determination of reaction constants in air at 230°C.

Table IV   Reaction Constants in Air at 230°C

Flax Type	k in Air and at 230°C $(10^{-3} \text{ min}^{-1})$
G1	6.5
G2	2.7
M	3.0
F	1.2
E	8.6

Table V   Calculated E_a Values

Flax Type	Measurements in Air		Measurements in Nitrogen	
	Slope	E_a (kJ/mol)	Slope	E_a (kJ/mol)
G1	−14,865	123.7	−14,091	117.2
G2	−14,633	121.7	−15,053	125.2
M	−14,707	122.4	−13,758	114.5
F	−24.382	202.9	−21,750	181.0
E	−9,095	75.7	−11,100	92.4
B	−15,560	129.5	−21,834	181.7

eventual result was equal, but the speed at which it was reached was clearly different.

In short, one can say that peak 2 was mainly caused by cellulose and peak 3 was caused by cellulose and noncellulosic compounds. This explains the aforementioned trends.

The observed ash content decreased with an increasing degree of retting. This could be partly due to the presence of smaller quantities of inorganic impurities. However, ash is mostly made up of polycyclic aromatic compounds, so the only logical conclusion is that noncellulosic components present in underretted flax account for the production of more ash than in pure cellulose.

Flax type G2, which was green (unretted), closely resembled M.

There was no noticeable tendency for peak 1 (Tables I and II), which was attributed to the loss of water (evaporation).

Looking at the isothermal TGA results (Table III), we can make the same conclusions we made earlier when studying peak 2 of the DTG curves. Increasing degrees of retting led to increasing amounts of residual mass. This phenomenon be-

came stronger at higher temperatures (especially at 230°C). This is explained by the fact that at lower temperatures, evaporation took place, and at higher temperatures, the degradation of cellulose became more and more important.

Flax type G2 was also, according to these experiments, more M-like than G1-like.

The obtained reaction constants confirmed all previous assumptions: the fully retted flax (F) degraded most slowly of all the samples, and G2 was much more M-like than G1-like.

A high value of E_a points to a stable substance because it is the energy needed for the reaction (degradation) of this substance. The E_a values determined here did not give any extra information about the nontreated fibers. Apparently, the cellulose in the nonfully retted flax samples was not completely freed. This led to E_a values that were lower than those mentioned in the literature (Table VI) because the simultaneous degradation
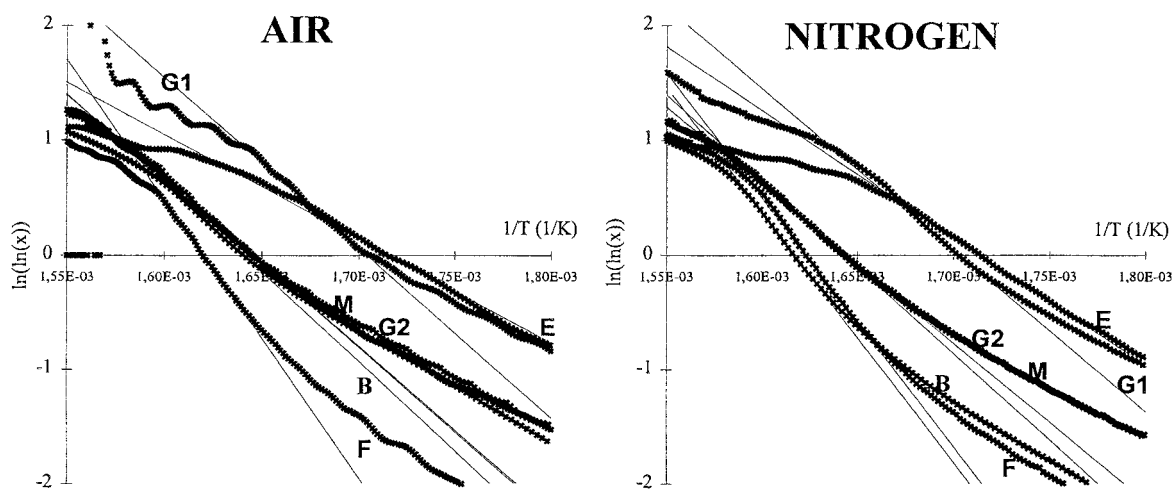

Figure 6   Determination of E_a.

Table VI E_a Values from the Literature

Reference	Atmosphere	Sample	Reaction Type	Number of Peaks in DTG	Peak 2	
					T (°C)	E_a (kJ/mol)
3	Nitrogen	Cellulose	Endotherm	2	339	182
6	Helium	Cellulose	(Not given)	2[a]	(Not given)	203
6	Helium	Retted flax	(Not given)	2[a]	377	188
4,7	Air	Cellulose	Exotherm	3	355–365	193–228

[a] Tests were stopped at 450 or 500°C. Hence, there was no opportunity to detect third peak.

of noncellulose and cellulose took place. On the basis of these E_a values, no significant differences could be found for G1, G2, and M. The fully retted flax, however, had an E_a value that could be compared with literature data for pure cellulose or retted flax (Table VI).

The obtained E_a values were comparable for air and nitrogen. This is because they were based on measurements above 300°C. Above this temperature, E_a for cellulose is equal in air and nitrogen.[1]

Elementary Fibers

Concerning the TGA data on elementary fibers (E), some unexpected results (especially for peak 2 in the DTG curves) were obtained (Tables I and II). First, however, those results that were expected are discussed.

Peak 1 in the DTG curves of E was comparable to that of the nontreated fibers, whereas the mass loss around peak 3 was comparable to that of flax type F. This last peak was barely detectable in nitrogen (as already explained). Furthermore, much like in tests with the nontreated flax types, the DTG curves did not become zero. This means that mass loss continued (because of slow reactions in nitrogen). Moreover, not only do reactions happen much faster in air, but the actual reactions also may differ (e.g., the formation of hydroperoxide in air and not in nitrogen).

As expected, the ash content continued decreasing in comparison with nontreated fibers.

The unexpected position of peak 2 and the accompanying mass loss could be explained by the conversion of cellulose I to cellulose II caused by the treatment with alkali. To what extent this conversion took place is not clear, as the literature[8] cites the use of sodium hydroxide, whereas in this study, sodium carbonate was used. Literature data on DSC tests on jute showed a drastic decline in thermal properties (a downward shift of the decomposition temperature, as observed in peak 2) due to treatment with sodium hydroxide. This was attributed to an increase in amorphous cellulose (with worse thermal stability) and a shortening of the crystallite length.

Furthermore, peak 2 had a slight shoulder. This shoulder was more prominent in the DTG curves of the nontreated fibers. This possibly is an indication of pectin removal (pectin is barely mentioned in the literature). The small remaining shoulder for E fibers (in which pectin should be nearly completely removed) can also be caused by the presence of hemicellulose, which degrades at lower temperatures than cellulose itself.[8]

In general, the treatment of cellulose can lead to a decrease in the onset temperature of degradation. This is due to a decrease in cellulose crystallinity. Moreover, during the pyrolysis of the treated (modified) cellulose, ring formation can take place, resulting in stable intermediary products.[3] Therefore, a portion of the E fibers was probably converted during the TGA measurements into more thermostable products. This would explain the presence of the extra peak (peak 4) in air. In nitrogen, however, reactions were so slow that no peak 2 or peak 3 could be detected (whereas the original TGA curves continued decreasing).

Therefore, the relatively low mass loss around peak 2 should be seen in connection with the appearance of an extra peak (peak 4) in the DTG curve in air. Moreover, when mass losses around peak 2 and peak 4 were summed, they slightly exceeded the mass loss in peak 2 of fully retted flax (F). This is another indication that peak 4 was the result of further degradation of intermediary products that originated from cellulose (mainly peak 2).

All the previous arguments lead to the conclusion that fibers of type E were almost entirely

made up of cellulose. Peak 2, which was already largely attributed to cellulose degradation, showed almost no shoulder, and peak 3 (attributed to noncellulose compounds) was smaller than the one observed with nontreated fibers.

Isothermal runs on E fibers (Table III) revealed that at lower temperatures (60 and 120°C), the thermal stability might still be called reasonable, whereas at higher temperatures, it seemed to be quite poor. At the highest tested temperature (230°C), some stabilization in mass set in after several hours. This might also be due to the formation of stable intermediary products that, after some time, started to degrade themselves.

The determination of the reaction constant at 230°C in air (Table IV) revealed that fibers of type E had even higher reaction constants then the unretted flax (G1 and G2). Apparently, degradation set in very fast and then stabilized because of the formation of intermediary products.

The determination of the E_a values (Table V) further confirmed all previous conclusions. Chemical treatments tend to lower E_a because of the degradation of the crystalline cellulose structure.

Boiled Flax

The TGA curves of the boiled flax fibers (B; see Tables I and II) show results similar to those of the fully retted flax fibers. Even though the degradation was already complete at 500°C (contrary to the nontreated fibers in nitrogen), it started at comparable temperatures. Therefore, one can say that the thermal stability of the B fibers was relatively good.

The composition of the B fibers was also quite comparable to that of the fully retted fibers. A lot of the pectin, however, was probably removed by boiling, which accounts for the slightly lower mass loss around peak 2 (compared with F).

The obtained E_a values (Table V), however, are somewhat strange. In nitrogen, E_a is comparable to that of fiber-type F. In air, however, E_a is clearly lower. Apparently, the B fibers were more sensitive to degradation in air than in nitrogen. This might be due to the boiling reaction.

However, when applied in composites, the reaction with air is very limited because only air available in the fiber bundles is available for degradation reactions, so the B fibers seem to be performing as well as the F fibers in terms of thermal stability.

CONCLUSIONS

The assessment of the retting degree of flax fibers is possible through the use of TGA. Both the original and differentiated curves (DTG) may be used for this purpose, as well as calculations of reaction constants and activation energies.

However, it is not possible to quantify the different components of flax with the aforementioned techniques because the degradation of flax is spread over a wide temperature range.

Nonetheless, the mass loss around peak 2 of the obtained TGA curves proved to be proportional to the amount of cellulose present in the flax. Literature data on the cellulose content in flax usually ranges from 54 to 63% cellulose in the green and fully retted flax (60–70% in dry flax), respectively. These figures correspond to the values found around peak 2, but it should be realized that cellulose degradation also continues after this peak; furthermore, peak 2 is also composed of hemicellulose and pectin (indicated by the observed shoulder peak). For fibers treated in alkali, an extra peak may also appear, which is also attributable to cellulose degradation.

In this specific case, both the fully retted and boiled fibers showed the best thermal stability. The boiled fibers, however, are most promising for use in composites because they provide better adhesion with a thermoplastic matrix.

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