Thermal Analysis of Different Cellulosic Fabrics

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SYNOPSIS

Thermal behavior of different cellolusic fabrics was investigated in air and nitrogen by TG, DTG and DTA. Kinetic parameters based on weight loss for the initial and major stages of thermal degradation were determined. The weight loss in the TG curve for the cellulosic fabrics can be divided into four stages. In general, E_a values in air are lower than those in nitrogen, and the enthalpy changes as well as rates of degradation in air are much larger than those in nitrogen. This indicates that the thermal degradation of cellulosic fabric is promoted by oxygen. The E_a values of regenerated cellulose fabrics (viscose and modal) at the rapid weight loss stage are relatively higher than those of the cotton and linen fabrics. The raw cotton has the lowest E_a of all cellulosic fabrics, but its frequency factor and rate of weight loss are also the lowest. The thermal behavior of linen is similar to that of the raw cotton. Bleached, boiled and antibacterially finished cotton fabrics are also compared. Thermal behavior and kinetic parameters for the different cellulosic fabrics are discussed in the light of their structural characteristics, including degree of polymerization, crystallinity, crystalline form, orientation and morphology. Also the effects of the impurities and additives on the fabric are considered. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

When cellulosic fibers are heated, a series of inter-related physical and chemical changes occur. The physical properties affected include enthalpy, weight, color, strength, crystallinity and orientation, while the chemical reactions involved can be grouped into three different pathways.[1] The first of these takes place below 300°C and results in a decomposition of the glycosyl units of cellulose by evolution of water, carbon dioxide and carbon monoxide, eventually forming a charred residue. Another reaction occurs between about 300 and 600°C and facilitates depolymerization of the molecule by cleavage of glycosyl units to form mainly 1,6-anhydro-β-D-glucopyranose (levoglucosan). This reaction is accompanied by some decomposition of the original polymer as well as the anhydro-sugar products. At still higher temperatures, direct fission of the substrate and the intermediate products takes place, forming lower molecular weight gaseous products,

including oxides of carbon, water, hydrocarbons, and hydrogen gas. However, all of these reactions overlap.

Pyrolysis of cellulosic fabric, at the molecular level, is a process of consecutive and competing reactions that are strongly influenced by the degree of polymerization, supermolecular structure of the fiber and its morphology, as well as by impurities and additives. Many authors have studied the global kinetics of thermal degradation based on weight losses of cellulosic samples; such weight changes can be conveniently followed by thermogravimetry (TG). Calahorra et al.[2] investigated cellulose fractions of different molecular weights by TG in nitrogen atmosphere and showed that thermal stability increases with the increase in molecular weight. They also found that the cellulose pyrolysis process cannot be described by a single value of activation energy over the whole pyrolysis range. Similar studies have been carried on other samples including powdered cellulose, Iraqi cotton fibers and grained extracted cellulose,[3] native and mercerized Egyptian cotton linters, viscose and bagasse pulp,[4] cotton, wood and flax,[5] cellulosic paper,[6] and cotton linters treated

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with fire retardants.[7] All of these studies invoked depolymerization reactions, differences in crystallinity and the presence of additives and impurities to explain the differences in the global kinetic parameters or the sample weight losses observed during pyrolysis.

In this article, we examine the thermal behavior of several different cellulosic fabrics, such as raw cotton (muslin and voile), regenerated cellulose (viscose and modal) and linen; also included are cotton fabrics that have been bleached, boiled or antibacterially treated. These samples are systematically investigated by thermogravimetry, differential thermogravimetric analysis (DTG) and differential thermal analysis (DTA) in air and nitrogen atmospheres, respectively. The thermal behavior of the various samples is compared, and the TG data is used to estimate the global kinetic parameters (Reich-Levi method[8]) for the initial stage and the subsequent major thermal degradation process of cellulose. The kinetic parameters are then related to the structural differences of the cellulosic fibers.

EXPERIMENTAL

Samples

Nine cellulosic fabrics were used in this study: (a) six different cotton fabrics including bleached and raw voile, bleached and raw muslin, boiled muslin as well as the antibacterial cotton fabric (China Textile University, Shanghai, PRC), (b) two regenerated cellulose fabrics including viscose and modal (high wet modulus fiber) and (c) linen fabric (School of Fibre Science and Technology, University of New South Wales, Sydney, Australia). Unless otherwise stated all fabrics were obtained from the Department of Industrial and Engineering Chemistry, ETH, Zürich, Switzerland.

Thermal Analyses

Thermogravimetry

TG analysis was conducted using a SETARAM TG · DTA 92 instrument. The fabric sample was cut into a fine powder to eliminate the effects of fabric thickness and yarn denier, and 8 ± 0.1 mg of sample was used. The TG curves were obtained in the temperature range of 35 to 700°C at a heating rate of 10°C/min under air and nitrogen atmospheres, respectively. A blank run was carried out to correct for the temperature-dependent buoyancy effect.

Derivative Thermogravimetric Analysis

DTG provides a derivative form of the thermogravimetric signal and was calculated by the PC92 computer. DTG plots were obtained by choosing an adaptable level of filtering to keep good resolution and reduce the noise.

Differential Thermal Analysis

DTA can be simultaneously measured with TG on a SETARAM TG · DTA 92 instrument, and calcined alumina was used as the reference.

RESULTS AND DISCUSSION

Changes of Thermal Behavior during Heating

When various cellulosic fabrics are submitted to TG and DTA analysis, the resulting thermoanalytical curves for the respective techniques are similar in shape. In general, the differences in thermal behavior of the various fabrics are reflected in 1) the temperatures corresponding to the onset of weight loss (later referred to as the "initial temperature"), 2) the rate of weight loss, 3) the magnitude of the enthalpy change and 4) the values of the peak temperature of the DTA curves.

We use the results of the boiled muslin sample (Fig. 1), subjected to thermal analysis in air, to elucidate the typical changes of thermal behavior of a cellulosic fabric. It can be seen from the TG curve in Figure 1 that the overall weight loss can be divided into four different stages: 1) the first weight loss that occurs below ca. 110°C; this is generally attrib-
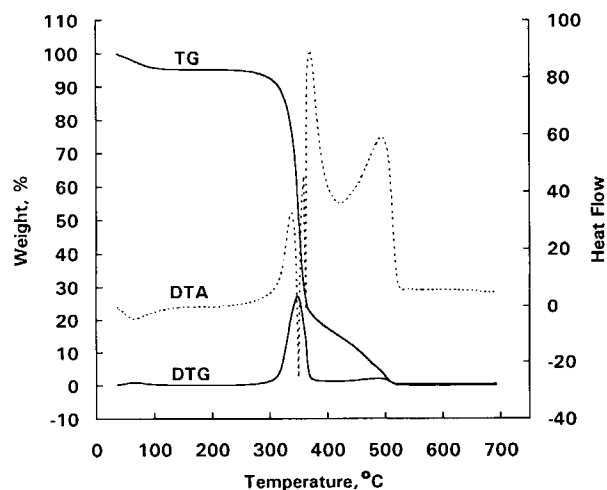

Figure 1   Thermal analysis of boiled muslin cotton fabric in air (DTG (%/min) has the same scale as TG).

uted to the evaporation of sorbed water from the fibers; 2) the second weight loss, which commences at about 270°C, and is reflected in a slow weight decrease represented by a shoulder; this is the initial stage of thermal degradation; 3) a rapid weight loss, reflecting major thermal degradation; and 4) a prolonged char oxidation stage.

The corresponding DTG curve contains the same information as TG, but it is much easier to interpret. Thus the onset of weight loss, maximum weight loss rate and the corresponding temperature are evident in the main features of the DTG trace (Fig. 1).

Information about enthalpy changes can be obtained from DTA measurements simultaneously with TG. For the boiled muslin sample, there is a small endothermic peak in the DTA curve (Fig. 1), which is consistent with the first weight loss stage; the peak temperature is about 65°C and the curve tapers off from approximately 120°C. It is suggested that the free noncrystalline water is essentially completely removed before 120°C. Between 120 and 265°C no obvious enthalpy changes are present, which indicates that no phase changes such as melting or recrystallization occur before the degradation of cellulosic fibers. The exothermic peak that appears after ca. 265°C is consistent with the initial weight loss of thermal degradation; it is followed by a sharp endothermic peak, with a peak temperature of ca. 350°C, which is coincident with the peak temperature of the DTG curve. A second sharp endothermic peak is observed at ca. 370°C. Most of the cellulosic fabrics in this study also show two endothermic peaks that correspond to the rapid weight loss stage. In general, such endothermic peaks are attributed to the formation and evolution of volatile pyrolysis products, and exothermic peaks are ascribed to the oxidation of the products.[9] Another exotherm begins at ca. 365°C, a temperature that is almost the same as that of the onset of the fourth weight loss stage. Usually two exothermic peaks (peak temperatures 370 and 495°C) are found in this last stage. They are evidently caused by the oxidation of the charred residue. The first sharp exotherm is associated with the oxidation of the aliphatic groups of the charred residue, and the second with the oxidation of the aromatic components in the residue.[10] The larger exotherm ends at 520°C; thereafter, no further heat effects are evident, and the mass of the sample approaches a constant weight.

Figure 2 shows the thermal behavior of the boiled muslin sample that was analyzed in a nitrogen atmosphere. Some TG differences between these results and those obtained from the analysis in air are
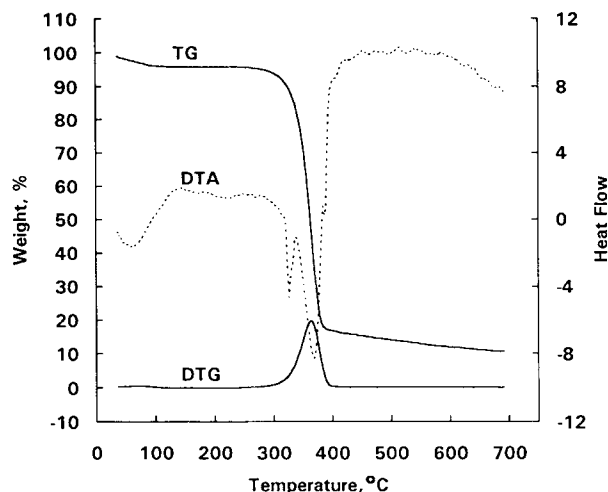
Figure 2   Thermal analysis of boiled muslin cotton fabric in nitrogen (DTG (%/min) has the same scale as TG).

as follows: 1) the initial temperature of degradation of the boiled muslin fabric analyzed in nitrogen atmosphere is higher than that in air (the former is ca. 275°C and the later is ca. 265°C); 2) the rate of degradation in the nitrogen experiment is lower than that in air; 3) the maximum rate of weight loss occurs at 365°C as compared with 350°C in air; and 4) the oxidation rate of the charred residue is relatively fast in air and very slow in nitrogen so that in this case the corresponding DTG curve levels off. There is much less residue after the fourth weight loss stage in air than in nitrogen. Up to 700°C only about 0.5% mass remains in air, but about 10% mass still remains in nitrogen. The end product in the inert atmosphere is carbon, but in air only inorganic impurities remain.[11]

There is a large difference between the heat effects measured in air and in nitrogen, as indicated by the DTA curves in Figures 1 and 2, respectively. The overall enthalpy change of the cellulosic fabric when it is heated in nitrogen is much less than that in air (note that the heat flow scale in Fig. 1 is nearly six times that in Fig. 2). Also it can be seen that the temperature of the endothermic peak related to the major weight loss stage in nitrogen is higher than that in air. The two large exothermic peaks, corresponding to the fourth weight loss stage, are present in the DTA curve from the experiment in air, but are absent from similar results in nitrogen. This is consistent with the TG results discussed above. The small exotherm in nitrogen is matched by a small weight loss at this stage. In the absence of oxygen, the oxidizing reaction for charred residue, especially for the relatively stable aromatic component in

Table I   Comparison of Structure Characteristics of Cellulosic Fibers[12]

Sample	Cotton	Linen	Viscose
Degree of polymerization	10,000–15,000	~36,000	300–500
Crystallinity (%)	65–70	~35	35–40
Birefringence (Δn)	0.047	0.062–0.068	0.024–0.030
Moisture regain (%)	7–8	7.0	12–14

charred residue is very slow,[1] and therefore, no re-solved exotherms appear in the DTA curve.

In the above discussion, it has been assumed that the thermal degradation of cellulose is similar to that of synthetic polymers and may therefore involve a free radical mechanism consisting of initiation, depropagation and termination.[7] Oxygen can accelerate thermal degradation by increasing the formation of free radicals and subsequent interactions with these initiators. Shafizadeh and Bradbury's results[9] show that a relatively larger number of gly-cosidic bonds are broken under oxidative conditions than under nitrogen. Therefore the lower initial temperature and the smaller heat effect in the pyrolysis process of cellulosic fabrics, as well as the lower weight loss rates observed under nitrogen atmosphere with our wide range of samples, are consistent with previous findings.

Comparison of Cotton, Viscose, and Linen

Cellulosic fibers such as cotton, viscose and linen contain the same basic cellobiose unit, but there are some differences in the degree of polymerization,

supermolecular structure and morphology as shown in Table I. Hence, the physical properties of these fabrics, such as tenacity, elongation, modulus, moisture regain and thermal behavior are also different.

Boiled muslin fabric was selected to represent the cotton fabrics because it was relatively cleaner than the raw muslin sample and had not been subjected to chemical treatments such as bleaching.

The TG and DTG curves of cotton, viscose and linen in air and nitrogen are shown in Figures 3 and 4, respectively. It can be seen from Figure 3 that during the first stage of thermal degradation, the weight loss of viscose fiber is somewhat larger than that of cotton and linen; this can be ascribed to the relatively high moisture regain of the viscose in comparison with the other two types of fibers. At the second weight loss stage, namely the initial stage of thermal degradation, the initial temperature of weight loss of linen is the lowest. Basch et al.[13] suggested that the weight loss of this stage is caused by pyrolysis in the amorphous region; consequently, the thermal behavior of the linen sample is consistent with the low crystallinity of its fiber. In addition,
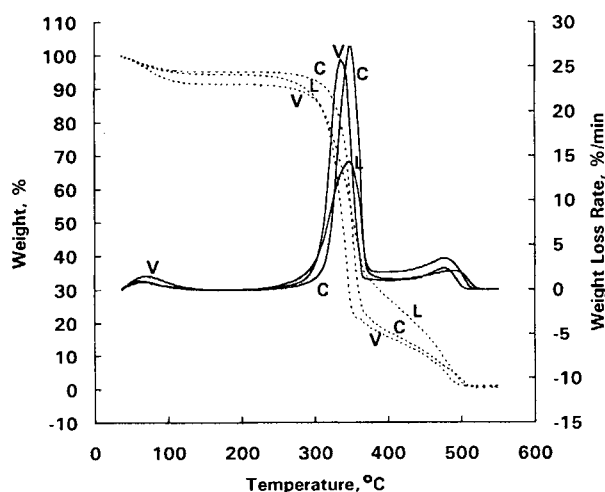

Figure 3   TG and DTG curves of cotton, viscose and linen in air. C, cotton; V, viscose; L, linen; ———, DTG; -----, TG.
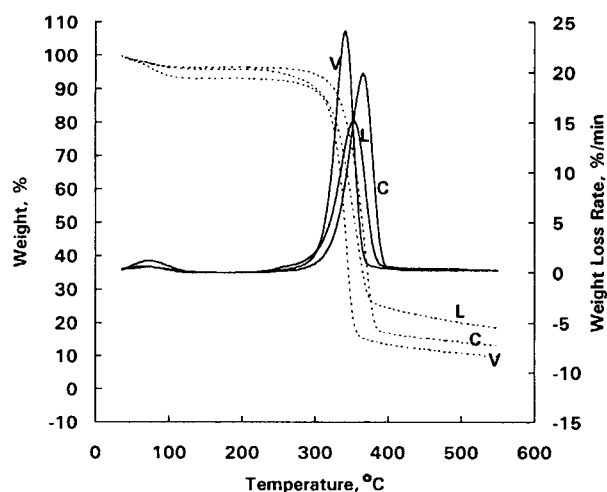

Figure 4   TG and DTG curves of cotton, viscose and linen in nitrogen. C, cotton; V, viscose; L, linen; ———, DTG; -----, TG.
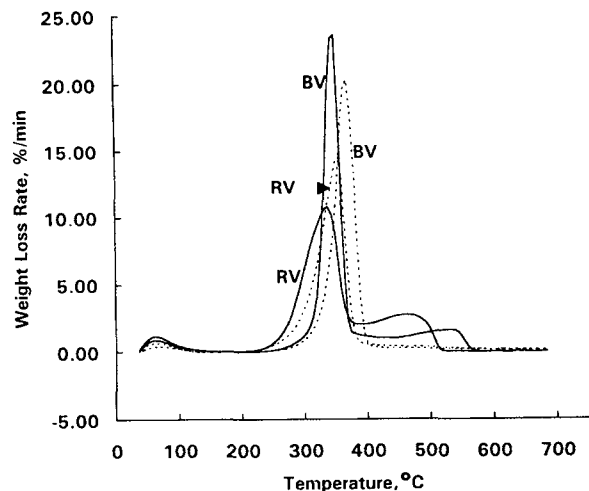
Figure 5 Comparison of DTG curves between in air and in nitrogen for raw and bleached voile. RV, raw voile; BV, bleached voile; ——, in air; ----, in nitrogen.

linen contains a comparatively large amount of impurities[14] that may initiate more active sites and accelerate the beginning of thermal degradation. Viscose also has low crystallinity, but because it has less impurities, its initial temperature of thermal degradation is higher than that of linen. Thus, it is apparent that the presence of impurities in cellulosic fibers can significantly affect the onset of thermal degradation. At the third and major weight loss stage, linen has the lowest rate of weight loss, and its maximum rate of weight loss is much lower than those of cotton and viscose, as shown in the comparison of the DTG and TG curves (Fig. 3). This may be related to the structural characteristics of linen. Although its crystallinity is low, both the degree of polymerization and orientation of macromolecules in this fiber are expected to have the highest values for the three types of fibers examined, (Table I); consequently, the intermolecular forces between the cellulose polymer chains in linen are relatively high, leading to a decrease in the rate of the degradation process. In addition, a linen fiber is rather firm with thick cell walls and this would also reduce the reaction rate. At the fourth weight loss stage, i.e., the char oxidation, the rate of weight loss for linen is relatively higher than that of cotton and viscose.

In a nitrogen atmosphere, the thermal behavior (Fig. 4) of the three types of fiber is basically similar to that in air, particularly in the first and second stages. At the rapid weight loss stage, the rate of weight loss for linen is still the lowest, and the viscose has a higher rate of weight loss than cotton. This could be attributed to the low degree of poly-

merization and orientation as well as a lower crystallinity of the viscose polymer. However, in air the rates of reaction for viscose and cotton are similar, because oxygen accelerates the reaction.

Comparison of Bleached and Raw Cotton Fabrics

Bleaching of a fabric is a major process in the textile industry and is used to eliminate the admixtures and coloring substances contained in fibers. After bleaching, the degree of polymerization of the macromolecule decreases, and the thermal behavior also changes. When oxidizing agents such as ClO_2^- and H_2O_2 are used for bleaching, content of the oxidized groups ($C=O$ and $COOH$) in a fabric increases.

The thermal analyses of raw and bleached fabrics carried out in air and in nitrogen are compared in Figures 5-7. The first weight loss stage is present for both raw and bleached fabrics, but there are distinct differences at the pyrolysis stage. As mentioned in the Introduction, Calahorra et al.[2] showed that lower initial temperatures of thermal degradation correlate with lower molecular weights. However, our experimental results indicate that although the raw fabric has a high molecular weight, its initial temperature of degradation is lower than that of the bleached one. This may be attributed to the presence of more impurities in the raw fabric. On the other hand, the rate of weight loss at the major degradation stage of the bleached fabric is much higher than that of the raw one (Fig. 5), and for the bleached fabric there are two sharp endothermic peaks in the DTA curves that correspond to the weight loss at this stage (Figs. 6 and 7). The results in Figs. 5-7
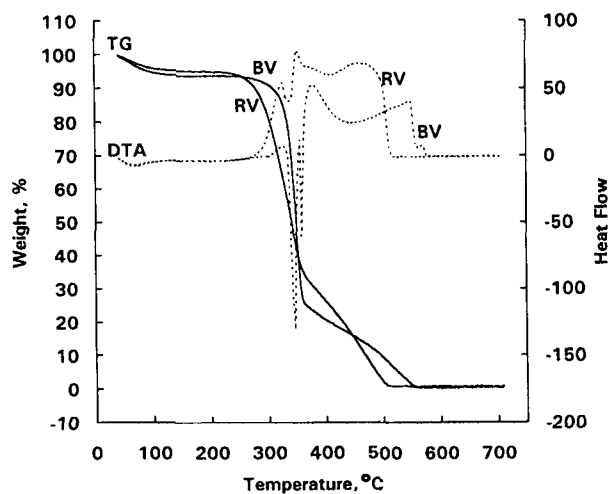

Figure 6 DTA curves corresponding to weight losses of raw and bleached voile heated in air. RV, raw voile; BV, bleached voile.
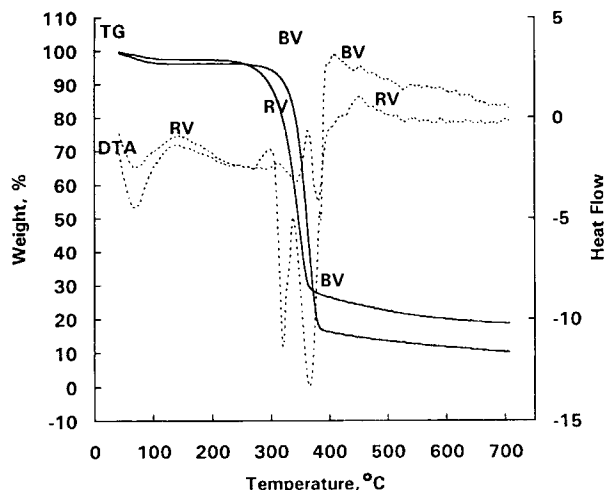
Figure 7 DTA curves corresponding to weight losses of raw and bleached voile heated in nitrogen. RV, raw voile; BV, bleached voile.

indicate that the pyrolysis reactions proceed rapidly through trans-glycosylation, formation and evaporation of the volatile pyrolysis products, mainly because the bleached fabric has a lower degree of polymerization and also because some carbonyl and carboxyl groups are introduced into the macromolecules by the bleaching process. After the rapid weight loss stage, pyrolysis products are almost completely oxidized in air, but the weight declines slowly in nitrogen, similar to the behavior of the other cellulosic fabrics.

A comparison of the DTG curves of the raw and bleached fabrics in air and nitrogen, (Fig. 5) shows that at the rapid weight loss stage of the raw fabric, the rate of weight loss in nitrogen is somewhat larger than that in air. This is unexpected because the reverse is the more common case. It is possible that oxygen accelerates the degradation reaction through the formation of peroxides. On the other hand, an activated center formed on a chain fragment can undergo accelerated termination by reacting with a peroxy radical to form a crosslink[7]; hence depropagation and termination of the reaction related to the formation of the active centers and crosslinking are competitive. For the raw fabric with its higher degree of polymerization, the effect of oxygen appears to favor the termination process and for the bleached fabric with its lower degree of polymerization, the effect of oxygen seems to promote the depropagation process; consequently the rate of weight loss in air is higher than that in nitrogen. At the fourth weight loss stage, for both the raw and bleached fabrics, the rate of weight loss in air is markedly higher than that in nitrogen. This indi-

cates that in this stage, oxygen plays a dominant role and the reaction is mainly one of oxidation of pyrolysis products. The results of raw muslin and bleached muslin show behavior that is very similar to the raw and bleached voile; hence their thermoanalytical curves are omitted.

Kinetics of Thermal Degradation

Thermogravimetry is widely used as a method for the determination of kinetic parameters such as activation energy, frequency factors and reaction order, to elucidate the thermal degradation mechanisms and the thermal stability of materials. Various methods for estimating kinetic parameters from thermogravimetric measurements are available.[15,16] They are classified into two groups: the integral methods and the differential ones. A summary of the general approach to these methods is provided here.

The isothermal rate of conversion, dC/dt, for a thermal degradation process is generally given by

$$dC/dt = kf(C) \tag{1}$$

$f(C)$ is expressed analogously to the simple case of homogeneous kinetics as

$$f(C) = (1 - C)^n \tag{2}$$

where n is the apparent order of reaction.

On the other hand, the reaction rate constant k is expressed by the Arrhenius equation

$$k = A \exp(-E_a/RT) \tag{3}$$

where E_a is the activation energy, A is the frequency factor and R is the gas constant. Substitution of expressions (2) and (3) into eq. (1) gives

$$\frac{dC}{dt} = A \exp\left(\frac{-E_a}{RT}\right)(1 - C)^n \tag{4}$$

In a TG measurement the heating rate, $\beta = dT/dt$, is generally kept constant; thus

$$\frac{dC}{(1 - C)^n} = \frac{A}{\beta} \exp\left(\frac{-E_a}{RT}\right) dT \tag{5}$$

Given the initial condition: $C = 0$ at $T = T_0$, the integral form of eq. (5) is

Table II Values of Activation Energy (E_a) and Frequency Factor (A) for Thermal Degradation of Cellulosic Fabrics in Air

| Sample | Initial Stage | | | Major Stage | | | |
	Temperature Range (°C)	E_a (kJ/mol)	r^2 *	Temperature Range (°C)	E_a (kJ/mol)	A (s^{-1})	r^2 *
RV	257–285	52.1	0.985	285–338	90.1	9.89×10^5	0.999
BV	285–318	39.3	0.970	318–344	147	3.28×10^{10}	0.964
RM	257–285	49.1	0.986	285–345	79.5	1.13×10^5	0.999
BM	285–318	39.0	0.972	318–345	158	3.08×10^{11}	0.981
OM	279–312	38.4	0.972	314–341	118	8.79×10^7	0.961
AB	280–312	69.8	0.980	312–340	182	5.81×10^{13}	0.969
V2	274–312	32.2	0.959	312–335	203	6.18×10^{15}	0.985
V1	274–312	31.4	0.939	312–335	211	3.67×10^{16}	0.967
L	275–312	47.8	0.987	312–343	115	9.03×10^7	0.997

* r^2, regression coefficient.[17]

$$\int_0^c \frac{dC}{(1 - C)^n} = \frac{A}{\beta} \int_0^T \exp\left(\frac{-E_a}{RT}\right) dT \qquad (6)$$

The integral methods are based on this equation, and the differential ones on eq. (6). In this study, the Reich–Levi integral method[8] is applied.

The weight loss of cellulose due to its thermal degradation has been shown empirically to obey the first-order reaction.[1,4,7] According to Reich and Levi,[8] the relationship between conversion and temperature when $n = 1$, can be represented by equation (7).

$$\ln \ln(1 - C) \cong -\frac{E}{RT} + \ln\left(\frac{A\Delta T}{\beta}\right) \qquad (7)$$

where ΔT is the temperature interval used for the estimation of C. Thus a plot of $\ln \ln(1 - C)$ against the reciprocal of temperature should give a straight line, from which the value of activation energy E_a and the frequency factor A can be determined. These parameters were calculated by a linear regression analysis using Microsoft Excel software. The initial and rapid weight loss parts of the thermal degradation process were investigated. In this case the ln ln$(1 - C)$ vs $1/T$ plot should yield two straight-line sections, one with a small slope in the low-temperature region, and the other with a large slope in the high-temperature region. Summaries of the E_a and A estimates for thermal degradation in air (Table II) and in nitrogen (Table III) are presented for all cellulosic fabric samples used in this work. When the activation energies of initial and major stages of thermal degradation processes are compared (Tables II and III), it is found that those for the air case are lower than those for nitrogen. This indicates

Table III Values of Activation Energy (E_a) and Frequency Factor (A) for Thermal Degradation of Cellulosic Fabrics in Nitrogen

| Sample | Initial Stage | | | Major Stage | | | |
	Temperature Range (°C)	E_a (kJ/mol)	r^2	Temperature Range (°C)	E_a (kJ/mol)	A (s^{-1})	r^2
RV	279–306	77.9	0.997	306–348	120	2.89×10^8	0.996
BV	295–328	67.0	0.982	328–364	178	9.13×10^{12}	0.991
RM	279–314	78.1	0.998	314–354	113	6.00×10^7	0.995
BM	295–328	70.1	0.984	328–364	185	3.14×10^{13}	0.991
OM	294–328	62.2	0.978	328–363	169	1.65×10^{12}	0.995
AB	290–330	89.5	0.996	330–358	181	1.85×10^{13}	0.992
V2	279–314	36.6	0.961	314–342	183	8.41×10^{13}	0.985
V1	279–314	32.7	0.949	314–342	196	9.90×10^{14}	0.987
L	284–322	58.7	0.985	322–353	132	2.06×10^9	0.996

that thermal degradation of cellulosic fibers is promoted by oxygen, which is consistent with the reported values of the activation energy for chain scission of the cellulose polymer in air (88 kJ mol^{-1}) and in nitrogen (113 kJ mol^{-1}).[1] The initial temperatures of thermal degradation in air are generally lower than those in nitrogen, as well. This also illustrates the fact that oxygen accelerates this reaction from the beginning, presumably by forming peroxides as discussed previously.

A comparison of E_a values for bleached voile and muslin fabrics with those of the raw ones, for the initial stage of thermal degradation (Fig. 8), shows that the E_a values of the bleached fabrics are lower than those of the raw ones. This is probably due to the lower degree of polymerization of the bleached samples. On the other hand, for the rapid weight loss stage, E_a values of the raw fabrics are much lower than those of the bleached ones (Fig. 9), and the corresponding initial temperatures follow the same trend. This could be accounted for by the presence of more impurities in the raw fabrics. However, as soon as the activation energy barrier is overcome, the rates of weight loss (Fig. 5), and the maximum weight loss rate of the bleached fabrics as shown by the DTG peak heights (Table IV), are higher than those of raw fabrics. Support for these results is also found in the values of the frequency factors A. According to the classical interpretation of the Arrhenius equation, the value of A is related to the number of collisions between the reacting molecules. Thus we would expect A for the bleached fabrics to be larger than that for the raw ones. This trend is
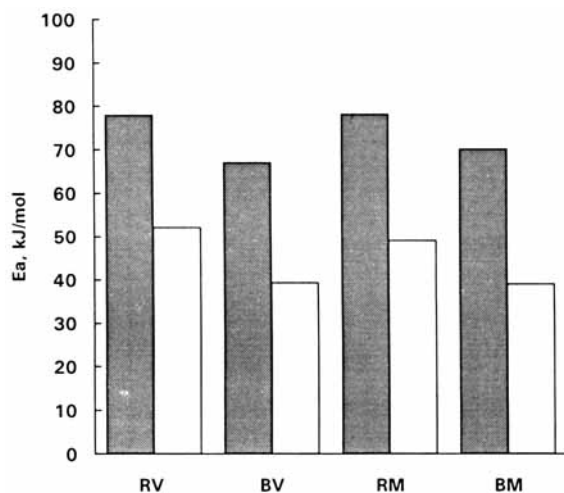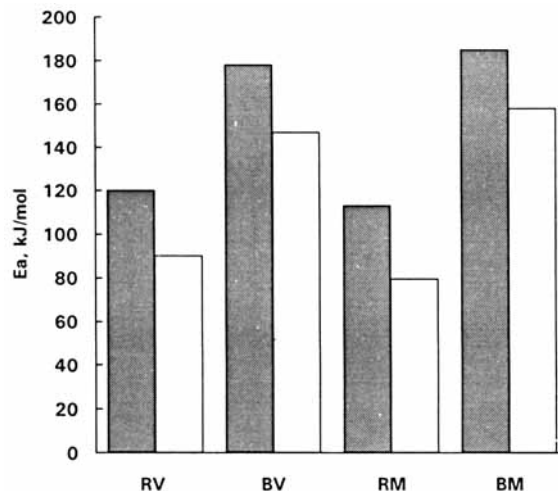

Figure 9 Comparison of activation energy between raw and bleached fabrics at the major stage. RV, raw voile; BV, bleached voile; RM, raw muslin; BM, bleached muslin; ▨, in nitrogen; ☐, in air.

observed in Tables II and III for samples BV and RV, as well as for BM and RM.

A comparison of viscose and modal with linen and all cotton fabrics used in this study shows (Table II) that at the initial stage of thermal degradation, the E_a values for regenerated cellulose fabrics are lower than those for cotton and linen both in air and nitrogen. This is consistent with the low crystallinity and low degree of polymerization for regenerated fabrics (Table I), and as a consequence of this, only comparatively weak bonding is present in the amorphous regions of the regenerated cellulose fibers. A different situation arises for the rapid weight loss stage. The E_a of the regenerated cellulosic fabrics are higher than those of cotton and linen. This is presumably due to higher stability of the lattice structure of cellulose II.[18] Cotton and linen fibers are known to have a cellulose I crystalline structure, but in the regenerated cellulose fibers, this changes to cellulose II. In cellulose I all of the CH_2OH side chains have the tg conformation. Each residue forms two intramolecular (O_3—H···O'_5 and O'_2—H···O_6) and one intermolecular (O_6—H···O_3) hydrogen bonds to the neighboring chain along the a axis; in cellulose II the CH_2OH groups have the gt conformation such that the intramolecular hydrogen bond between O'_2—H and O_6 cannot form. These two hydroxyl groups form intermolecular hydrogen bonds, and the additional intermolecular hydrogen bond contributes to a somewhat tighter packing of the chains in cellulose II, leading to a lattice structure of higher stability.[19] On the other hand, the presence of more impurities

Figure 8 Comparison of activation energy between raw and bleached fabrics at the initial stage. RV, raw voile; BV, bleached voile; RM, raw muslin; BM, bleached muslin; ▨, in nitrogen; ☐, in air.

Table IV   Temperature and Height of DTG Curve Peaks for Cellulosic Fabrics at the Major Weight Loss Stage

Sample	DTG Peak (in air)		DTG Peak (in nitrogen)	
	Temperature (°C)	Height (%/min)	Temperature (°C)	Height (%/min)
RV	336	10.8	346	14.6
BV	347	24.3	362	20.4
RM	342	11.1	351	14.0
BM	348	24.6	362	20.6
OM	348	27.5	365	19.9
AB	338	25.4	361	21.9
V2	333	25.9	342	24.2
V1	332	27.2	342	25.1
L	343	14.4	354	15.2

in cotton (especially in raw cotton) and linen as compared with the regenerated fabrics also could contribute to the smaller E_a values of this stage.

Modal is a high wet modulus regenerated cellulose fiber and has higher crystallinity than viscose[20]; hence the E_a of its rapid weight loss stage is somewhat higher than that of viscose. Although the E_a values of regenerated cellulose fibers are higher, as soon as the respective activation energy barriers are overcome, the rates of degradation increase relative to those of the natural cellulose fibers (Table IV). This is consistent with the higher values of the frequency factors A, as shown in Tables II and III. These results are similar to those observed for the bleached fabrics, as described above. However, for the raw fabrics, because their macromolecules have a high degree of polymerization and correspondingly low frequency factors, their rates of weight loss are much smaller than those of the other cellulosic fabrics. The E_a value of raw cotton fabric is the lowest, followed by that of linen (Table II).

The antibacterial fabric sample used in this study had a finish based on the medical bleached cotton gauze. Its E_a value of the initial degradation stage is rather higher than those of the other cellulosic fabrics, presumably because of the chemical treatment. The E_a and A values of the rapid degradation stage are close to those of the bleached fabric, particularly to the bleached muslin under nitrogen atmosphere (Table III).

CONCLUSION

The thermal behavior of cellulosic fabrics measured in air is evidently different from that in nitrogen.

In general, the initial temperature of thermal degradation and the activation energies of degradation (both for the initial stage and for the rapid weight loss stage) in air are lower than those in nitrogen. The rates of the degradation, in most cases, have a similar trend. Corresponding enthalpy changes observed in air are much larger than those in nitrogen, and the residue mass after the TG measurement in air is less than that in nitrogen. All of these indicate that the thermal degradation of cellulosic fabrics is promoted by oxygen.

A comparison of natural and regenerated cellulosic fabrics shows that at the rapid weight loss stage, regenerated fabrics (viscose and modal) have relatively higher E_a values because they have a comparatively stable lattice structure. However, their degradation rates are higher than those of natural fabrics (cotton and linen) because of their low degree of polymerization, which is supported by the higher A values of regenerated cellulose fabrics. The linen fabric has high degree of polymerization and orientation, and therefore has the lowest rate of thermal degradation in comparison with the regenerated cellulose and the cotton fabrics. The linen and raw cotton fabrics contain a large amount of impurities, and their initial temperatures are lower than those of the other cellulosic fabrics used in this study. It is apparent that impurities in a fabric significantly affect the beginning of the thermal degradation. The thermal behavior of raw cotton fabrics is similar to that of linen because the two textile fibers have structural similarities.

The bleached fabrics have higher E_a values relative to raw fabrics at the major thermal degradation stage, but once the E_a barriers are overcome, the

weight loss rates of bleached fabrics are higher than those of raw fabrics.

REFERENCES

1. F. Shafizadeh, in *Cellulose Chemistry and Its Application,* T. P. Nevell and S. H. Zeronian, Eds., Thomas Percy, Horwood, Chichester, UK, 1985, p. 267.
2. M. E. Calahorra, M. Cortazar, J. I. Eguiazabal, and G. M. Guzman, *J. Appl. Polym. Sci.,* **37,** 3305 (1989).
3. A. A. Hanna, A. Abd-El-Wahid, and M. H. Abbass, *Cellulose Chem. Technol.,* **18,** 11 (1984).
4. M. Z. Sefain and F. El-Kalyoubi, *Thermochim. Acta,* **75,** 107 (1984).
5. A. M. Shishko, L. G. Pesnyakevich, I. N. Abranpal'skii, S. M. Volkovich, and N. M. Selitskaya, *Vesti Akad. Navuk BSSR, Ser. Khim. Navuk,* **1,** 30 (1989).
6. K. Takashi and N. Hidesaburo, *Chem. Phys. Processes Combust.,* 91-1/91-4, (1991).
7. T. Hirata and K. E. Werner, *J. Appl. Polym. Sci.,* **33,** 1533 (1987).
8. L. Reich and D. W. Levi, *Makromol. Chem.,* **66,** 106 (1963).
9. F. Shafizadeh and A. G. W. Bradbury, *J. Appl. Polym. Sci.,* **23,** 1431 (1979).
10. Y. Sekiguchi and F. Shafizadeh, *J. Appl. Polym. Sci.,* **29,** 1267 (1984).
11. D. Dollimore and B. Holt, *J. Polym. Sci., Polymer Phys. Ed.,* **11,** 1703 (1973).
12. H. R. Wu and L. F. Wu, *Structure and Properties of Textile Fibres,* Ministry of Textile Industry Press, Beijing, P. R. China, 1985, p. 182.
13. A. Basch and M. Lewin, *J. Polym. Sci., Polymer Chem. Ed.,* **12,** 2053 (1974).
14. F. P. G. Gohl and L. D. Vilensky, *Textile Science,* 2nd ed., Longman Cheshire, Melbourne, Australia, 1983, p. 55.
15. L. Reich and D. W. Levi, *Macromol. Rev.,* **1,** 173 (1967).
16. H. Nishizaki, K. Yoshida, and J. H. Wang, *J. Appl. Polym. Sci.,* **25,** 2869 (1980).
17. Function Reference, Microsoft Excel, Version 4.0, Microsoft Corporation, USA, 225 (1992).
18. T. Yurugi, H. Iwata, and M. Okuma, *Nippon Kagaku Kaishi,* 733 (1975).
19. J. C. Artnur, in *Cellulose Chemistry Technology,* ACS Symposium Series, American Chemical Society, Washington, DC, 1977, Chapt. 14, p. 207.
20. J. E. McIntyre, *The Chemistry of Fibres,* Edward Arnold Publications, London, 1971, p. 27.