Thermal Degradation of Cellulose and Cellulose Esters

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ABSTRACT: Cellulose, cellulose diacetate (CDA), cellulose triacetate (CTA), cellulose nitrate (CN), and cellulose phosphate (CP) were subjected to dynamic thermogravimetry in nitrogen and air. The thermostability of the cellulose and its esters was estimated, taking into account the values of initial thermal degradation temperature T_d, the temperature at the maximum degradation rate T_{dm}, and char yield at 400°C. The results show that these polymers may be arranged in the following order of increasing thermostability: CN < CP < regenerated cellulose < filter cotton < CDA < CTA. The activation energy (E), order (n), and frequency factor (Z) of their degradation reactions were obtained following the Friedman, Chang, Coats–Redfern, Freeman–Carroll, and Kissinger methods. The dependence of T_d, T_{dm}, E, n, Ln Z, and char yield at 400°C on molecular weight and test atmosphere is also discussed. © 1998 John Wiley & Sons, Inc. J Appl Polym Sci 68: 293–304, 1998

Key words: cellulose; cellulose ester; dynamic thermogravimetry; thermostability; thermal degradation; decomposition kinetics

INTRODUCTION

Cellulose is one of the most important classes of natural polymers. There is considerable industrial and academic interest in cellulose and cellulose derivatives.[1–4] Cellulose-based paper is widely used as electrical insulation in large electrical power transformers and cables. Cellulose esters are extensively used as separation membrane materials.[5,6] Their thermal oxidative degradation may determine the ultimate life of the insulation system or membrane module at an elevated temperature.[6] Because of the practical importance of the phenomena of flame and heat resistance, thermogravimetry (TG) of cellulose and cellulose derivatives should be made. The

TG of pulp and regenerated cellulose or viscose rayon have been studied.[7–19] Despite the importance of the TG investigation of cellulose derivatives, there have been few reports on the subject. The objective of this work was to gather information on the thermostability and thermal decomposition kinetics of cellulose and four cellulose esters by using a dynamic TG analysis through investigating the TG, derivative thermogravimetry (DTG), the second derivative thermogravimetry (2DTG) thermograms, and calculating various thermal parameters, taking also into account the influence of the molecular weight and test atmosphere.

EXPERIMENTAL

Regenerated cellulose fiber or viscose rayon having the degree of polymerization (DP) of 350–
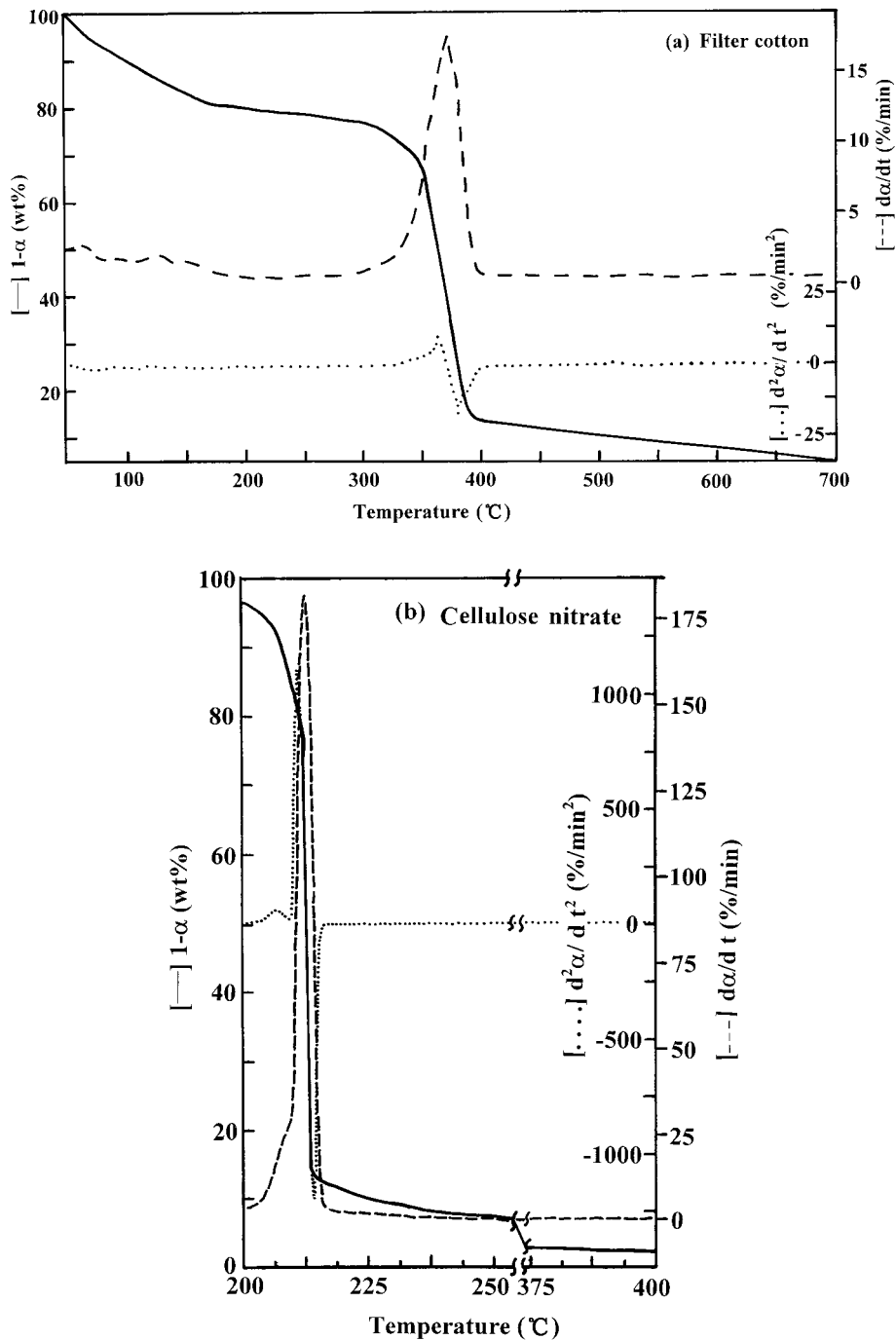

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Figure 1 Residual weight TG (—), derivative weight loss DTG (– – –), and second derivative weight loss (2DTG) (· · · · ·) plotted as a function of temperature for (a) filter cotton, (b) cellulose nitrate, (c) cellulose diacetate, and (d) cellulose triacetate at 10°C/min in nitrogen.

400 was provided by Tianjin Man-Made Fiber Factory of China. Filter cotton pulp having the DP of approximately 800 was supplied by Gaomi

Chemical Fiber Factory of Shandong Province of China. Cellulose diacetate (CDA) with high and low molecular weights were purchased from
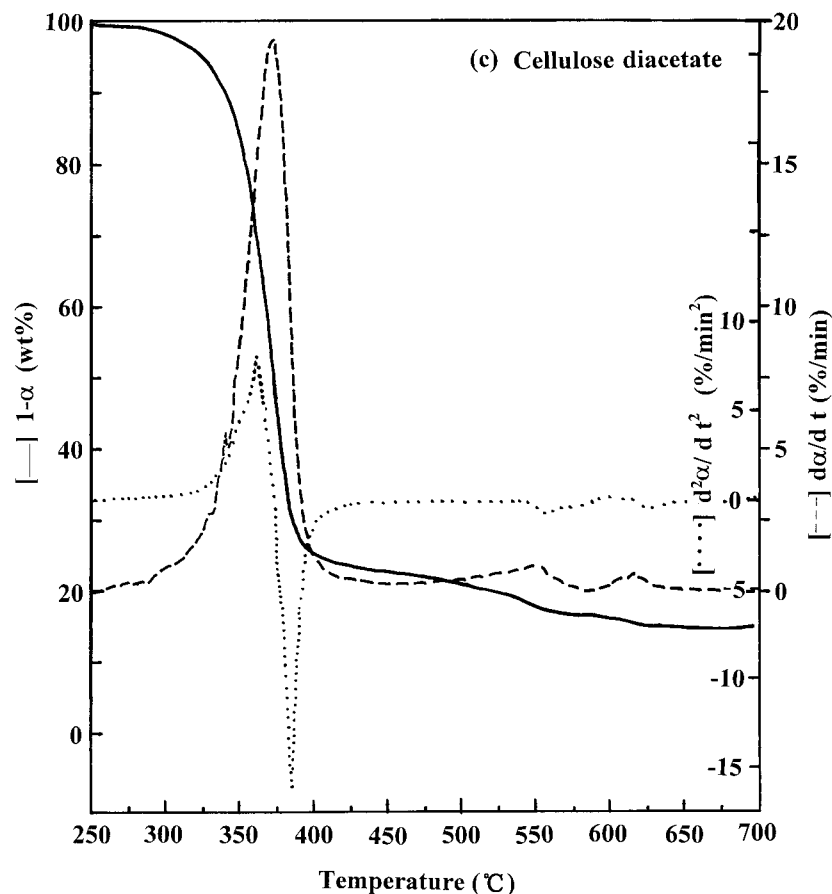
Figure 1 (*Continued from the previous page*)

Shanghai Cellulose Factory and Wuxi Film Factory of China, respectively. The intrinsic viscosity of the low-molecular-weight CDA in chloroform is 0.28 dL/g. The cellulose triacetate (CTA) having the degree of substitution and $\bar{M}_n$ of 2.7 and 315, respectively, was obtained from Daicel Chemical Company of Japan. Cellulose nitrate (CN), whose falling sphere viscosity is 25 s and whose nitrogen content is 12%, was made in the Seventh Dyeing Chemicals Factory of Shanghai.

The TG measurements were carried out with a Hi-Res TGA 2950 thermogravimetric analyzer (Du Pont model 2000) made by TA Instruments. The TG assembly TGA 2950 consisted of the thermobalance itself (balance, furnace, gas circuit, and power), a controller, Thermal Analyst 2000, and an IBM PS/2 53 486 SLC 2 computer. The thermal decomposition was carried out in an inert atmosphere of ultrahigh pure nitrogen or an air at a flow rate of 30 mL/min with sample weight of 0.9–1.1 mg, raised at 10°C/min from room temperature to 800°C.

The differential methods are to determine the kinetic parameters (activation energy E, order n, and frequency factor Z) of thermal degradation by using the relationship between the weight-loss rate $d\alpha/dt$ and absolute temperature T. There have been several differential techniques, which are different in the approximation. Only five methods are used in this article.

The Friedman method uses the following equation[20]:

$$\text{Ln } d\alpha/dt = \text{Ln } Z + n \text{ Ln}(1 - \alpha) - E/RT \quad (1)$$

where α is the fractional weight loss and R is the gas constant. The value of $\text{Ln } d\alpha/dt$ can easily be obtained from the DTG curve. The value of $\text{Ln}(1$
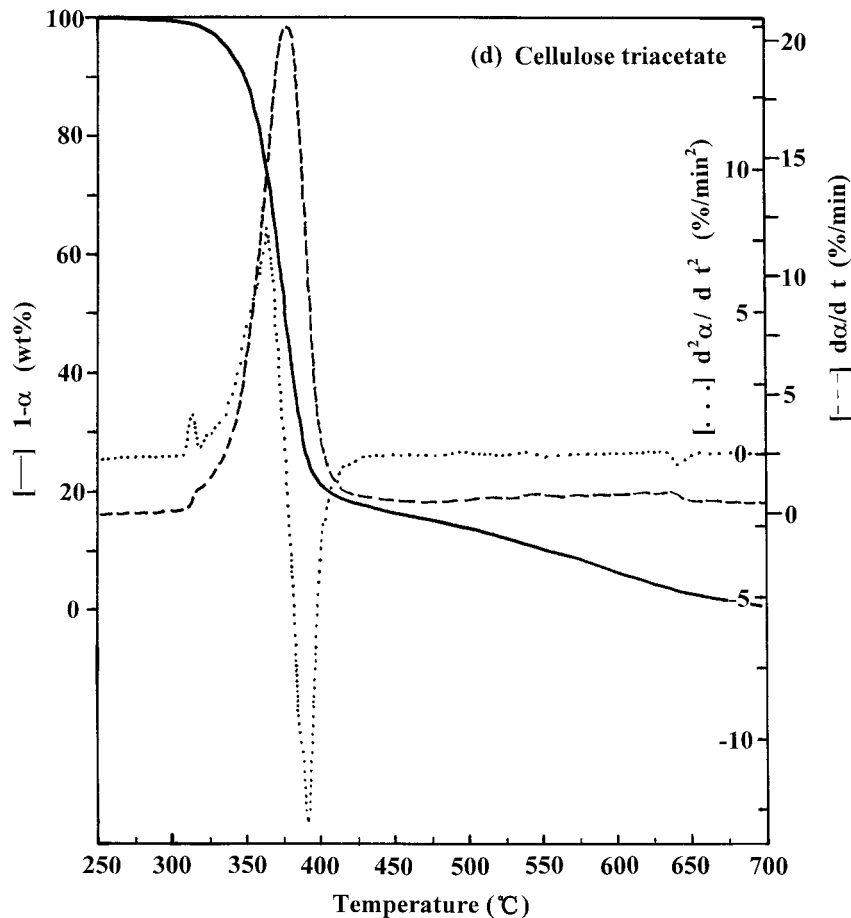
Figure 1 (*Continued from the previous page*)

$- \alpha$) can be obtained from the TG curve. The values of $\mathrm{Ln}(d\alpha/dt)$ were plotted against $1/T$, and then E can be determined from the slope of the plot. The plot of $\mathrm{Ln}(1 - \alpha)$ versus $1/T$ will give the n value from the maximum slope of the line. Finally, the $\mathrm{Ln}\, Z$ can readily be calculated through eq. (1) at a certain temperature.

The Chang method involves the following expression[21]:

$$\mathrm{Ln}[(d\alpha/dt)/(1 - \alpha)^n] = \mathrm{Ln}\, Z - E/RT \quad (2)$$

A plot of $\mathrm{Ln}[(d\alpha/dt)/(1 - \alpha)^n]$ as a function of $1/T$ will offer a straight line if the assumed n value is correct, and the E value can be calculated from the slope of the straight line. The derived E value can be used to calculate $\mathrm{Ln}\, Z$ from the intercept value.

The Coats–Redfern method involves the following equations[22]:

$$\mathrm{Ln}\{[1 - (1 - \alpha)^{1-n}]/[T^2(1 - n)]\}$$

$$= \mathrm{Ln}[ZR(1 - 2RT_{dm}/E)/qE] - E/RT$$

$$(n \neq 1) \quad (3)$$

Table I Thermal Degradation Data of Cellulose and Cellulose Esters at 10°C/min in Nitrogen

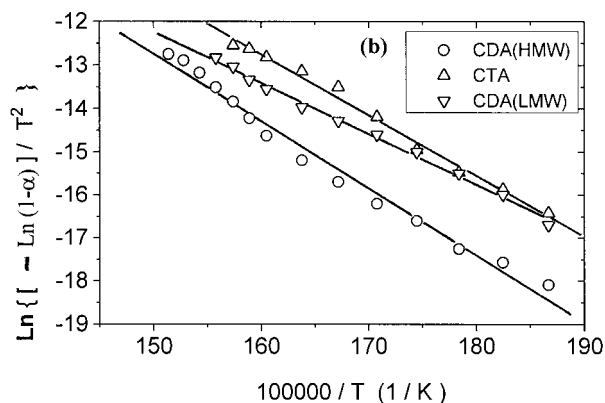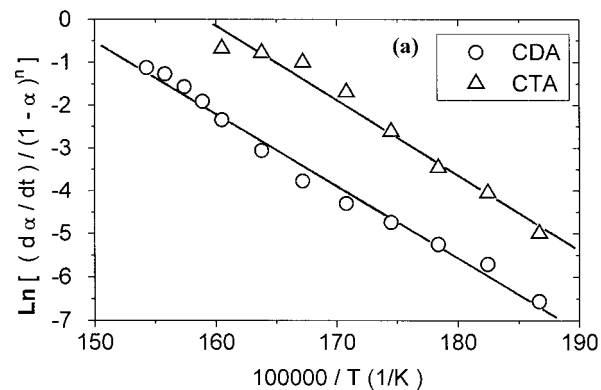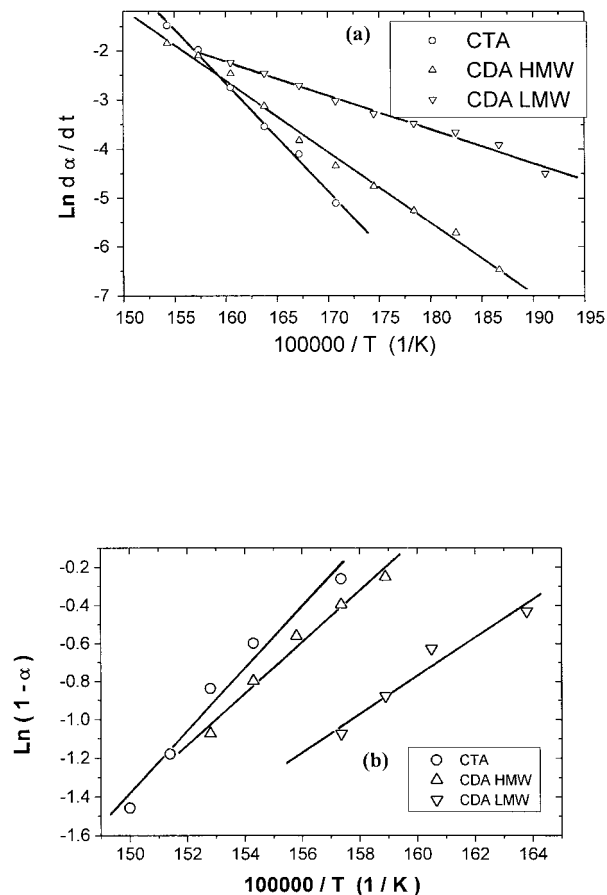| Sample	T_d (°C)	T_{dm} (°C)	Char Yield at 400°C (wt %)	$(d\alpha/dt)_m$ (%/min)
CN	212	213	5.3	183.1
FC	342	367	17.9	17.2
CDA[a]	345	371	25.2	19.2
CTA	350	376	20.0	20.7

[a] High-molecular-weight sample.

Figure 2 Typical Friedman plots of Ln $d\alpha/dt$ versus $1/T$ (a) and Ln$(1 - \alpha)$ versus $1/T$ (b) for determination of activation energy and order of thermal degradation in nitrogen of ($\bigcirc$) CTA (correlation coefficient 0.9976 and 0.9846), ($\triangle$) CDA with high molecular weight (correlation coefficient 0.9967 and 0.9895), and ($\triangledown$) CDA with low molecular weight (correlation coefficient 0.9930 and 0.9968).

$$\text{Ln}\{[-\text{Ln}(1 - \alpha)]/T^2\}$$
$$= \text{Ln}[ZR(1 - 2RT_{dm}/E)/qE] - E/RT$$
$$(n = 1) \quad (4)$$

The plot of the first member of eqs. (3) and (4) versus $1/T$ will form a straight line if the n value selected is correct. From the slope and intercept of this straight line, the kinetic parameters E and Z can be calculated.

The Freeman–Carroll method involves the following equation[23]:

$$\Delta[\text{Ln}(d\alpha/dt)]/\Delta[\text{Ln}(1 - \alpha)]$$
$$= n - (E/R)[\Delta(1/T)/\Delta \text{ Ln}(1 - \alpha)] \quad (5)$$
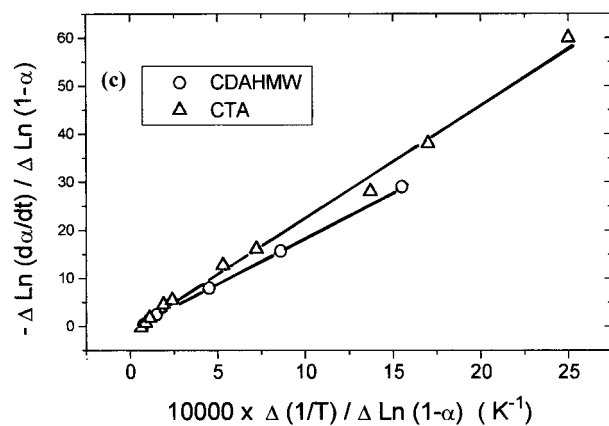

Figure 3 Representative Chang plots (a), Coats–Redfern plots, (b) and Freeman–Carroll plots (c) for thermal decomposition of ($\bigcirc$) CDA (high molecular weight), ($\triangle$) CTA, and ($\triangledown$) CDA (low molecular weight) in nitrogen. Note the activation energy and frequency factor as the slope and Y-axis intercept of the straight lines, respectively.

Table II   Thermal Decomposition Kinetic Parameters for the Cellulose and Cellulose Esters Using Four Techniques at 10°C/min in Nitrogen

Sample	Friedman E/n/Ln Z (kJ mol^{-1}/–/min^{-1})	Chang E/n/Ln Z (kJ mol^{-1}/–/min^{-1})	Coats–Redfern E/n/Ln Z (kJ mol^{-1}/–/min^{-1})	Freeman–Carroll E/n/Ln Z (kJ mol^{-1}/–/min^{-1})	Kissinger n
CN	690/0.1/208	670/0.1/180	680/0.1/168	650/1.4/148	1.7
FC	151/1.0/27	159/1.0/29	121/1.0/22	160/1.0/27	1.2
CDA	125/1.1/22	140/0.7/25	130/1.0/23	159/0.7/29	1.0
CTA	183/1.3/33	146/1.0/28	121/1.0/23	195/1.0/35	1.2

The n and E were obtained from the intercept and slope of a plot of $\Delta[\mathrm{Ln}(d\alpha/dt)]/\Delta[\mathrm{Ln}(1-\alpha)]$ versus $\Delta(1/T)/\Delta\,\mathrm{Ln}(1-\alpha)$ at the same $\Delta(1/T)$ value of approximately 0.00002.

The Kissinger method presents the following equation to calculate the shape index (S) of the TG curve:

$$S = [d^2\alpha/dt^2]_l/[d^2\alpha/dt^2]_r \qquad (6)$$

The $d^2\alpha/dt^2$ value can be obtained from the 2DTG curve. The n value can be calculated from the following equation[23]:

$$n = 1.88 \times S \qquad (7)$$

RESULTS AND DISCUSSION

Thermal Degradation in Nitrogen

Figure 1 shows dynamic TG–DTG–2DTG curves of filter cotton (FC) and three cellulose esters in nitrogen. Table I lists the T_d, T_{dm}, and char yield at 400°C. The thermal degradation of cellulose and its esters consists of a series of degradation reaction, such as dehydration below 100°C; denitration at 207°C for CN; deacetylation at 320°C for CDA and CTA; and thermal pyrolysis of cellulose skeleton at 213°C for CN and at 370°C for FC, CDA, and CTA. The thermal decomposition of CN is much faster at a much lower temperature than those of other three samples. CN of 90% was burned at 212°C within only 1 min whereas it takes at least 15 min to burn the filter cotton, CDA, and CTA of 90% at 340–350°C. In the temperature range of 342–350°C, the filter cotton, CDA, and CTA are decomposed. CTA ex-

hibits the highest thermostability, but CDA has the highest char yield at 400°C. Obviously, the presence of the substituted groups on the cellulose skeleton is expected to influence the thermostability. The degradation of nitro group occurs at a much lower temperature because of its highly thermally instability but the degradation of acetate group occurs at a higher temperature than that of cellulose; that is to say, the nitro group can initiate very fast decomposition of cellulose at a lower temperature. On the contrary, acetate group may make the cellulose more stable. In conclusion, the four different samples have the following order of thermostability: CN < FC < CDA < CTA. All four cellulose samples decompose totally at around 700°C.

Thermal Degradation Kinetics in Nitrogen

There are several techniques on the determination of kinetic parameter of TG data of polymer. Five techniques that can calculate the decomposition order based on the single run TG were selected since it is unknown which technique is the best fit to dynamic TG data of cellulose and its esters. The thermal decomposition kinetics of four samples were assessed by the Friedman, Chang, Coats–Redfern, Freeman–Carroll, and Kissinger techniques, as shown in Figures 2 and 3 for the principal stage of pyrolysis of fractions as an example. The values of E, n, and Ln Z are summarized in Table II with the correlation coefficient larger than 0.985. Extremely high E ($\sim$ 690 KJ/mol) and Ln Z($\sim$ 208 min^{-1}) were observed for CN. FC, CDA, and CTA exhibit much lower E and Ln Z values than CN, and their decomposition could be roughly believed to follow the first order during a significant portion of their weight loss.
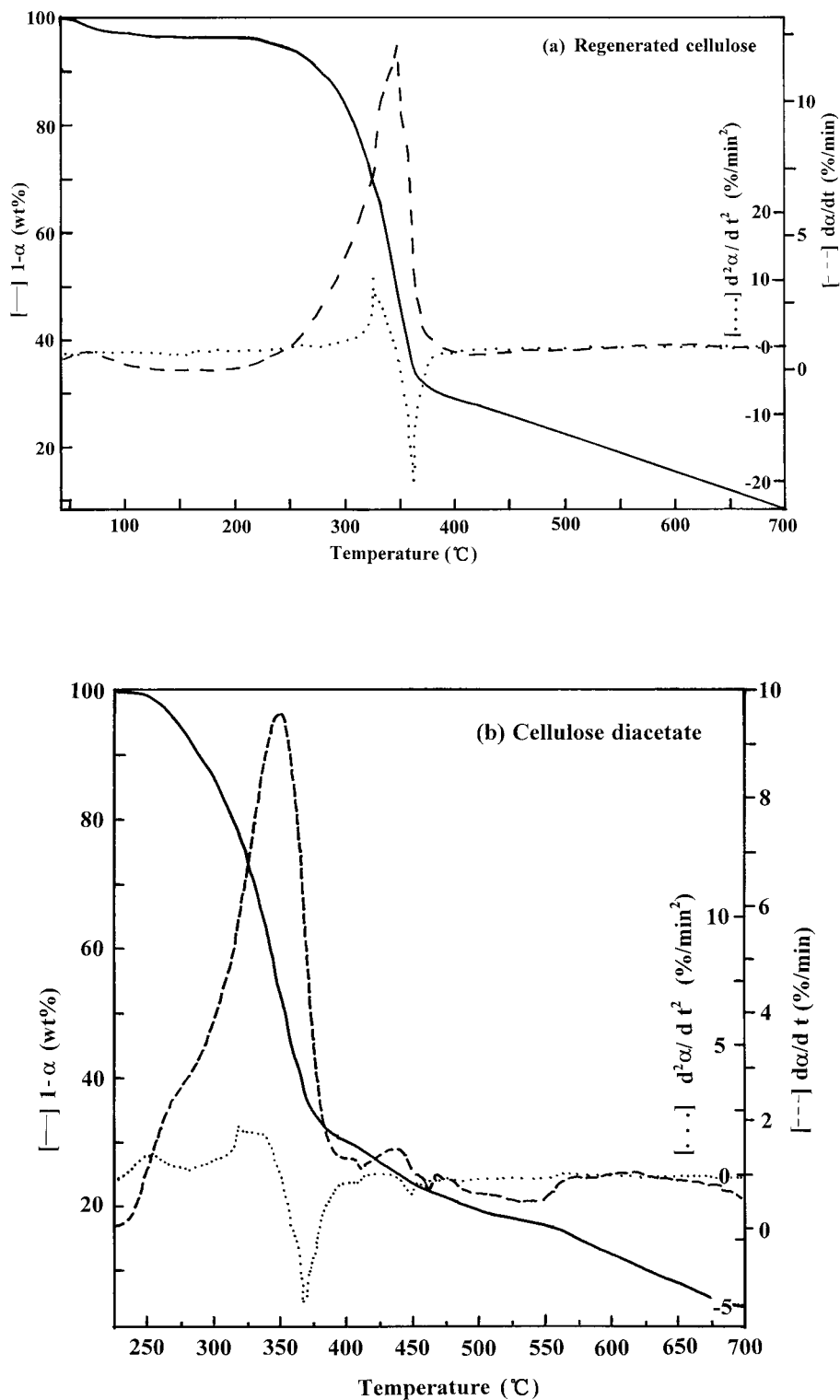
Figure 4 TG (—), DTG (– – –), and 2DTG (·····) traces for the samples with lower-molecular-weight (a) regenerated cellulose and (b) CDA in nitrogen at 10°C/min.

It should be noted from Table II that different calculating methods on the same TG curves produce essentially the same results. It appears that the activation energy values obtained by the Freeman–Carroll method were a little larger than those by other three methods. A similar difference has been observed in the thermal degradation of other polymers and might be attributed to the different mathematical approaches employed in different methods.[8,20]

Effect of Molecular Weight on Thermal Degradation

Thermal degradation of cellulose and its derivatives at molecular level is a process of consecutive and competing reactions that are strongly influenced by their molecular weight and supermolecular structure and by impurities and additives.[24] Figure 4 exhibits the dynamic TG–DTG–2DTG traces of regenerated cellulose and CDA with low molecular weight in nitrogen. As can be seen in Figures 1 and 3, the thermal pyrolysis of two kinds of cellulose samples in nitrogen takes place in two stages. The first stage in the temperature range of 50–160°C corresponds to the phenomenon of physical dehydration because the samples were not dried prior to the test, and the second stage from 240 to 370°C (depending on the molecular weight) is attributed to the thermal cleavage of the glycosyl units and scission of other C—O bonds via a free radical reaction.[7] Note that a shoulder peak on the DTG curve of CDA with lower molecular weight in the temperature range from 240 to 290°C might be attributed to the intramolecular dehydration from the CDA unit and to deacetylation from the CDA. As shown in Tables III and IV, the decomposition reaction for the cellulose and CDA begins at a higher temperature and shows larger E and Ln Z values with high molecular weight than with low molecular weight, but the n value exhibits little variation with molecular weight or the calculating method. Furthermore, a relative agreement was obtained between n values calculated by four methods. Generally, the lower the molecular weight or the crystallinity, the more readily degradable the polymers are because the percentage of crystallinity decreases as the molecular weight decreases. It has been reported that the molecular weight or crystallinity has a stabilizing effect on the thermal degradation of cellulose.[6] It may be noticed from Table III that char yields at 400°C for both cellulose and

Table III Effect of Molecular Weight of Cellulose and Cellulose Diacetate on Their Thermal Decomposition in Nitrogen at 10°C/min

Sample	T_d/T_{dm} (°C)	Char Yield at 400°C (wt %)	$(d\alpha/dt)_m$ (%/min)	Friedman $E/n/$Ln Z (kJ mol$^{-1}/$–/min^{-1})	Chang $E/n/$Ln Z (kJ mol$^{-1}/$–/min^{-1})	Coats–Redfern $E/n/$Ln Z (kJ mol$^{-1}/$–/min^{-1})	Kissinger n
Cellulose							
LMW[a]	300/344	27.4	12.1	75/1.1/13	88/1.0/16	84/1.0/15	1.0
HMW[b]	343/368	17.9	17.2	151/1.1/27	159/1.0/29	121/1.0/22	1.2
CDA							
LMW[a]	298/350	29.8	9.5	61/0.7/10	73/1.0/14	98/1.0/17	0.8
HMW[b]	345/371	25.2	19.2	121/1.1/22	140/0.7/25	130/1.0/23	1.0

[a] LMW = lower molecular weight.
[b] HMW = higher molecular weight.

Table IV   Thermostability Results of Cellulose with Different Molecular Weights at a Heating Rate 5°C/min by the Friedman Method

Sample	DP	Test Environment	T_d/T_{dm} (°C)	Char Yield at 400°C (%)	E (KJ/mol)	n	Ln Z (min^{-1})	Reference
Bagasse pulp	74	Nitrogen	273/330	42	88	1.0	—	25
Viscose rayon[a]	400	Air	313/333	15	186	1.0	36	24
Viscose rayon[a]	400	Nitrogen	320/335	13	181	0.8	34	24
Cellulose pulp	1240	Nitrogen	308/340	10	259	0.9	—	8
Cotton linter[b]	2530	Nitrogen	337/360	10	178	1.0	33	12
Cotton linter[b]	2530	Air	326/345	10	251	1.1	48	12
Cotton[a]	12500	Air	333/345	17	190	1.2	36	24
Cotton[a]	12500	Nitrogen	339/361	17	142	0.9	26	24
Linen[a]	36000	Air	310/343	27	120	1.5	22	24
Linen[a]	36000	Nitrogen	322/354	25	112	1.1	20	24

[a] Heating rate: 10°C/min.
[b] Heating rate: 15°C/min.

CDA decreases with an increase in their molecular weights. The results are in good agreement with those in the literature (Table IV). The bagasse, linen, and some cellulose pulp exhibit lower initial thermal decomposition temperatures and activation energies because they contain a large number of impurities in spite of their higher DP and orientation. Apparently, the impurities in the samples significantly effect the beginning of the thermal degradation and even the total degradation process.[24]

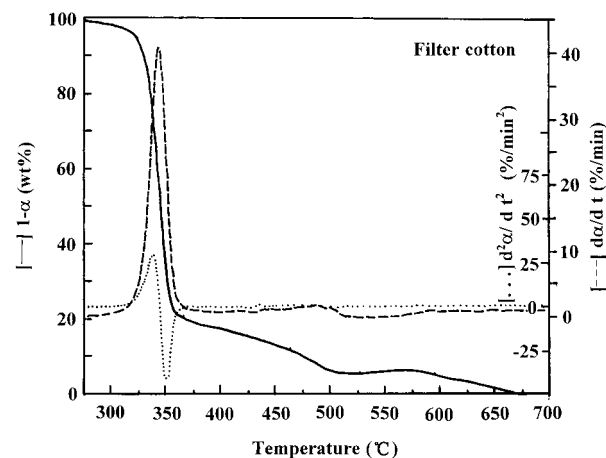Figure 5 shows the TG–DTG–2DTG traces of the filter cotton in air. Obviously, there is a strong

Figure 5   TG (—), DTG (– – –), and 2DTG (·····) traces for filter cotton in air at 10°C/min.

influence of test atmosphere on thermal decomposition for cellulose and its derivatives, as shown in Tables IV–VII. The cellulose is more stable in nitrogen than in an oxidative atmosphere on the basis of its higher T_d and T_{dm} in nitrogen because the oxygen plays the roles of a catalyst in accelerating the thermal degradation of cellulose. It can be seen from Figure 5 that there is an additional thermo-oxidative decomposition at approximately 475°C in air as compared with Figure 1(a). It was reported that the oxidative decomposition accompanied the thermal pyrolysis of the cellulose when the oxygen contamination of the nitrogen exceeds 0.5%.[18] On the contrary, the cellulose, especially mercerized cotton, is the least thermally stable in the pure oxygen flow. Cellulose and its esters have much higher E and Ln Z values in pure oxygen than in air or nitrogen; particularly, the mercerized cotton exhibits the highest E and Ln Z values of thermal decomposition in oxygen. The E and Ln Z values obtained in air are generally higher than those in nitrogen. Note that cellulose phosphate (CP) in flowing atmosphere shows the lowest E and Ln Z values, suggesting that the CP exhibits the lowest thermostability. It is of interest that the n values remain almost constant in a narrow range of 0.8–1.2 and do not vary either with the chemical structure or with test atmosphere, except for that in the oxygen.[14,17,18,27]

Additionally, the char yields at 400°C in nitrogen are ordinary higher than those in air, and the char yields in pure oxygen are the low-

Table V Effect of Test Atmosphere on the Thermal Decomposition of Filter Cotton with DP of 800 at 10°C/min

Test Atmosphere	T_d/T_{dm} (°C)	Char Yield at 400°C (wt %)	$(d\alpha/dt)_m$ (%/min)	Friedman $E/n/\mathrm{Ln}\ Z$ (kJ mol⁻¹/–/min⁻¹)	Chang $E/n/\mathrm{Ln}\ Z$ (kJ mol⁻¹/–/min⁻¹)	Coats–Redfern $E/n/\mathrm{Ln}\ Z$ (kJ mol⁻¹/–/min⁻¹)	Kissinger n
Nitrogen	343/368	17.9	17.2	151/1.1/27	159/1.0/29	121/1.0/22	1.2
Air	331/343	17.4	40.8	281/1.1/54	293/1.0/56	275/1.0/53	1.3

est (Table VII). It may be attributed to the further pyrolysis and combustion of the residual materials in the air or oxygen and the formation of volatile char products due to the oxidation of char residues after the thermal decomposition stage at a relatively low temperature. It is also found from Table VII that the acetylated cotton exhibits slightly high T_d and E values as compared with benzoylated cotton (BC), indicative that the acetylated cotton is more thermally stable in spite of high aromatics of BC.

In conclusion, the cellulose and its esters have a lower thermostability in an oxidative atmosphere than in an inert atmosphere because oxygen can greatly favor or even accelerate their thermal decomposition. When the thermostability of cellulose and its esters was compared in different atmospheres, the following trend of increasing thermostability was evident: in oxygen < in air < in nitrogen. Quite the contrary, the E and Ln Z values of thermal decomposition of cellulose and its esters decrease in the following order: in oxygen > in air > in nitrogen.

Thermal decomposition rates in nitrogen were found to be higher than in air for filter cotton, but quite the contrary for the CP, as shown in Figure 6. The predicted lifetime t_f (weight loss 5%) was calculated according to the equations reported in Ref. [20]. It was found from Fig. 6 that the estimated lifetime at 150°C increases in the following order: CN < CP < CDA < CTA < FC. An exponential reduction of the estimated lifetime of the CDA, CTA, CP, and filter cotton was observed with an increase in temperature from 25 to 350°C, and, at 350°C, they all exhibit the lifetime shorter than 1 min once the estimated lifetime of CN declines dramatically with increasing temperature from 25 to 150°C. According to the thermal decomposition temperature (T_d and T_{dm}), the thermostability of cellulose and its esters can be ranked in the following order: CN < CP < CDPP < CEP < Cellulose < BC < CDA < CTA.

CONCLUSIONS

The thermal degradation of cellulose and cellulose acetate in the temperature range from room temperature to 700°C was observed to follow the first order with an activation energy range of 60–400 kJ/mol, but the activation energy of the thermal decomposition of CN is increased to 690

Table VI   Effect of Test Atmosphere on Thermal Decomposition of Cellulose and Its Phosphates[a]

Test Atmosphere	Heating Rate (°C/min)	$T_d/T_{dm1}T_{dm2}$ (°C)	Char Yield at 400°C (wt %)	E (kJ mol^{-1})	n	Ln Z (min^{-1})
Cellulose						
Flowing N$_2$	9	360/400/620	38	214	1.0	39
Flowing air	9	275/321/480	25	213	1.1	46
Flowing air	10	285/321/482	23	238	—	49
Static air	10	305/334/—	17	262	1.1	56
Cellulose phosphate (CP) (DS = 1)						
Flowing N$_2$	9	218/255/630	61	96	0.9	21
Flowing air	9	176/194/505	47	98	1.1	28
Flowing air	10	179/222/508	42	60	—	15
Static air	10	255/262/300	52	197	1.0	47
Cellulose diethylphosphate (CEP)						
Flowing N$_2$	9	325/365/630	55	153	1.1	29
Flowing air	9	245/255/510	38	139	1.1	32
Cellulose diphenylphosphate (CDPP)						
Flowing N$_2$	9	327/355/650	57	148	1.0	28
Flowing air	9	225/243/500	39	130	1.0	34

[a] See Jain et al.[14,15] and Franklin et al.[16]

KJ/mol. The rate of thermal degradation of CN is very high at approximately 210°C in a very narrow range of temperature. The thermal decomposition reaction of CN is the fastest. It was found that the nitration onto cellulose makes the cellulose thermally the lowest stable, but the acetylation onto cellulose makes the cellulose thermally more stable. The thermostability of cellulose and cellulose diacetate will enhance with increasing their molecular weights or with the variation of environment from oxidative to inert. On the contrary, the samples with lower molecular weight or air have higher char yield at 400°C. Filter cotton at 250°C exhibit estimated a lifetime longer than 6500 min. The above thermostability results led us to the conclusion that the nature of macromolecular structure of cellulose and its esters plays an important role in changing the thermostability of cellulose.

Table VII   Thermal Degradation Results of Cellulose and Cellulose Esters[a]

Sample	Atmosphere/Heating Rate/Method (°C/min)	T_d/T_{dm} (°C)	Char Yield at 400°C (wt %)	E (kJ mol^{-1})	n	Ln Z (min^{-1})
Cotton	Flowing O$_2$/40/Friedman	310/311	1.8	882	3.3	185
Scoured cotton	Flowing O$_2$/40/Friedman	333/337	0.9	852	1.8	171
Mercerized cotton	Flowing O$_2$/40/Friedman	277/289	4.7	1110	4.7	242
Acetylated cotton						
DS = 0.75	Flowing O$_2$/40/Friedman	326/337	0.8	640	1.7	129
DS = 1.72	Static air/10/Broido	320/355	15.4	237	—	45
Benzoylated cotton						
DS = 0.42	Flowing O$_2$/40/Friedman	325/339	1.1	654	2.0	132
DS = 1.88	Static air/10/Broido	305/360	14.8	136	—	25

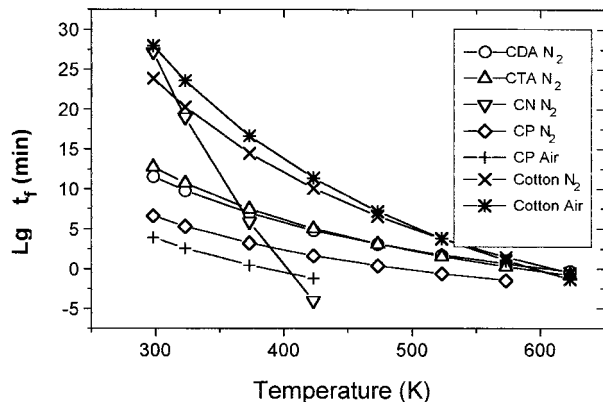[a] See Subramaniam et al.[27] and Jain et al.[28]

Figure 6 Predicted lifetime $\{t_f = [(0.95^{1-n} - 1) \exp(E/RT)]/[(n-1)Z]$ $(n \neq 1)$; $t_f = [0.0513 \exp(E/RT)]/Z$ $(n = 1)\}$ based on the average activation energy, order, and frequency factor of thermal degradation of ($\bigcirc$) CDA in nitrogen, ($\triangle$) CTA in nitrogen, ($\triangledown$) CN in nitrogen, ($\diamond$) CP in flowing nitrogen, ($+$) CP in flowing air, ($\times$) filter cotton in nitrogen, and ($*$) filter cotton in air.

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