High-Resolution Thermogravimetry of Cellulose Esters

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ABSTRACT: Cellulose dinitrate (CDN), cellulose diacetate (CDA), and cellulose triacetate (CTA) were subjected to high-resolution thermogravimetry (TG) at a variable heating rate in air. The TG curves, the derivative TG curves, the second derivative TG curves, and heating rate curves are discussed. The thermal degradation temperature and kinetic parameters are presented and compared to those obtained with traditional TG at a constant heating rate. The degradation process of the cellulose esters is speculated. Among the three cellulose esters, CDN exhibits the lowest degradation temperature of (213°C) but the largest degradation activation energy of (237–269 kJ/mol). © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 71: 573–578, 1999

Key words: cellulose ester; high-resolution thermogravimetry; thermostability; thermal degradation; degradation kinetics; thermooxidative degradation

INTRODUCTION

Among all cellulose derivatives, the cellulose esters are the most widely used for separation membrane materials, transparent film, man-made fiber, coating, plastics, and smokeless powder. A few papers have addressed the thermal degradation of cellulose esters by traditional thermogravimetry (TG) at a constant heating rate in nitrogen.[1–5] In our earlier paper, the thermal degradation of the cellulose esters in nitrogen by the conventional TG was demonstrated.[6] However, to date, no high-resolution TG of cellulose esters in air has been reported, nor is the thermal degradation kinetics of the cellulose esters understood.

This article reports some preliminary studies on the thermal degradation and kinetics of three cellulose esters in air by a recently developed high-resolution TG technique.

EXPERIMENTAL

Fibrous cellulose dinitrate (CDN) made in Shanghai, China has a falling ball viscosity, degree of substitution, and molecular weight of 25 s, ∼ 2.3, and ∼ 60,000, respectively. The degree of substitution and molecular weight of the pelletized cellulose diacetate (CDA) used in this paper, which was made in Shanghai, China, are ∼ 2.3 and ∼ 70,000, respectively. The degree of substitution and molecular weight of cellulose triacetate (CTA) random particle, obtained from Daicel Chemical Company in Japan, are 2.7 and 86,751, respectively.

TG analyses were performed under a 35 mL/min air flow on a high-resolution TGA 2950 thermal analyzer (Hi-Res™ TGA) produced by TA Instruments Inc., New Castle, Delaware, using the high-resolution mode interfaced to a TA Instruments 2000 controller with a General V.4.1C microprocessor. The sample sizes were 0.62 mg for both CDN and CDA and 1.26 mg for CTA. The initial heating rate and resolution were fixed at 50°C/min and 3.0, respectively. The sensitivity was fixed at its default value of 1 in the temperature range of 25–740°C. The thermal degrada-

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Table I   Thermal Degradation Data of Cellulose Esters at an Initial Heating Rate of 50°C/min in Air Using HRTG with a Resolution of 3.0

Sample	$T_d/T_{dm1}/T_{dm2}$ (°C)	$(d\alpha/dt)_m$ 1st/2nd (%/min)	$(d\alpha/dT)_m$ 1st/2nd (%/°C)	Char Yield at 400°C (wt %)
Cellulose dinitrate	213/213/546	37.4/2.2	7.4/0.1	12.2
Cellulose diacetate	340/352/525	15.7/4.5	5.9/0.2	12.8
Cellulose triacetate	341/355/490	11.2/3.5	3.4/0.2	16.6

tion temperatures and kinetic parameters were determined using the techniques described previously.[6] The degradation temperature, T_d, was obtained by extrapolating the initial degradation portion of the TG curve. These data were compared to values in the literature. The T_{dm} means the temperature at the maximum weight-loss rate determined by the DTG curves.

RESULTS AND DISCUSSION

Figure 1 shows the high-resolution thermogravimetry (HRTG), derivative thermogravimetry (DTG), second derivative thermogravimetry (2DTG), and heating-rate curves for three cellulose esters at an initial heating rate of 50°C/min in air. The thermal decomposition results are given in Table I. Comparing the thermal decomposition parameters in air to those obtained in nitrogen,[6] shows that the thermostability of each cellulose ester differs. CDA and CTA exhibit slightly lower T_d, T_{dm}, and char yield at 400°C in air except for almost unchangeable T_d and T_{dm} values in both conditions for CDN. This suggests that onset of the bond cleavage in the CDA and CTA is basically thermal in nature and is slightly influenced by the presence of oxygen, but the onset of the degradation of the CDN is entirely thermal in nature and not influenced by oxygen at all. These differences in thermal decomposition parameters may be also attributed to different measuring modes. It was found that the T_d, T_{dm1}, and char yield at 400°C increase with the variation from CDN, CDA to CTA, but that T_{dm2}, $(d\alpha/dt)_{m1}$ and $(d\alpha/dT)_{m1}$ decrease. That is, CTA is the most thermostable and CDN is the least

thermostable. CDN has a 2.4 times and 3.3 times greater $(d\alpha/dt)_{m1}$ than CDA and CTA, respectively. The much greater decomposition rate and much lower T_d of CDN are due to the thermal instability of nitro groups on the CDN molecules. The thermolabile nitro group on CDN leads to weight loss of 60% in a narrow temperature range of 200–223°C, whereas weight loss of 60% occurs in wider temperature ranges of 260–352°C for CDA and 275–360°C for CTA.

Figure 2 shows that the high-resolution $(d\alpha/dt)$ plots generally exhibit higher resolution than the high-resolution $(d\alpha/dT)$ plots and traditional $(d\alpha/dt)$ plots obtained at a fixed heating rate of 10°C/min in nitrogen.[6] The $(d\alpha/dT)$ and traditional $(d\alpha/dt)$ plots look smoother than the high-resolution $(d\alpha/dt)$ curves, which exhibit three and four shoulder peaks on the left sides of the major DTG peaks. The weight loss corresponding to the third shoulder peak on the high-resolution $(d\alpha/dt)$ curve of CDA is 39.0%, which is close to the weight loss of 38.2% after the complete loss of whole acetyl groups on CDA. In the traditional $(d\alpha/dt)$ curve of CDA obtained at 10°C/min, two shoulder peaks correspond to the weight losses of 5.9% and 10.9%. The weight loss of 5.9% is slightly higher than the theoretical weight loss (5%) of the 0.3 molar acetyl group on the most reactive position—the sixth carbon on the cellulose unit in CDA. The first shoulder peak on the high-resolution $(d\alpha/dt)$ plot of CTA corresponds to the weight loss of 9.4%. This weight loss is slightly lower than theoretical loss (10.9%) of 0.7 molar acetyl groups on the most reactive position, (i.e., the sixth carbon on the cellulose unit) in the CTA molecules. This first stage of thermal deacetylation shows much lower activation en-

Figure 1   High-resolution TG (–), DTG (– – –), 2DTG (· · ·), and heating rate (– · – ·) curves of cellulose esters in air flow at an initial heating rate of 50°C/min and resolution 3.0. (a) Cellulose dinitrate; (b) cellulose diacetate; (c) cellulose triacetate.

(a) Cellulose nitrate

(b) Cellulose diacetate

(c) Cellulose triacetate

Figure 2 Comparisons of high-resolution ($d\alpha/dt$) curves (——) with ($d\alpha/dT$) curves (– – –) in a high-resolution TG mode in air or ($d\alpha/dt$) curves ($\cdots$) obtained in a traditional TG mode at a constant heating rate of 10°C/min in nitrogen. (a) Cellulose diacetate; (b) cellulose triacetate.

ergy of 64 kJ/mol, as listed in Table II. The weight loss at the fourth shoulder peak is 42%, which is the same as the theoretical weight loss (42.3%) of the total abstraction of the acetyl group on CTA. These may imply that the thermal degradation of CDA and CTA begins with the cleavage of the ester linkage and simultaneous removal of the acetyl group. After the whole loss of the acetyl group, the weight loss rates of CDA and CTA both reach the maximum, then decrease dramatically. The decomposition of CDN, CDA, and CTA are a complex set of reactions; the denitration and deacetylation; scission of O—N (only for CDN), C—O, C—C, and C—H bonds to form gases such as nitrogen dioxide for CDN and ethylene ketone[7] for CTA and CDA, and intermolecular condensations to form carbonaceous char. Figures 1 and 2 show that a two-stage degradation was clearly found in air. After the first stage of thermal degradation, the respective char yields for CDN, CDA, and CTA are 18.1% at 317°C, 18.6% at 361°C, and 17.4% at 397°C, which all are equivalent to the char residue of four carbons per structural unit.

As compared to the degradation of CDN, CDA and CTA in nitrogen,[6] an obvious additional decomposition process at an elevated temperature was observed, as shown in Figure 2. This process may be assigned to the evaporation of the volatile products formed by the combustion or thermooxidative degradation of residual carbon after the plateau. The plateaus observed at 310–450°C for CDN and CDA and 380–440°C for CTA are attributed to aromatization oxidation and burning of the high-molecular-weight charred residues after the initial depolymerization of the cellulose esters at about 370°C.[8] The three cellulose esters were entirely burned out in air at 629°C for CDN and at 550°C for CDA and CTA, but the temper-

Table II   Kinetic Parameters of the Major Thermal Degradation for the Cellulose Esters in Air by HRTG

Sample	Freeman–Carroll $E/n/\ln Z$[a]	Friedman $E/n/\ln Z$	Chang $E/n/\ln Z$	Coats–Redfern $E/n/\ln Z$	Kissinger n	Average $E/n/\ln Z$
Cellulose dinitrate	240/0.3/58	237/0.8/58	269/0.5/65	537/0.3/132	1.8	321/0.7/78
Cellulose diacetate	118/1.3/21	106/0.5/18	131/1.0/24	189/1.0/36	1.4	136/1.0/25
Cellulose triacetate	180/1.0/33	193/1.1/36 (64/5.0/10)[b]	140/1.0/25	197/1.0/37	1.2	178/1.1/33

[a] The units of E and $\ln Z$ are kJ mol^{-1} and min^{-1}, respectively.
[b] Kinetic parameters of first stage of thermal deacetylation of cellulose triacetate.

Figure 3 Application of the Freeman–Carroll method to the high-resolution TG data of (□) cellulose dinitrate, (○) cellulose diacetate, and (△) cellulose triacetate.

ature at which they were totally burned out in nitrogen is up to 700°C for CDN and CTA, and the char yield of ∼ 20 wt % was observed even at 700°C for CDA.[6]

The kinetic parameters of thermal degradation for CDN, CDA, and CTA obtained from Figures 3–6 by the Freeman–Carroll, Friedman, Chang, Coats–Redfern, and Kisinger methods are presented in Table II. This Table II shows that the average decomposition order obtained is almost the same as that obtained in nitrogen by traditional TG at 10°C/min. The average E and ln Z values in this article are basically consistent with those in nitrogen[6] and in vacuum (E = 188

Figure 5 Application of the Chang method to the high-resolution TG data of (□) cellulose dinitrate, (○) cellulose diacetate, and (△) cellulose triacetate.

kJ/mol for CTA),[9] except that the E and ln Z values for CDN are much smaller than those in nitrogen.[6] This is because HRTG can decrease the heating rate automatically and rapidly whenever the weight loss rate of the polymer increases rapidly. It should be noticed that the correlation efficient of four kinds of plots of calculating kinetic parameters are 0.967–0.990 for the Coats–Redfern plots, 0.985–0.989 for the Chang plots, 0.996–0.999 for the Friedman plots, and 0.995–0.999 for the Freeman–Carroll plots. Among the five methods, only the Freeman–Carroll method permits the simultaneous determination of E and n values. However, the slopes of TG and DTG traces are often steep, requiring extreme care in obtaining data from both curves. Further, at low weight loss, considerable scatter is often encountered in the plots due to the magnification of the experimental scatter resulting from the use of the difference of the DTG traces.[10]

Figure 4 Application of the Friedman method to the high-resolution TG data of (□) cellulose dinitrate, (○) cellulose diacetate, and (△) cellulose triacetate.

Figure 6 Application of the Coats–Redfern method to the high-resolution TG data of (□) cellulose dinitrate, (○) cellulose diacetate, and (△) cellulose triacetate.

CONCLUSIONS

High-resolution TG can provide more information of thermal degradation of CDN, CDA, and CTA in a shorter time than a traditional TG. The first stage of deacetylation of the CTA seems to be clearly observed. The first thermal degradation and the second thermooxidative degradation processes on the HRTG and DTG of the three cellulose esters are obviously resolved. The degradation of cellulose esters in air is a complex set of reactions: denitration or deacetylation; scission of N—O, C—O, C—C, and C—H to form volatile compounds such as nitrogen dioxide for CDN and ethylene ketone for CDA and CTA; intermolecular condensations to form carbonaceous char at a relatively low temperature; and further oxidation and combustion of the residual char at an elevated temperature. The HRTG and DTG curves can be used to calculate the kinetic parameters of thermal degradation of cellulose esters through conventional kinetic equations deduced for the conventional TG at a constant heating rate.

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