Thermal Decomposition of Cellulose Ethers

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ABSTRACT: The thermostability and thermal decomposition kinetics of methyl cellulose (MC), ethyl cellulose (EC), carboxymethyl cellulose (CMC), hydroxyethyl cellulose (HEC), and hydroxypropyl-methyl cellulose (HPMC) were characterized in nitrogen and air by thermogravimetry (TG). Various methods of kinetic analysis were compared in case of thermal degradation of the five cellulose ethers. The initial decomposition temperature (T_d) , temperature at the maximum decomposition rate (T_{dm}) , activation energy (E), decomposition reaction order (n), and pre-exponential factor (Z) of the five cellulose ethers were evaluated from common TG curves and high-resolution TG curves obtained experimentally. The decomposition reactions in nitrogen were found to be of first order for MC, EC, and HPMC with the average E and $\ln Z$ values of 135 kJ/mol and 25 min⁻¹, although there were slight differences depending on the analytical methods used. The thermostability of cellulose ethers in air is substantially lower than in nitrogen, and the decomposition mechanism is more complex. The respective average E, n, ln Z values for HEC in nitrogen/air were found to be 105/50 kJ/mol, 2.7/0.5, and $22/8.3 \text{ min}^{-1}$, from constant heating rate TG method. The respective average E, n, and $\ln Z$ values for three cellulose ethers (EC/MC/HPMC) in air are 123/144/147 kJ/mol, $2.0/1.8/2.2, 24/28/28 \text{ min}^{-1}$ by using high-resolution TG technique. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 73: 2927-2936, 1999

Key words: cellulose ether; alkyl cellulose; thermogravimetry; thermostability; thermal decomposition; decomposition kinetics; high-resolution thermogravimetry

INTRODUCTION

Cellulose ethers represent a large class of cellulose materials. The ether structure in the cellulose ethers is responsible for relatively good sol-

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vency, low melting temperature, excellent liquid crystallinity, and good processability.^{1,2} The cellulose ethers are widely used for many important applications such as coating, painting, food additive, fiber, plastics film, separation membranes, and functional materials. For example, carboxymethyl cellulose has been used as the controlledrelease monolithic formulations of various larvicides³ and also as high-performance ion-exchange resin which can form a complex with gold ion in dilute $AuCl_4^-$ solution.⁴ Consequently, the cellulose ethers may encounter elevated temperatures in compounding and processing, as well as in service. Apparently, the thermostability of the cellu-

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Figure 1 TG (——), DTG (– – –), and 2DTG (· · ·) curves at 10°C/min heating rate in nitrogen for four cellulose ethers, (a) HEC; (b) MC; (c) EC; (d) HPMC.



Figure 1 (Continued from the previous page)

lose ethers are important from both practical and academic points of view, but so far, the thermostability and thermal decomposition kinetics of the cellulose ethers have not been critically studied.

In this article, the thermal stability and degradation kinetics of five cellulose ethers have been investigated by performing detailed thermogravimetry (TG), derivative thermogravimetry (DTG), and second derivative thermogravimetry (2DTG) kinetic analyses of the thermal decomposition.

EXPERIMENTAL

Methyl cellulose (MC) powder made in Britain has a degree of substitution (DS) of $\sim 1.6-2.0$,

and a molecular weight of $\sim 50,000-80,000$. The viscosity of water solution containing 2 wt % MC is $\sim 0.35-0.55$ Pa s. Hydroxypropyl-methyl cellulose (HPMC) powder produced by Japan has a DS for methoxyl group of ca. 1.8 and for hydroxypropoxyl group of ca. 0.2. Low molecular weight ethyl cellulose (EC) (DS = $\sim 2.3-2.4$) was made by Shantou Xinning Chemicals Work of Guangdong Province, China, and its 5 wt % solution viscosity in ethanol/toluene (50/50) is $\sim 0.04 - 0.08$ Pa s. High molecular weight EC (DS $= \sim 2.4$) was imported from Roth Chemicals and its solution viscosity is ca. 0.2 Pa s. Hydroxyethyl cellulose (HEC) (DS = ~ 0.2) was purchased from the 6th Harbin Chemicals Work of Heilongjiang Province, China. The source of cellulose for preparing the lower molecular EC, MC, and HEC is linter.

Table I Results of Thermogravimetry for Cellulose Ethers at 10°C/min in Nitrogen

Sample	T_d (°C)	T_{dm} (°C)	$T_{df} (^{\circ}\mathrm{C})$	Char Yield at 400°C (wt %)	$(d \alpha/dt)_m$ (%/min)	
HEC	239	280	320	35.5	8.2	
MC	308	342	361	17.8	16.4	
EC	325	352	375	7.8	20.9	
HPMC	336	368	390	12.9	17.1	

Table II Initial Thermal Degradation
Temperatures of Wholly Substituted Cellulose
Ethers Synthesized from Regenerated Cellulos
with the Degree of Polymerization (DP)
of 250 in Helium

T_d (°C)
125
260
290
310
320
330
330
390

Sample weight, 10 mg; heating rate, 5°C/min.^{8,9}

^a DP is 110 and test atmosphere is air.

For TG measurements, TA Instrument 2000 thermal analyzer with a high-resolution TGA 2950 module was used to evaluate the thermostability of samples. The thermal analyzer consists of a printer plotter, professional computer, and TG standard software-general V 4.1c. The measurements were taken in nitrogen or airflow of 25 mL/min at a heating rate 10°C/min and an initial 50°C/min in a high-resolution mode with a sample weight of ~ 0.4 –1.2 mg. The initial decomposition temperature (T_d) and final decomposition temperature (T_{df}) were obtained by extrapolation. The temperature at the maximum rate of weight loss (T_{dm}) , the maximal weight-loss rate $(d\alpha/dt)_m$, and char yield at 400°C were obtained from DTG and TG traces, respectively.

Table III Thermostability of Carboxymethyl Cellulose (CMC) and Its Derivates in Nitrogen at 20°C/min Heating Rate^{3,4}

Sample	T_d (°C)	T_{dm} (°C)	T_{df} (°C)	Char Yield at 400°C (wt %)
FeCMC	200	255	350	47.1
CuCMC	235	263	280	42.5
NaCMCX ^a (S, 2.7 wt %)	253	260	267	50.7
NaCMC	274	322	341	63.1
$\mathrm{CMC}^{\mathrm{a}}$	292	300	308	47.1

 $^{\rm a}$ CMCX means carboxymethyl cellulose xanthate with the degree of esterification at 3.3 mol %. The original degree of substitution of CMC is 0.44.



Figure 2 Friedman (a) and Chang (b) plots for the determination of kinetic parameters of thermal decomposition in nitrogen at 10°C/min for three cellulose ethers, (\Box) methyl cellulose; (\bigcirc) ethyl cellulose; (\triangle) hydroxypropyl-methyl cellulose.

Kinetic Analysis

The kinetics of thermal decomposition of cellulose ethers were examined by four methods: Friedman, Chang, Coats–Redfern, and Kissinger. The first method, by Friedman, uses the equation^{5,6}

$$\ln(d\alpha/dt) = \ln Z + n \, \ln(1-\alpha) - E/RT \quad (1)$$

where $d\alpha/dt$ is the weight-loss rate which is obtained from DTG curve; *Z* is the frequency factor of decomposition reaction; *n* is the reaction order; $1 - \alpha$ is the residual weight of sample at a certain

		Friedman		Chang					
Sample	E (kJ/mol)	n	ln Z (L/min)	E (kJ/mol)	n	ln Z (L/min)	$\frac{\text{Kissinger}}{n}$		
FeCMC ^a	76	9.8	18	117	7.0	29	_		
HEC	88	2.9	18	122	3.0	25	2.0		
NaCMC ^a	100	7.2	20	145	6.0	32	_		
HPMC	112	0.9	20	135	0.8	24	0.9		
MC	127	1.1	24	135	1.0	26	0.8		
EC^{b}	130	0.7	24	169	1.0	32	1.7		
CuCMC ^a	271	7.3	63	356	5.0	84	—		

Table IVThermal Decomposition Kinetic Parameters for the Cellulose Ethers Using ThreeCalculating Methods at 10°C/min in Nitrogen

^a Their TG/DTG curves were obtained at 20°C/min from ref. 3.

 $^{\rm b}$ Its solution viscosity is \sim 0.04–0.08 Pa s.

temperature which is obtained from TG curve; E is the activation energy; R and T are the gas constant and absolute temperature recorded on the thermogram, respectively. E or n values can be calculated from the plots of $\ln(d\alpha/dt)$ or $\ln(1 - \alpha)$ against 1/T.

The second method, by Chang, uses the following equation 5,6 :

$$\ln[(d\alpha/dt)/(1-\alpha)^n] = \ln Z - E/RT \qquad (2)$$

The plot of $\ln[(d\alpha/dt)/(1 - \alpha)^n]$ versus 1/T must give a straight line if the *n* value assumed is correct. Thus, *E* and $\ln Z$ values can be obtained from the slope and intercept of the straight line, respectively.

The third method, by Coats–Redfern, employs the equation⁷

$$\ln\{[1 - (1 - \alpha)^{1-n}]/[T^2(1 - n)]\} = \ln[ZR(1 - 2RT_{n}/E)/aE] - E/RT \quad (n \neq 1) \quad (3)$$



Figure 3 TG (——), DTG (– –), and 2DTG (· · ·) curves of hydroxyethyl cellulose at 10°C/min heating rate in air.

Test Atmosphere	T_d (°C)	T_{dm} (°C)	(<i>T_{df}</i> (°C)		Char Yield at (wt %)	t 400°C	$(d \alpha/dt)_m$ (%/min)
Nitrogen Air	239 230	280 281		320 335		$35.5 \\ 38.6$		$\begin{array}{c} 8.2\\ 5.8\end{array}$
		Friedman				Chang		
Test Atmosphere	E (kJ/mol)	n	ln Z (L/min)		E (kJ/mol)	n	ln Z (L/min)	$\frac{\text{Kissinger}}{n}$
Nitrogen Air	88 44	$2.9\\0.4$	18 6.8		$\begin{array}{c} 122 \\ 57 \end{array}$	$\begin{array}{c} 3.0\\ 0.5\end{array}$	25 9.7	2.3 0.5

Table VEffect of Test Atmosphere on the Thermal Decomposition of HydroxyethylCellulose at 10°C/min

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

where q is the heating rate. Plotting the first member of eqs. (3) and (4) against 1/T should give a straight line and allow us to obtain the E and Zvalues if the n value employed is correct. The additional advantage of the Coats-Redfern method is that only one TG curve is required.

In the Kissinger method,⁸ the peak shape or shape index of the DTG curve was quantitatively described. Defined as the absolute value of the ratio of the slopes of tangents to the curve at the left and right inflection points, the shape index can be expressed analytically as

$$S = |(d^2 \alpha / dt^2)_L| / |(d^2 \alpha / dt^2)_R|$$
(5)

where subscripts L and R refer to the value of these quantities at the left and right inflection points (i.e., where $d^3\alpha/dt^3 = 0$). As a matter of fact, the value of $d^2\alpha/dt^2$ can easily be obtained from 2DTG curve. This Kissinger technique allows a rapid calculation of n value from two points (two maximal $d^2\alpha/dt^2$ values at the left positive peak and at the right negative peak on the 2DTG curve at a single heating rate). The shape of DTG curves based on decomposition order (n) via simulation shows the shape indices (S) are 0.17, 0.60, 1.15, and 1.57 for n = 0.5, 1, 2, and 3, respectively, from which the n value can be calculated from the following empirical equation as a function of S value:

$$n = 1.88S \quad (S \ge 0.45)$$
 (6)

$$n = 1.26S^{0.5} \quad (S \le 0.45) \tag{7}$$

RESULTS AND DISCUSSION

Figure 1 gives the TG/DTG/2DTG curves of four cellulose ethers. Comparison of the thermal decomposition parameters in Table I shows that the thermostability of cellulose ethers exhibits a strong dependency on substituted groups. HEC has the lowest T_d , T_{dm} , T_{df} , and $(d\alpha/dt)_m$, but the largest char yield at 400°C among the cellulose ethers listed in Table I. This might be understood from the contribution of a little hydroxyethyl group in the system. The hydroxyethyl group may significantly decrease the pyrolytic temperature, retard carbonization of polymer, and increase pyrolysis residue. The thermostability of a series of cellulose ethers has been studied earlier.⁹⁻¹¹ Their thermal decomposition parameters are summarized in Tables II and III. The significance of the effect of substituted groups on the thermostability of the cellulose ethers is apparent. The thermal stability of cellulose ethers in an inert atmosphere increases on the order of FeCMC, CuCMC, NaCMCX, HEC, TAC, NaCMC, TBEC, CMC, MC, TPC, TMC, EC, TEC, TBC, HPMC, and TMAC.

Further information on the thermal degradation of the cellulose ethers was obtained from the kinetic parameters calculated by the Friedman, Chang, and Kissinger methods (Fig. 2 and Table IV). On the basis of the results obtained by the three calculating methods, the FeCMC has the lowest E and the highest n values, but CuCMC exhibits the highest E value.



Figure 4 High-resolution TG (——), DTG (– – –), and 2DTG (· · ·) curves and accompanying variable heating rate curve (– · – · –) at an initial heating rate of 50°C/min in air and resolution 3 for the cellulose ethers, (a) EC (0.04–0.08 Pa s); (b) HPMC; (c) MC.

The E and $\ln Z$ values obtained by Friedman method are smaller than by Chang method, whereas the n values are slightly larger by Friedman than by other methods except for the EC. The thermal decomposition reaction of FeCMC, NaCMC, and CuCMC in nitrogen may be the fifth-tenth order; the decomposition reaction of HEC might be the third order, but the decomposition reactions of HPMC, MC, and EC may be the first order in nitrogen.

Additionally, there is a significant dependence on the thermal decomposition of cellulose ethers on test atmosphere and measuring mode. Figure 3 shows dynamic TG/DTG/2DTG curves of HEC in air. In the temperature ranges of $\sim 34-100$ and \sim 190–250°C (shoulder peak), the physical desorption of water (intermolecular dehydration) in the sample and intramolecular dehydration from the HEC unit occur, respectively. However, there is no apparent dehydration process of HEC in nitrogen (Fig. 1). Table V compares the thermal decomposition parameters in nitrogen with those found in air. This comparison suggests that the T_d , $(d\alpha/dt)_m$, E, n, and $\ln Z$ values for the thermal decomposition of HEC are larger in nitrogen than in air, indicating the thermostability of HEC in nitrogen is higher than in air, although the T_{dm} , T_{df} , and the char yield at 400°C are slightly lower in nitrogen than in air.

The highest char yield of 38.6% denoted for HEC in air may be the result of the advancement of dehydration reaction. The dehydration may enhance the thermostability of HEC against its decomposition, reduce the formation of flammable volatile, and result in less loss of carbon from the char. Consequently, a product of higher char yield is obtained.¹¹ The highest char yield of ~ 42.5 -63.1% was observed when CMC and its derivatives decomposed thermally and was believed to be the result of the combined effects of $\sim 10-16$ wt % dehydration, inhibition of depolymerization, and inflammable metal ion.¹¹ From Table V, it is noted that the *n* value changes from \sim 2.3–3.0 to $\sim 0.4-0.5$ with the change in test atmosphere from nitrogen to air. This change could be attributed to the change in mechanism of the overall thermal decomposition, including intramolecular dehydration and inhibition of depolymerization.¹¹

High-resolution TG/DTG/2DTG curves in air are shown in Figure 4. The typical Chang and Coats-Redfern plots from the high-resolution TG data are shown in Figure 5. An additional sharp peak at higher temperature was observed for three samples and contributed to the thermal ox-



Figure 5 Typical Chang (a) and Coats–Redfern (b) plots for the calculation of kinetic parameters of thermal degradation of HPMC (\bigcirc) and MC (\triangle) from the high-resolution TG curves shown in Figure 4.

idation and burning of thermal cleavage or scission compounds produced at a relatively low temperature. The thermal decomposition parameters are listed in Tables VI and VII. Almost all of the four thermal degradation temperatures and $(d\alpha/dt)_m$ decrease as compared to those obtained at 10° C/min in nitrogen listed in Table I, because there is a very slow heating rate (the lowest heating rate is ca. 2.8°C/min) in thermal decomposition zone when the high-resolution mode was used. As can be seen in Figure 4, the heating rate decreases sharply with the increase in weight loss and reaches the minimum heating rate at the maximum weight-loss rate to enhance the resolution of the thermograms and derivatograms.

Sample	T_d (°C)	$\begin{array}{c} T_{dm1} \\ (^{\circ}\mathrm{C}) \end{array}$	$T_{dm2} \ (^{\circ}\mathrm{C})$	$\begin{array}{c} T_{df} \\ (^{\circ}\mathrm{C}) \end{array}$	Char Yield at 400°C (wt %) 4.9 16.6		$(dlpha/dt)_m$ (%/min)
EC ^a HPMC	$294 \\ 309$	$301 \\ 329$	411 494	$\begin{array}{c} 323\\ 344 \end{array}$			$12.0 \\ 9.9$
MC	309	328	492	342	1	5.5	10.2
		Friedman			Chang		
Sample	E (kJ/mol)	n	ln Z (L/min)	<i>E</i> (kJ/mol)	п	ln Z (L/min)	$\frac{\text{Kissinger}}{n}$
EC HPMC MC	130 106 102	0.7 0.7 0.6	25 19 19	119 117 107	$1.8 \\ 2.0 \\ 1.5$	23 22 20	$3.5 \\ 3.1 \\ 2.5$

Table VIResults of Thermogravimetric Analyses for Cellulose Ethers at an Initial Heating Rate50°C/min in Air by a High-Resolution TG Mode with a Resolution 3

^a Solution viscosity is 0.04–0.08 Pa s.

However, the E and $\ln Z$ values listed in Tables VI and VII for the major thermal decomposition maintain an early constant in comparison with those listed in Table IV in spite of the variation of test atmosphere from nitrogen to air, except for those values of HPMC and MC obtained by Coats-Redfern method. Only n values are larger in air than in nitrogen. Different kinetic parameters obtained by different methods were observed on other polymer degradation¹²⁻¹⁴ and are generally ascribed to the different mathematical approaches used to evaluate the kinetic parameters in a different temperature range.

There may be no effect of molecular weight on the thermal decomposition temperatures and kinetic parameters of EC, as shown in Figure 4(a)and 6 and Table VIII.

CONCLUSIONS

Conventional constant heating rate TG and highresolution TG with a variable heating rate were

Table VII Kinetic Parameters of Thermal Decomposition of Cellulose Ethers at an Initial Heating Rate of 50°C/min in Air by High-Resolution TG Obtained by Coats-Redfern Method

Sample	E (kJ/mol)	n	ln Z (L/min)	Correlation Coefficient
EC HPMC MC	$120 \\ 218 \\ 224$	$2.0 \\ 3.0 \\ 2.5$	$23 \\ 43 \\ 45$	0.9141 0.9921 0.9978

used to determine the thermal stability and degradation kinetics in both nitrogen and air. In an inert atmosphere, the cellulose ethers exhibit thermal degradation temperatures ranging from 260 to 390°C and seem to follow the first-order decomposition reaction with the activation energy and natural logarithm frequency factor of 110–



Figure 6 High-resolution TG (——), DTG (–––), 2DTG (· · ·) variable heating rate (· – · – ·) curves for ethyl cellulose with solution viscosity of 0.2 Pa s at an initial heating rate of 50°C/min and resolution 3 under air.

Solution Viscosity of EC (Pa s)	T_d (°C)	$T_{dm1} \ (^{\circ}C)$	$T_{dm2} \ (^{\circ}C)$	<i>T_{dm3}</i> (°C)	T_{df} (°C)	Char Yield at 400°C (wt %)	$(dlpha/dt)_m$ (%/min)
0.04-0.08	294	242	300	410	325	2.9	12.0
0.2	265	269	304	433	328	17.0	8.5
		Friedman			Chang		
Solution Viscosity of EC	E		$\ln Z$	E		$\ln Z$	Kissinger
(Pa s)	(kJ/mol)	n	(L/min)	(kJ/mol)	n	(L/min)	n
0.04-0.08	130	0.7	25	119	1.8	23	3.5
0.2	87	0.9	16	92	1.8	18	3.6

Table VIII Effect of Molecular Weight on the Thermal Degradation of Ethyl Cellulose in Air at an Initial Heating Rate of 50°C/min by a High-Resolution TG Mode with a Resolution 3

170 kJ/mol and $20-30 \text{ min}^{-1}$, except for HEC, CMC, and its derivates, the degradation temperature and activation energy of which are down to 200°C and 76 kJ/mol, respectively, but the thermal decomposition order are up to 9.8. The thermal degradation temperatures and activation energies obtained by the same calculating technique for the cellulose ethers are usually lower in air than in nitrogen. The thermal decomposition data depend on the substituent, degree of substitution, molecular weight of the cellulose ethers, test mode, and calculating method.

REFERENCES

- 1. Li, X.-G.; Huang, M.-R. Polym Bull (Beijing) 1990, 213.
- Huang, M.-R.; Li, X.-G. J Appl Polym Sci 1994, 54, 463.

- Prasad, M. P.; Kalyanasundaram, M. J Appl Polym Sci 1994, 54, 1879.
- Zeng, H.; Li, W.; Li, Z. J Appl Polym Sci 1994, 54, 1989.
- Li, X.-G.; Huang, M.-R.; Bai, H. Angew Makromol Chem 1998, 256, 9.
- Li, X.-G.; Huang, M.-R.; Guan, G.-H.; Sun, T. Polym Int 1998, 46, 289.
- 7. Coats, A. W.; Redfern, J. P. Nature 1964, 201, 68.
- 8. Kissinger, H. E. Anal Chem 1957, 29, 1702.
- 9. Kondo, T.; Isogai, A.; Ishizu, A.; Nakano, J. J Appl Polym Sci 1987, 34, 55.
- Isogai, A.; Ishizu, A.; Nakano, J. J Appl Polym Sci 1985, 30, 345; J Appl Polym Sci 1986, 31, 341.
- Venkateswaran, R.; Babu, S.; Kumar, S. S.; Pillai, M. A.; Sharma, P. V. J Appl Polym Sci 1990, 41, 2783.
- Eguiazabal, J. I.; Calahorra, M. E.; Cortazar, M. M.; Guzman, G. M. J Polym Sci, Polym Lett Ed 1986, 24, 77.
- Huang, M.-R.; Li, X.-G. J Appl Polym Sci 1998, 68, 293.
- 14. Li, X.-G. J Appl Polym Sci 1999, 71, 573.