Kinetics of Hydrolysis and Thermal Degradation of Polyester Melts

KAB S. SEO and JAMES D. CLOYD

Eastman Kodak Company, Eastman Chemical Company, Research Laboratories, Kingsport, Tennessee 37662

SYNOPSIS

Polyester melts exhibit two discrete degradation rates depending on the moisture content in the solid state. The initial fast rate is very sensitive to the moisture content while the later slow rate is not sensitive to the moisture content. The former is attributed to hydrolysis and the latter is attributed to thermo-oxidative degradation. A combined kinetic equation which represents both hydrolysis and thermo-oxidative degration of the polyester melt is proposed. The model equation agrees well with the experimental data. A method to determine hydrolytic and thermal degradation rate constants, moisture content, molecular weight for polyesters by means of a melt viscometry is discussed.

INTRODUCTION

The degradation rate of polymer melts, in the opposite sense of thermal stability, is often defined as the rate of chain breakage as represented in the following equation[1]

$$\frac{1}{\overline{DP}} = \frac{1}{\overline{DP}_o} + kt \qquad (1)$$

where $\overline{DP}_o$ and $\overline{DP}$ are the initial and final number average degree of polymerization, respectively. The degree of polymerization can be monitored by various methods including end-group analysis, gel permeation chromatography (GPC), osmometry, ebuliometry, or viscometry. The solution methods usually require a periodic measurement of the chain length at different degradation stages and can be employed only for soluble polymers in an appropriate solvent. On the other hand, the melt viscometry can continuously monitor the chain length and is useful for insoluble polymers. When only one degradation rate is involved, the thermal degradation rate constant for a linear polymer may be determined from the melt viscosities at different times[2]

$$\frac{1}{\eta^a} = \frac{1}{\eta_o^a} + kt \qquad (2)$$

where η_o is the initial melt viscosity of the polymer and η is the viscosity at time t, k is the thermal degradation rate constant, and a is a constant equal to $1/3.4$ from the 3.4th power relationship of molecular weight and melt viscosity. Eq. (2) predicts a straight line for $\frac{1}{\eta^a}$ vs. time plot for a single degradation rate. However, polyester melts usually show dual slopes consisted of an initial fast rate and a later slow rate. Our preliminary experimental results for polyethylene terephthalate (PET) have shown that the initial rate is very sensitive to the moisture content in the sample while the later slow rate is much less sensitive to the moisture content. Therefore, the initial fast rate is attributed to hydrolysis driven mainly by the residual water in the sample while the later slow rate is attributed to thermo-oxidative chain breakdown initiated by the thermal energy.[3] We refer to the latter as "thermal degradation" hereafter. The rate of hydrolysis of ester links has been reported to be several orders of magnitude higher than thermal breakdown rate.[4,5] Thus, the initial hydrolysis contribution is often expressed as a constant term in a degradation kinetic equation for molten polyesters, or neglected for the dry sample.[6] As industrial processes show trends of moving to shorter extrusion melt residence times, the simplification of treating hydrolysis in this manner will not be appropriate. In the present study we derive a kinetic equation which combines both hydrolysis and thermal degradation of polyester melts.

EXPERIMENTAL

Materials

The polyethylene terephthalate (PET) samples Eastman Chemical Company with weight average molecular weights ($\overline{M_W}$) ranging from 40,000 to 45,000 were used in this study. The moisture content of sample was controlled by drying time and measured by Karl Fischer method. Samples were dried at 100°C under the vacuum.

Rheology

The melt viscosity change of the sample at 285°C was monitored with a Rheometrics Mechanical Spectrometer (RMS 7220) with eccentric rotational disks (ERD) at 25 rad/sec. The sample was heated for 3 min before measurements.

Experimental Results

Typical plots of melt viscosity versus time for dried and undried PET samples are shown in Figure 1. Two degradation rates are clearly seen especially for the undried sample. There is a substantial difference in the initial degradation rates between dried and undried samples while the degradation rates at the later stage are close to each other.

DEGRADATION KINETICS

In view of the experimental results, the degradation of the polyester melt is considered to have two contributions, namely hydrolysis and thermal degradation. The oxidative reaction and alcoholysis which will affect the degradation rate in any stage of degradation is not considered separately from the two
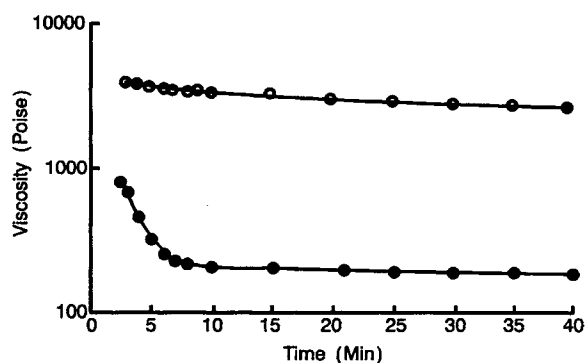
Figure 1   Melt viscosity of PET at 285°C, (O) dried for 24 hours; (●) undried.

contributions in this study. A random scission of ester links is assumed in any case.

Hydrolysis

The rate of breakdown of ester links by hydrolysis may be expressed as[5,7]

$$\left[\frac{d\phi}{dt}\right]_H = -k_H(\phi_o - r)(x_o - r) \qquad (3)$$

where ϕ is the number of available ester links at time t, ϕ_o is the initial number of ester links, r is the number of moles of water reacted, x_o is the initial number of moles of water, and k_H is the rate constant. The subscript H represents hydrolysis. All the parameters here are in number density, e.g., number per unit volume. Rewriting eq. (3), we have

$$\left[\frac{d\phi}{dt}\right]_H = -k_H\phi_x \qquad (4)$$

where x is the number of moles of unreacted water. We assume that all the water molecules react with ester links without drying, i.e., the rate of water consumption is same as the rate of ester link breakdown by hydrolysis. Then the rate of water consumption can be written as

$$\frac{dx}{dt} = \left[\frac{d\phi}{dt}\right]_H = -k_H(\phi_o - x_o + x)x \qquad (5)$$

Since $(\phi_o - x_o) \gg x$ for a moisture content less than 0.5% (by weight) and the number average degree of polymerization $\overline{DP}$ much greater than unity, eq. (5) becomes

$$\frac{dx}{dt} = -k_H(\phi_o - x_o)x \qquad (6)$$

The solution for eq. (6) gives the concentration of unreacted water at time t as

$$x = x_o\exp[-\xi t] \quad \text{where} \quad \xi = k_H(\phi_o - x_o) \qquad (7)$$

By combining eqs. (4) and (7), the rate of hydrolysis can be written as

$$\left[\frac{d\phi}{dt}\right]_H = -k_Hx_o\phi \exp[-\xi t] \qquad (8)$$

Thermal Degradation

If the thermal breakdown reaction is assumed to be a first order reaction the concentration of ester links can be written as[3,8]

$$\left[\frac{d\phi}{dt}\right]_T = -k_T\phi \qquad (9)$$

where k_T is the thermal breakdown rate constant. The subscript T represents thermal degradation.

Hydrolysis and Thermal Degradation

The overall breakdown rate of ester links may be represented as the sum of hydrolysis and thermal breakdown contributions. Combining eqs. (8) and (9) we have

$$\frac{d\phi}{dt} = -k_H x_o \phi \exp[-\xi t] - k_T\phi \qquad (10)$$

Solving the differential eq. (10) we get

$$\ln\frac{\phi}{\phi_o} = -\frac{x_o}{\phi_o - x_o} + \frac{x_o}{\phi_o - x_o}\exp[-\xi t] - k_T t \qquad (11)$$

The number of ester links ϕ in eq. (11) can be replaced by the number average degree of polymerization $\overline{DP}$ through the following relationship[8]

$$\phi = N\left(1 - \frac{1}{\overline{DP}}\right) \qquad (12)$$

where N is the total number of monomer units. Using the following approximation when $\overline{DP} \gg 1$

$$\ln\left(1 - \frac{1}{\overline{DP}}\right) \cong -\frac{1}{\overline{DP}}$$

eq. (11) can be written as

$$\frac{1}{\overline{DP}} - \frac{1}{\overline{DP}_o}$$

$$= \frac{x_o}{\phi_o - x_o} - \left(\frac{x_o}{\phi_o - x_o}\right)\exp[-\xi t] + k_T t \qquad (13)$$

Using the following relationship[9]

$$\overline{DP} = \overline{M_n}/M_o$$

$$\eta = KM^{3.4}$$

where M = molecular weight of polymer; M_o = molecular weight of monomer, e.g., 96 for polyethylene terephthalate (PET); and K = a front factor, eq. (13) can be expressed as

$$\frac{1}{\eta^a} = \frac{1}{\eta_o^a} + A - A\exp[-\xi t] + k_2 t \qquad (14)$$

where

$$a = 1/3.4$$

$$A = x_o/[M_o K^a(\phi_o - x_o)]$$

$$k_2 = k_T/M_o K^a$$

Here we assume that the polydispersity ($\overline{M_W}/\overline{M_n}$) does not change during degradation. Eq. (14) represents the viscosity as a function time and includes both hydrolysis and thermal degradation contributions. When time t is small, more strictly $\xi t \ll 1$, eq. (14) can be approximated into an equation which represents the hydrolysis only. Neglecting the thermal degradation term ($k_2 t$) and expanding the exponential term we get

$$\frac{1}{\eta^a} = \frac{1}{\eta_o^a} + A\xi t \qquad (15)$$

or

$$\frac{1}{\eta^a} = \frac{1}{\eta_o^a} + k_1 t \qquad (16)$$

where $k_1 = A\xi = k_H x_o/(M_o K^a)$. The apparent hydrolysis rate constant k_1 is determined from the slope of $\frac{1}{\eta^a}$ vs. t plot when t is small. It is noted that k_1 is proportional to k_H and the initial water content x_o but independent of the molecular weight. On the other hand, at the later stage when t is long enough, eq. (14) can be reduced to

$$\frac{1}{\eta^a} = \frac{1}{\eta_o^a} + A + k_2 t \qquad (17)$$

Eq. (17) represents the thermal degradation after completion of hydrolysis. The thermal degradation rate constant k_2 depends only on the degradation rate constant k_T as defined in eq. (9). It is noted that the term A in eq. (17) is the difference in intercepts of eqs. (16) and (17). If there is no initial water in the sample, A is zero and eq. (17) represents thermal degradation only as in eq. (2).
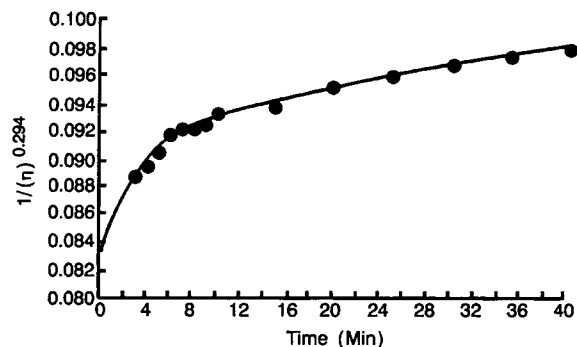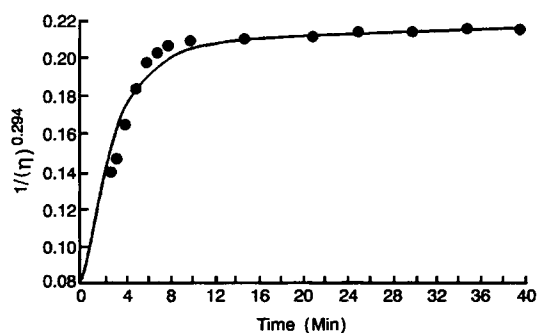
Figure 2 Curve fitting of eq. (14) for dried PET. (●) experiment; (——) $0.0920-0.0095 \cdot \exp(-0.32 \cdot t)$ $+ 0.000181 \cdot t$.

DISCUSSION

In Figure 2 is shown a curve fitting result of eq. (14) to experimental data for a dried PET sample. The model equation agrees well with the experimental data for the dried PET. In Figure 3 was made a curve fitting for the undried sample using the values of η_o, ξ, and k_2 estimated for the dried sample as in Figure 2. Although the lack of fitting of the model equation to the experimental data is noticable for the undried sample the qualitative agreement is very good. The discrepancy can be attributed to many things such as evaporation of water, generation of small bubbles during test resulting in erroneous viscosity values and self-catalytic effect of end-groups produced by hydrolysis.

The initial viscosity η_o estimated from the curve fitting can be converted to the weight average molecular weight of the virgin polymer by using 3.4th power law and a known front factor. Instead of using eq. (14) with four unknown parameters, one may want to use simpler forms as in eqs. (16) and (17)

Figure 3 Curve fitting of eq. (14) for undried PET. (●) experiment; (——) $0.20875-0.12626 \cdot \exp(-0.32 \cdot t)$ $+ 0.000181 \cdot t$.

Table I Comparison of Molecular Weights Measured by GPC and Those Determined from Intercepts of Eq. (16)

Sample	$1/\eta_o^a$	$\overline{M_w}$ (RMS)	$\overline{M_w}$ (GPC)
B1	.0908	47072	43342
B2	.0875	48836	41140
B3	.0823	51944	44231
B4	.0907	47114	44649
B5	.0930	45984	42543
B6	.0878	48708	43751

to estimate η_o, ξ, A, k_1, and k_2. In Table I, the molecular weights determined from the initial melt viscosity η_o estimated from the intercept of eq. (16) using three initial data points and those determined by GPC are compared. For the estimation of molecular weight from η_o the relationship $\eta_o = 4.46 \times 10^{-13} \, (\overline{M_w})^{3.4}$ was used. The front factor 4.46 $\times 10^{-13}$ was estimated comparing the melt viscosity and the GPC molecular weight for several PET samples. Although the agreement between two methods is reasonably good, care must be taken to estimate the molecular weight from the melt viscosity η_o. There exists an uncertainty in degradation rate at the very early stage of the experiment when the sample does not reach the exact test temperature. More detailed work for the induction period at the very early stage of degradation is necessary to predict an accurate molecular weight from the present kinetic equations. The effect of the test temperature and additives such as plasticizers on melt viscosity should also be taken into account before converting the initial melt viscosity to the molecular weight. In Table II are listed the hydrolysis rate constant (k_1) and the thermal degradation rate constant (k_2) determined by eqs. (16) and (17), respectively. The estimation of k_1 was based on the data when $t \leq 5$ min and k_2 was estimated when $t \geq 15$ min. It is clearly seen that the hydrolysis rate constant is very sensitive to the moisture content

Table II Effect of Moisture on Hydrolysis Rate Constant (k_1) and Thermal Degradation Rate Constant (k_2) of PET

Moisture Wt %	k_1	k_2
0.274	0.0150	0.00076
0.063	0.0081	0.00042
0.007	0.0016	0.00032

while the thermal degradation rate constant is relatively insensitive to the moisture as predicted in the present kinetic equations. It is also noticed that the hydrolysis rate constant is at least an order of magnitude higher than the thermal degradation rate constant depending upon the moisture content.

It is trivial to estimate k_H from ξ determined from the curve-fitting result. In Figures 2 and 3 we had ξ value of 0.32 and in eq. (7) we defined

$$\xi = k_H(\phi_o - x_o) \cong k_H\phi_o$$

Since $\phi_o \cong 200$ for the PET with the molecular weight of about 40,000 ($\overline{M_n} = 20,000$), $k_H = 1.6 \times 10^{-3}/(\text{mole min})$. This value is an order of magnitude lower than the literature[5,7] values of k_H measured for the solid PET film and extrapolated to 285°C. Similarly, k_T defined in eq. (9) can be estimated using the relationship in eq. (14). For example,

$$k_T = k_2 M_o K^a \cong 1.44 \times 10^{-5}$$

for the dried PET in Table II with $k_2 = 0.00032$, $M_o = 96$, $K = 4.71 \times 10^{-12}$, and $a = 0.294$. The values for A estimated from Figures 2 and 3 are 0.0095 for the dried PET and 0.1262 for the undried PET. They can be easily converted into the initial moisture content using the following relationships

$$A = x_o/[M_o K^a(\phi_o - x_o)] \cong x_o/[M_o K^a\phi_o]$$

$$\% \ H_2O = 1800 x_o/\overline{M_n}$$

When $M_o = 96$, $K^a = (4.71 \times 10^{-12})^{0.294}$, $\phi_o \cong 200$, and $\overline{M_n} \cong 20,000$, the A values give 0.008% H_2O and 0.102% H_2O, respectively, which are comparable to the typical moisture content of PET in Table II. The lower value of the calculated moisture content than the measured for the undried PET is probably due to the drying effect of moisture during the melt viscosity measurement.

CONCLUSION

The hydrolysis and thermal degradation rates of molten polyesters can be expressed in a single kinetic equation. The hydrolysis rate strongly depends on the moisture content in the solid state while the thermal degradation rate is insensitive to the moisture. The suggested model equation describes well the melt viscosity change of polyesters as a function of time and can be used to determine hydrolysis rate constant, thermal degradation rate constant, initial moisture content, and molecular weight of polyesters.

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