

Thermal and Hydrolytic Degradation of Poly(1,4-cyclohexylenedimethylene Terephthalate)

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Synopsis

The kinetics of simultaneous thermal and hydrolytic degradation of poly(1,4-cyclohexylenedimethylene terephthalate) (PCHDT) were evaluated by using a 1.5-in.-diam. melt extruder ($\approx 20/1$ length/diameter ratio) as a reactor. The effects of extrusion temperature (295°–330°C), residence time (2.6–17.5 min), and moisture content (<0.001% to 0.2%) of the supply polymer on degradation were determined. The rate of degradation was measured in terms of the rate at which inherent viscosity (I.V.) decreased and the rate at which carboxyl endgroup concentration increased. The contributions of both thermal and hydrolytic degradation to the total degradation of PCHDT could be separated because the hydrolysis was rapid enough that it could be considered as occurring prior to thermal degradation. Thus, the hydrolysis merely adjusted the initial properties of the supply polymer, which was then subjected to thermal degradation. Equations were developed from an analysis of the kinetic data based on a random chain scission mechanism. The activation energies for decrease in I.V. and increase in carboxyl endgroup concentration of PCHDT from thermal degradation were determined as 33.5 and 41 kcal/mole, respectively.

INTRODUCTION

Poly(1,4-cyclohexylenedimethylene terephthalate) (PCHDT) is a synthetic polyester which was discovered by Tennessee Eastman Company¹ and became the basis for Kodel polyester fiber. It currently finds extensive use as a carpet fiber.

During the melt extrusion of PCHDT to produce fibers, the extrusion temperature and the moisture in the supply polymer cause degradation. In this paper, we discuss the thermal and hydrolytic degradation of this polyester during passage through a 1.5-in.-diam. melt extruder.

In earlier work, Gregory and Watson used a laboratory extruder to determine the effects of oxygen and temperature on the degradation of PCHDT.² They found that the oxygen content of the gas used to purge the polymer during drying prior to extrusion had no measurable effect on degradation when I.V. and carboxyl endgroup concentration were used as responses. Gregory and Watson² also showed that the overall kinetic equations describing thermal degradation of PCHDT were in agreement with a random chain scission mechanism.

Several workers have investigated the thermal degradation of poly(ethylene terephthalate) (PET)³⁻⁶ and other polyesters.⁷ Investigations by Ritchie³ on the mechanism of thermal degradation of PET, using related model compounds, showed that the initial breakdown in the decomposition is a primary alkyl-oxygen scission of the β -hydrogen type. Pohl⁴ interpreted his chemical and infrared examinations of the products of degradation of PET as typical of random chain scission to produce new endgroups and shorter chains. Marshall and Todd⁵ studied the kinetics of degradation of PET in an oxygen-free atmosphere by measuring the change of melt viscosity as a function of time. They calculated the initial rate of degradation from the decrease in melt viscosity and found it to be in good agreement with that calculated from the standard equations for random chain scission. Goodings⁶ measured the rate of thermal degradation of PET in terms of the following rates: gas evolution; decrease of hydroxyl endgroups, melt viscosity, and intrinsic viscosity; and increase of carboxyl endgroups and color. The equations he developed were in general agreement with random chain scission. Goldfarb and McGuchan⁷ investigated the overall degradation of eight polyesters using thermogravimetry, mass-spectral thermal analysis, infrared-spectral studies, and product and residue analyses by gas chromatography and mass spectrometry. The overall kinetics were consistent with a random chain scission mechanism.

Gregory and Watson,² in their kinetic analysis of the thermal degradation of PCHDT, developed the following equation in terms of I.V. based on random chain scission:

$$\frac{1}{[\text{I.V.}_{(t)}]^{1.37}} - \frac{1}{[\text{I.V.}_{(0)}]^{1.37}} = \frac{k_{\text{I.v.}}}{2(4.98 \times 10^{-4})^{1.37}} t \quad (1)$$

where $\text{I.V.}_{(t)}$ is the inherent viscosity at time t , in dl/g; $\text{I.V.}_{(0)}$ is the inherent viscosity of the supply polymer, in dl/g; $k_{\text{I.v.}}$ is the reaction rate constant, in moles of random chain breaks/g-min; and t is the residence time, in min.

The reaction rate constant was related to temperature through the Arrhenius equation²:

$$k_{\text{I.v.}} = \exp\left(21.373 - \frac{19,500}{T}\right) \quad (2)$$

where T is the temperature, in °K.

In this investigation, the following equation was developed to relate the I.V. of PCHDT to residence time, moisture content, and temperature:

$$\frac{1}{[\text{I.V.}_{(t)}]^{1.37}} - \frac{1}{[\text{I.V.}_{(p)}]^{1.37}} = \frac{k_{\text{I.v.}}}{2(4.98 \times 10^{-4})^{1.37}} t \quad (3)$$

where $\text{I.V.}_{(p)}$ is the inherent viscosity after reaction with the initial moisture present, assuming the most probable molecular weight distribution. Moore presented equations from which $\text{I.V.}_{(p)}$ can be calculated.⁸ They are

$$\text{I.V.} = 4.98 \times 10^{-4}(\bar{M}_w)^{0.73} \quad (4)$$

and

$$(\bar{M}_w)_n = \frac{3600(\bar{M}_w)_0}{3600 + (X)(\bar{M}_w)_0} \quad (5)$$

where \bar{M}_w is the weight-average molecular weight; $(\bar{M}_w)_n$ is the weight-average molecular weight after hydrolysis; $(\bar{M}_w)_0$ is the weight-average molecular weight before hydrolysis; and X is the moisture in the supply polymer, in wt.-%.

Equation (5) was derived assuming that 1 mole of water results in the formation of lower molecular weight PCHDT. By solving the previous equations, we obtained the following equation for calculating I.V._(p) from inherent viscosity and moisture data:

$$\text{I.V.}_{(p)} = [394.5 \text{ I.V.}_{(0)}][3600 + (X)(2008 \text{ I.V.}_{(0)})^{1.37}]^{-0.73} \quad (6)$$

A rate expression is not required in eq. (6) because hydrolytic degradation is much faster than thermal degradation for PCHDT in the melt. Thus, the initial I.V. required for calculating thermal degradation is that I.V. which remains after hydrolytic degradation. The Arrhenius equation relating $k_{\text{I.V.}}$ and temperature is

$$k_{\text{I.V.}} = \exp\left(16.912 - \frac{16,840}{T}\right) \quad (7)$$

A plot of the Arrhenius equation for $k_{\text{I.V.}}$ is presented in Figure 1.

Goodings,⁶ in his kinetic analysis of thermal degradation of PET, and Gregory and Watson,² in their kinetic analysis of thermal degradation of PCHDT, used the integrated form of the following differential equation (zero-order model) for carboxyl endgroup buildup:

$$\frac{dC}{dt} = k_c \quad (8)$$

where C is the carboxyl endgroup concentration, in equiv/10⁶ g; and k_c is the specific reaction rate based on carboxyl end group concentration, in equiv/10⁶ g-min. The integrated form is

$$C_{(t)} - C_{(0)} = k_c t \quad (9)$$

where $C_{(t)}$ is the carboxyl endgroup concentration at time t , in equiv/10⁶ g; $C_{(0)}$ is the carboxyl endgroup concentration in supply polymer, in equiv/10⁶ g; and t is the residence time, in min.

In this investigation, the following equation was developed to relate buildup of carboxyl endgroup concentration in PCHDT extrudate to temperature and residence time in the extruder and to moisture content and carboxyl end group concentration in the supply polymer:

$$C_{(t)} = C_{(0)} + C_{(H)} + tAe^{-E_a/RT} \quad (10)$$

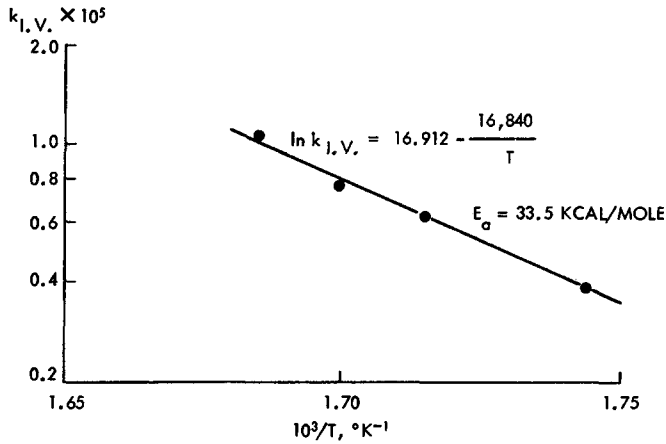


Fig. 1. Arrhenius plot: reaction rate constant based on inherent viscosity.

The $C_{(H)}$ (carboxyl endgroup concentration due to hydrolysis, in equiv/ 10^6 g) is calculated as follows:

$$C_{(H)} = 555.6 (X). \quad (11)$$

The equation of $C_{(H)}$ was derived assuming that, for each mole of water which reacts, a mole of carboxyl endgroups is formed.⁹

The Arrhenius equation relating k_c and temperature is

$$k_c = \exp \left(37.0 - \frac{20,552}{T} \right). \quad (12)$$

An Arrhenius plot relating k_c and temperature is presented in Figure 2.

There is a paucity of data in the literature regarding the rate at which PET or PCHDT hydrolyzes in the melt. Marshall and Todd⁶ found that

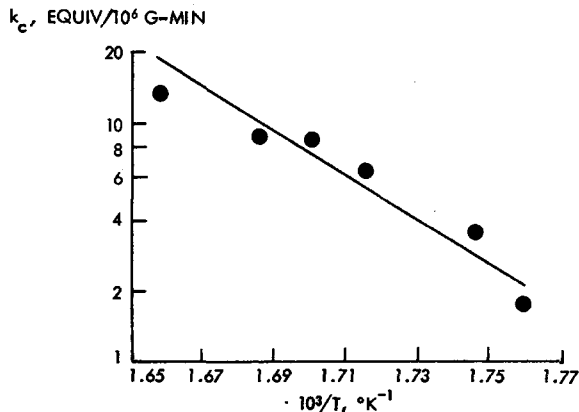


Fig. 2. Arrhenius plot: reaction rate constant based on carboxyl endgroup concentration.

water in molten PET was used virtually instantaneously in hydrolysis. McMahon et al.¹⁰ reported that at 100% R.H., hydrolysis of PET at 100° to 120°C proceeds 10,000 times faster than thermal degradation.

The objective of this work was to determine the effects of residence time, extrusion temperature, and moisture content of the supply polymer on the degradation of PCHDT during melt extrusion, when I.V. and carboxyl endgroup concentration were used as responses; and further, to develop kinetic equations that would enable us to predict these properties of the extrudate accurately.

This work should have relevance to thermoplastic processing because of the analytical method that was devised. By this method, contribution of both hydrolytic and thermal degradation to the total degradation of PCHDT could be separated. The analysis should be applicable to any polymer where conditions are such that hydrolytic degradation is much faster than thermal degradation.

EXPERIMENTAL

In the experimental design, moisture levels of 0.012%, 0.027%, and 0.055% in the supply polymer, average extrusion temperatures of 300°, 310°, and 320°C, and average residence times of 3.5, 7.0, and 17.5 min were included. All combinations of the above variables were also included, and each combination was replicated three times. Additional evaluations were made for temperatures of 295°, 315°, and 330°C, residence times of 2.6, 5.0, and 10 min, and 0.2% moisture in the polymer.

PCHDT produced as pellets by standard procedures¹ was used in each evaluation. Moisture levels in the supply polymer, except for 0.2%, were adjusted by drying PCHDT in a double-cone tumble dryer for various lengths of time. PCHDT containing 0.2% moisture was obtained by submerging the pellets in water for three days. Sufficient polymer for an entire moisture level evaluation was prepared at one time.

PCHDT pellets were fed by gravity to a laboratory 1.5-in.-diam. melt extruder equipped with a gear pump. Melt temperature was controlled to within $\pm 1^\circ\text{C}$ for all temperatures investigated, and pump speed was controlled to $< \pm 0.5$ rpm. Moisture content in the supply polymer was controlled to about $\pm 40\%$ of the average value.

Three samples of supply polymer and extrudate were collected for each experimental condition and were analyzed for I.V. and carboxyl endgroup concentration. The method of determining carboxyl endgroup concentration was essentially the same as that described by Pohl.¹¹ Inherent viscosities were determined by the method of Smith and co-workers.¹² Moisture contents were determined with a Consolidated Electroynamics Corporation moisture analyzer. A carrier gas was used to sweep the moisture into an electrolytic cell. The cell current was integrated with time to provide a measurement of total moisture.¹³

RESULTS AND DISCUSSION

Residence time, temperature, and moisture all contributed significantly to the degradation of PCHDT during melt extrusion. Experimental results are given in Table I. Some results for I.V. breakdown of PCHDT during melt extrusion are also presented in Figure 3. These curves show I.V. as a function of residence time for various temperatures and one moisture content (0.012%). As expected, on increase in residence time or extrusion temperature caused a decrease in I.V.

The results for carboxyl endgroup buildup as a function of residence time for various temperatures and one moisture level (0.027%) are presented in Figure 4. Carboxyl endgroup concentration increased as temperature or residence time increased.

The method used to analyze data allowed us to separate the contributions of both thermal and hydrolytic degradation to total degradation of PCHDT.

TABLE I
Experimental Results for Thermal and Hydrolytic Degradation of PCHDT

PCHDT moisture content, %	I.V. _(t) , dl/g	I.V. _(p) , dl/g	Temp., °C	Resi- dence time, min	I.V. _(t) , dl/g	$\frac{1}{[I.V.(t)]^{1.37}}$	C _(t) , equiv/ 10 ⁶ g	C _(p) , equiv/ 10 ⁶ g
0.012	0.770	0.729	300	3.5	0.676	1.710	11.0	22.5
				7.0	0.617	1.938		31.4
				17.5	0.501	2.578		74.6
			310	3.5	0.641	1.839		26.8
				7.0	0.566	2.181		42.8
				17.5	0.412	3.370		112.4
			320	3.5	0.593	2.046		30.4
				7.0	0.485	2.695		55.0
				17.5	0.338	4.420		179.0
0.027	0.812	0.716	300	3.5	0.657	1.778	12.6	42.5
				7.0	0.581	2.104		58.3
				17.5	0.441	3.070		103.0
			310	3.5	0.632	1.875		48.7
				7.0	0.516	2.476		75.3
				17.5	0.372	3.876		161.2
			320	3.5	0.551	2.263		64.9
				7.0	0.454	2.950		111.0
				17.5	0.303	5.134		214.2
0.005	0.772	0.686 ^a	300	3.5	0.599	2.018	14.3	43.7
				7.0	0.595	2.037		56.6
				17.5	0.462	2.880		93.1
			310	3.5	0.590	2.060		49.5
				7.0	0.505	2.550		66.0
				17.5	0.357	4.101		143.6
			320	3.5	0.553	2.251		67.2
				7.0	0.432	3.158		111.7
				17.5	0.296	5.301		212.0

^a Calculated from eq. (6) using 0.027% moisture content; extruder acted as dryer to reduce moisture level to 0.027%.

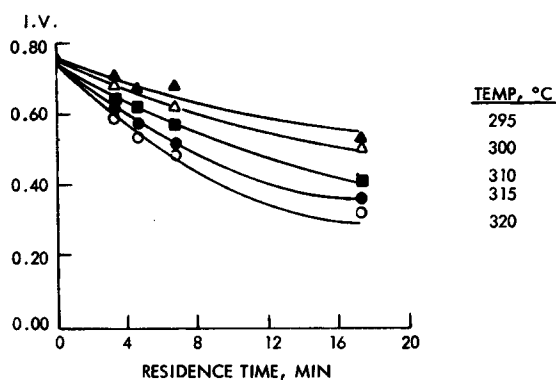


Fig. 3. Inherent viscosity breakdown during melt extrusion. Moisture in supply polymer, 0.012%.

Although the kinetics of hydrolysis are not included or are not even required (except that hydrolysis is rapid), the method of analysis is effective because hydrolytic degradation is much more rapid than thermal degradation in the melt. In fact, the hydrolysis is rapid enough that, for practical purposes, it can be assumed to occur prior to thermal degradation during melt extrusion. The hydrolysis can be thought of as merely adjusting the initial properties of the supply polymer, which is then subjected to thermal degradation. Extrapolation of experimental data ($1/[I.V.(t)]^{1.37}$ and carboxyl endgroup concentration versus residence time with temperature as a parameter) to zero residence time should yield these initial properties as intercepts on the ordinate independent of temperature. The difference between intercept values and those of the supply polymer before extrusion should equal the degradation attributable to hydrolysis.

Specifically, based on eqs. (3) and (10), $1/[I.V.(t)]^{1.37}$ is plotted in Figure 5 versus residence time for various temperatures, and carboxyl endgroup con-

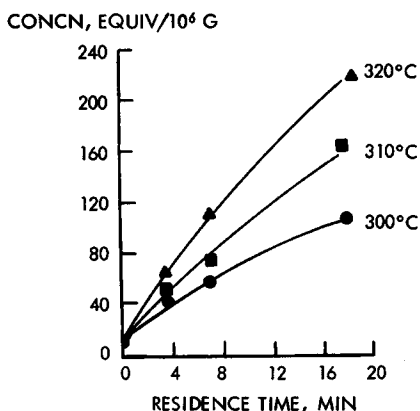


Fig. 4. Carboxyl endgroup buildup during melt extrusion. Moisture in supply polymer, 0.027%.

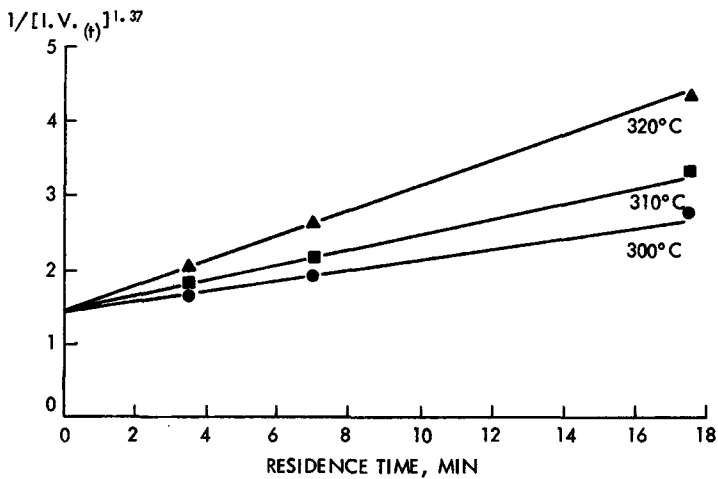


Fig. 5. Kinetic analysis based on inherent viscosity. Moisture in supply polymer, 0.012%.

centration is plotted in Figure 6 versus residence time for various temperatures. When this procedure was repeated for each moisture level, a family of straight lines with different slopes resulted. These data were extrapolated to zero residence time, where they did in fact intersect at a point on the ordinate at zero residence time. The differences (in both I.V. and carboxyl endgroup concentration) between these extrapolated points of intersection and their values in the supply polymer were equal to the calculated differences from hydrolysis alone (assuming 100% reaction of water present). Thus, the method of analysis used in this investigation was justified, because hydrolysis of PCHDT is indeed much more rapid than thermal degradation.

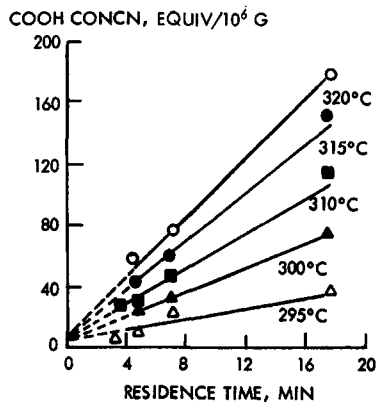


Fig. 6. Kinetic analysis based on carboxyl endgroup concentration. Moisture in supply polymer 0.012%.

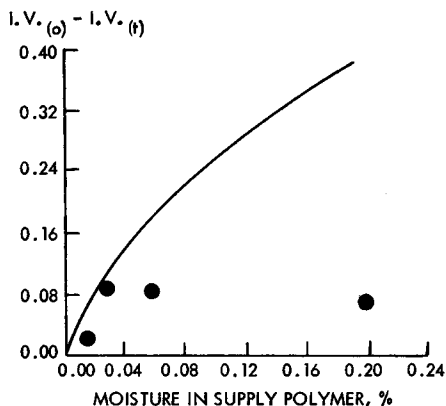


Fig. 7. Effect of moisture in supply polymer on inherent viscosity breakdown. Theoretical breakdown based on 100% conversion of water during hydrolysis.

For moisture contents above 0.027% in the supply polymer, experimental values (based on intercept of measured response at zero residence time) of hydrolytic breakdown and theoretical values of hydrolytic breakdown (based on complete reaction of all moisture in the supply polymer) did not agree. These data are shown in Figures 7 and 8. In Figure 7, the theoretical and experimentally determined values of I.V. are plotted versus per cent moisture in the supply polymer. Theoretical values are based on 100% reaction of water present.⁸ As shown for moisture levels above 0.027% in the supply polymer, the experimental values for I.V. breakdown attributable to hydrolysis remained constant with increased moisture in the supply polymer. The same effect is shown in Figure 8, in which experimental and theoretical values of carboxyl endgroup concentration buildup are plotted against moisture content of the supply polymer. It was assumed that either the extruder was acting as a dryer or 100% of the moisture present was not reacting.

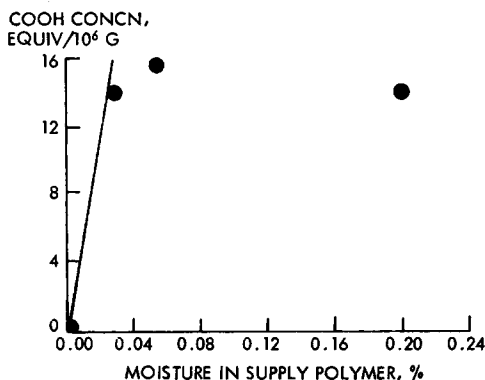


Fig. 8. Effect of moisture in supply polymer on carboxyl endgroup buildup. Theoretical concentration based on 100% conversion of water during hydrolysis.

A subsequent experiment in a sealed tube indicated that hydrolysis would be practically complete for the concentrations of moisture present in the polymer.¹⁴ We therefore concluded that the extruder was acting as a dryer. Thus, to use the equations developed herein most effectively, one needs to know the extent to which the extruder dries the supply polymer before hydrolysis takes place. This information can be determined experimentally from a prototype extruder under normal conditions by extruding supply polymer having various moisture contents and determining I.V.'s of the extrudate. The moisture level above which additional moisture in the supply polymer does not affect the extrudate I.V. would be the moisture level to which the extruder dries the polymer before appreciable hydrolysis takes place. As shown in Figure 7, the particular extruder used in this investigation apparently dried the polymer to about the same moisture level regardless of the initial moisture content of the supply polymer. Whether the water removed by the extruder is surface moisture only or a combination of surface and internal moisture is not known.

Activation energies E_a for I.V. breakdown of PCHDT and for increase in carboxyl endgroup concentration of PCHDT were determined as 33.5 and 41 kcal/mole, respectively. These values compare well with values of 38.7 and 40 kcal/mole determined in a previous investigation by Gregory and Watson² for thermal degradation of PCHDT. For PET, Marshall and Todd⁵ obtained a value of 32 kcal/mole, and Goodings⁶ obtained values of 37.4 to 41.7 kcal/mole.

The correlation equations reported here hold for temperatures ranging from 295° to 330°C, moisture contents ranging from < 0.001% to 0.2%, and residence times ranging from 3.5 to 17.5 min; they can be used with caution for other conditions (in the melt) outside these ranges. Although hydrolysis takes place rapidly in the melt and is virtually complete in 3.5 min or less, the exact time that the hydrolysis terminates is not known. Therefore, the equations for predicting I.V. and carboxyl endgroup concentration should be used with caution for residence times under 3.5 min when hydrolytic degradation is occurring.

CONCLUSIONS

The method of analysis that was developed allows separation of hydrolytic and thermal degradation from total degradation of PCHDT in the melt. This method is generally applicable where rates of competing reactions differ greatly.

Residence time, temperature, moisture content of supply polymer, and their interaction all contribute significantly to the degradation of PCHDT. The equations developed enable accurate prediction of I.V. and carboxyl endgroup concentration in the extrudate.

The extruder used in this experiment acted as a dryer for moisture contents of the supply polymer greater than approximately 0.027%. Supply polymers having moisture contents greater than 0.027% were dried to about 0.027% in the extruder prior to significant hydrolysis.

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