Hydrolytic Degradation of Poly(ethylene terephthalate)

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ABSTRACT: Molecular weight is an important factor in the processing of polymer materials, and it should be well controlled to obtain desired physical properties in final products for end-use applications. Degradation processes of all kinds, including hydrolytic, thermal, and oxidative degradations, cause chain scission in macromolecules and a reduction in molecular weight. The main purpose of this research is to illustrate the importance of degradation in the drying of poly(ethylene terephthalate) (PET) before processing and the loss of weight and mechanical properties in textile materials during washing. Several techniques were used to investigate the hydrolytic degradation of PET and its effect on changes in molecular weight. Hydrolytic conditions were used to expose fiber-grade PET chips in water at 85°C for different periods of time. Solution viscometry and end-group analysis were used as the main methods for determining the extent of degradation. The experimental results show that PET is susceptible to hydrolysis. Also, we that as the time of retention in hydrolytic condition increased, the molecular weight decreases, but the rate of chain cleavage decreased to some extent, at which point there was no more sensible degradation. The obtained moisture content data confirmed the end-group analysis and viscometry results. Predictive analytical relationships for the estimation of the extent of degradation based on solution viscosity and end-group analysis are presented. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 103: 2304–2309, 2007

Key words: hydrolytic degradation; poly(ethylene terephthalate); viscosity; moisture content; end-group analysis

INTRODUCTION

Thermoplastic fibers, including polyesters, polyolefins, and nylons, have been used mostly in the past in various applications. In recent years, considerable progress has led to improved process yields, efficiency, and physical properties of poly(ethylene terephthalate) (PET) products. PET has already carved out a leading position in applications as diverse as fibers, films, and molded products. Although other polyesters are produced, PET is the unquestioned leader among thermoplastic polyesters and ranks quite high among thermoplastics, and its market is expanding continuously. Among the three principal products made of PET, that is, fibers, films, and bottles, still commodity fibers have traditionally provided the largest outlet for this polymer. PET has some noteworthy properties that affect its processing behavior and also its products. PET, because of its microstructure, is sensitive to humid conditions at temperatures above the glass-transition temperature (T_g) and usually undergoes degradation. Polymer degradation is often defined as molecular chain scission in the polymer during which the length of macromolecules and the degree of polymerization decreases. The extent of degradation strongly depends on the polymer structure and the environmental conditions of the polymer.

Hydrolytic, thermal, and oxidative mechanisms are the three main mechanisms of degradation that occur during the melt processing of PET.[1,2] Hydrolytic degradation usually takes place for a broad range of hydrolysable polymers, including PET, polycarbonate, and nylons.[3] Hydrolysis causes the most serious problems, including a loss of properties in PET.[2] Many of these problems are encountered in the extrusion, melt spinning, and processing of PET and during the washing of textiles made from PET fibers. The hydrolytic degradation processes that occur in PET have received continuing attention in the literature.[4–13] The hydrolytic degradation of a polyester includes chain scission reactions at ester linkages. During this process, each water molecule breaks down one ester bond. This leads to the creation of one carboxyl and one hydroxyl end group. It is expected that an increase in the time of hydrolysis will causes an increase in the concentration of carboxyl end groups. Therefore, end-group analysis can be implemented as a suitable technique for investigating the rate of degradation in PET.[6] Zimmerman and Kim[4] used an increase in carboxyl groups as a measure of the chain scissions per unit time.
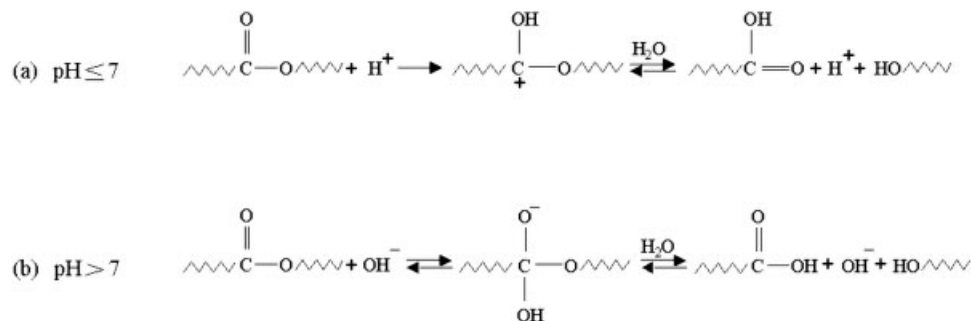
Figure 1 Hydrolytic cleavage of an ester bond under (a) acidic or neutral conditions and (b) alkaline conditions.[5]

During degradation, smaller chain fragments are increased. It seems that this is caused by reverse esterification.[14] Because of some complexities, the real kinetics for the hydrolytic degradation of polyester have not yet been understood, and authors have proposed different kinetic schemes.[5,15–18] General mechanism schemes for the hydrolytic degradation of polyester in acidic, neutral, and alkaline environments are shown in Figure 1.

As shown in Figure 1, the degradation kinetics in both cases are different, and this issue shows the dependency of the degradation mechanism on the environmental conditions.

Under acidic conditions, the accelerated hydrolysis involves protonation of the in-chain oxygen atom of the ester group followed by a reaction with water to produce equivalent amounts of hydroxyl and carboxyl end groups. Under alkaline conditions, the hydroxide anion attacks the carboxyl oxygen atom to produce equivalent amounts of hydroxyl and carboxyl end groups. Furthermore, under acidic or basic conditions, the rate of hydrolysis increases significantly.[6,14] In unbuffered neutral water, pH of the postreaction mixture amounts to 3.5–4.0. This is due to the presence of acid ends of terephthalic acid and monoglycol ester that result from hydrolysis, whereas the chain cleavage of ester linkages in polyesters by traces of water in the melt state is an extremely rapid reaction.[17] On the other hand, degradation in alkaline conditions primarily causes chain scission at polymer chains and is confined to the polymer surface. This kind of hydrolysis usually takes place in aqueous sodium hydroxide, and it has been attributed to a so-called topochemical degradation.[18] There seems to be unanimous agreement among researchers that the reaction between an aqueous solution of NaOH and polyester takes place at the fiber surface and not in the interior.[19–22] It appears that in this situation, short-chain molecules located at fiber surfaces are removed in hydrolysis and leave the undissolved part of the fiber unaffected.

Some researchers have proposed that the PET degradation mechanism is an autocatalytic reaction and that the concentration of carboxyl end groups controls the hydrolytic degradation.[5,16,23–27] They suggest that an increase in the number of end groups during degradation leads to an increase in hydrophilicity and the penetration of more water into the system. This provides the conditions for an autocatalytic reaction. However, some other researchers have considered the case of diffusion-controlled kinetics,[15] and mostly, it has been observed that PET hydrolysis is a random-chain scission.[9] The mechanism of the thermal degradation of PET is mainly random-chain scission, too,[10,28,29] but the rate of hydrolysis is higher by several orders than that of thermal breakdown.[30]

PET is a semicrystalline polymer, and the crystalline fraction is nonreactive toward hydrolysis because of its impermeability to water. With regard to PET microstructure, water molecules can diffuse into the amorphous regions, and chain scission occurs in this area. This provides the conditions for small chains to mobilize and realign in the polymer media and increase the polymer crystallinity. This phenomenon is known as *chemicrystallization,* and it is estimated that this phenomena will cause five to six monomer units incorporate into the crystalline phase per chain.[5] Therefore, the rate of hydrolytic degradation strongly depends on the degree of crystallinity and polymer morphology.[6,14–16,31,32]

On the other hand, changes in crystallinity will affect polymer density. These changes in the morphological characteristics of PET will obviously affect the processibility and the physical and mechanical properties of the polymer. Observation of Fourier transform infrared (FTIR) analysis has been reported,[33] and a gradual decrease in crystallinity occurred after the completion of the degradation process. This is in contradiction to the results obtained by other workers, as mentioned previously.

It has been fairly well established that improved thermal and hydrolytic stability for a polyester can be achieved by a reduction in the acid content. In this regard, different types of additives have been introduced, including carboimides, ketonimides, and cyclic acetals.[2] Although a survey showed that diethylene

TABLE I
Characterization of the Virgin PET Sample

[IV] (dL/g)	0.557
M_v	27,311
[COOH] (mequiv/kg)	25.8
Melting point (°C)	256.3
TiO_2 (%)	0.311
DEG content (%)	0.85
Color values	$L* = 82.23$
	$a* = -2.77$
	$b* = 1.49$
Size (mm)	$2.49 \times 3.59 \times 3.82$

According to international standard for color measurements (CIE), $L*$ is lightness component; $a*$ (range from green to red) and $b*$ (range from blue to yellow) as two chromatic components.

glycol (DEG) content had no significant influence on the hydrolysis of polyester,[6] there was another report indicating that increasing DEG content promotes hydrolysis and thermal and oxidative degradation.[34]

Changes in the molecular weight of polyesters resulting from degradative reactions can be monitored by various techniques, including gel permeation chromatography, size exclusion chromatography, osmometry, end-group analysis, light scattering, and viscometry. Solution methods usually require a periodic measurement of chain length at different degradation process stages and can be used only for soluble polymers such as PET in an appropriate solvent.[12,35] The hydrolytic degradation of PET has been evaluated by the implementation of gravimetric, FTIR, and microcalorimetric techniques.[35]

EXPERIMENTAL

Materials

Fiber-grade PET granules were supplied by Yazd Polyester Co. (Yazd Iran). Fiber-grade PET contains some titanium dioxide to reduce luster and provide whiteness. The PET specifications are shown in Table I.

Phenol and 1,1,2,2-tetrachloroethane used for viscometry analysis were purchased from Hopkins and Williams (Chadwell Heath, England) and Fluka (Buchs, Switzerland), respectively. Orthocresol for end-group analysis obtained from Merck (Darmstadt, Germany).

Sample preparation

Virgin PET granules were exposed to water within a bath containing demineralized water at 85°C, which was above T_g of PET. During conditioning, samples were completely immersed in water. Samplings were performed at 5-day intervals in a final experimental

period of 0–25 days. All samples were dried with a soft cloth after they were removed from water.

Determination of moisture content

Moisture content analyses were performed in water content analyzer model WD-202 made by FAPA. This instrument consisted of a U-shaped tube filled with mercury and connected to the test tube containing the sample. All the connections were tested for any leakage. After the test was run, the samples were heated at 200°C for about 30 min. Measurement in this instrument was based on the manometric pressure difference between the two columns (ΔP). The degree of moisture content was directly proportional to the measured pressure difference value and was calculated with the following relationship:

$$M(\%) = \frac{\Delta P \times f}{Wt} \qquad (1)$$

where M is the moisture content (%), f is the calibration factor, and Wt is the sample weight. The calibration of the analyzer was performed by the implementation of sodium molibidate.

End-group analysis

Some methods for the rapid determination of the carboxyl end groups of polyester (PET) have been reported.[36] In the method used in these experiments, PET samples (~0.2 g) were dissolved in 40 mL of Orthocresol at a temperature of 90°C for a period of 45 min with a magnetic stirrer. The concentration of end groups was determined in a Mettler Toledo (Ohio, USA) DL-50 automatic titration system with a solution of 0.05N KOH as the titrant. To improve the titration sensitivity, about 2 mL of 0.1% KCl was added to the titration solution. This instrument was equipped with a digital indicator to monitor the pH of the solution during titration. The amount of KOH consumed in the titration for each sample was reported at pH = 7.3. Then, the concentration of carboxyl end groups was calculated by the following formula:

$$[COOH] = \frac{(V \times N \times f - M) \times 100}{Wt} \qquad (2)$$

where [COOH] is the amount of carboxyl end groups (mequiv/kg), V is the volume of consumed KOH (μL), N is the normality of KOH, f is the KOH normality factor (0.9874), M is the amount of reagent blank (mmol), and Wt is the sample weight (g). Three separate titration analyses were done for each sample.

TABLE II
Experimental Results of PET Samples Treated Under Hydrolytic Conditions

Sample	Moisture content (%)[a]	[COOH] (mequiv/kg)[b]	η^{int} (dL/g)[c]	M_v[d]
1	0.195	25.8	0.5576	27,311
2	0.278	28.2	0.5338	25,533
3	0.283	31.5	0.4851	22,029
4	0.284	35.6	0.4437	19,196
5	0.285	40.0	0.4117	17,100
6	0.285	45.1	0.3906	15,768

[a] Determined by a manometric water content analyzer.
[b] Measured by the titration method.
[c] Intrinsic viscosity. Data were obtained at 25°C with phenol/tetrachloroethane (60/40 w/w) mixture as the solvent.
[d] Calculated with the Mark–Houwink equation: $\eta = K[M_V]^a$, where $K = 7.44 \times 10^{-6}$ mL/g and $a = 0.648$.[38]

Viscometry analysis

Viscometry analysis was performed with a capillary Ubbelohde IC viscometer. PET samples were dissolved in a solvent mixture with a 60/40 weight ratio of phenol to 1,1,2,2-tetrachloroethane at a temperature of 110°C for at least 30 min. The procedure was carried out according to ASTM D 4603. The concentration of the PET samples in solutions was adjusted to 0.5 g/dL. The temperature was set to 25°C for all of the samples. The intrinsic viscosity [IV] of the solutions was calculated by the Billmeyer relationship:[37]

$$\eta = 0.25\frac{(\eta_r - 1 + 3\ln\eta_r)}{C} \qquad (3)$$

where $\eta_r = \eta/\eta_0$ and η_0, η, and η_r are the viscosities of the solvent and the polymer solution and the relative viscosity, respectively. Also, C is the concentration (g/mL). All of the samples were dried in an oven at temperature of 65°C for 2 h before test. The molecular
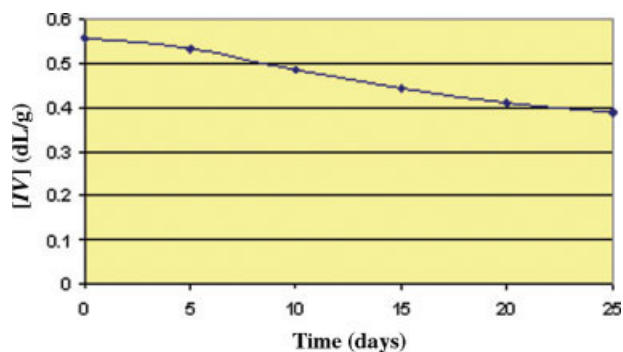

Figure 2 Changes in [IV] of PET samples as a function of retention time in water. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]
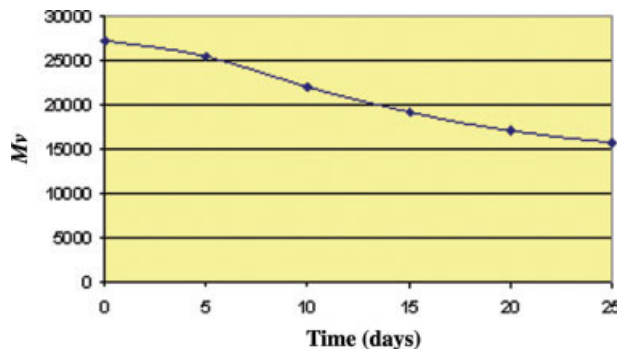

Figure 3 Changes in M_V as a function of retention time in water. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

weight is usually expressed in terms of its equivalent [IV].

The viscosity-average molecular weight (M_V) of the samples could be calculated on the basis of the viscosity data with the Mark–Houwink equation: $\eta = KM_V^a$, where $K = 7.44 \times 10^{-6}$ mL/g and $a = 0.648$.[38]

RESULTS AND DISCUSSION

The results obtained from the experiments and polymer characterization data are summarized in Table II.

Changes under hydrolytic degradation for [IV] are presented in Figure 2. This curve shows the variations in [IV] of PET samples as a function of retention time in water.

As expected, an increase in retention time caused a decrease in [IV]. The effects of residence time in humid conditions on chain scission and M_V are shown in Figure 3.

The molecular weight decreased exponentially with the retention time of hydrolysis. As shown in Figures 2 and 3, trends of [IV] and molecular weight values were toward an asymptotic value. This means that there would be limitations on further hydrolytic degradation of PET. This issue can be explained by PET morphology. Myagi and Wunderlich[39] proposed that a chain-folded model could represent the crystalline structure of PET. This model is shown in Figure 4,[39] in
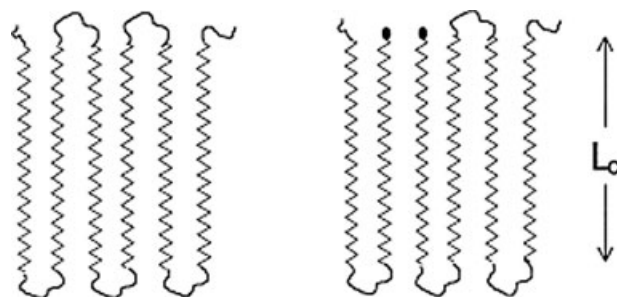

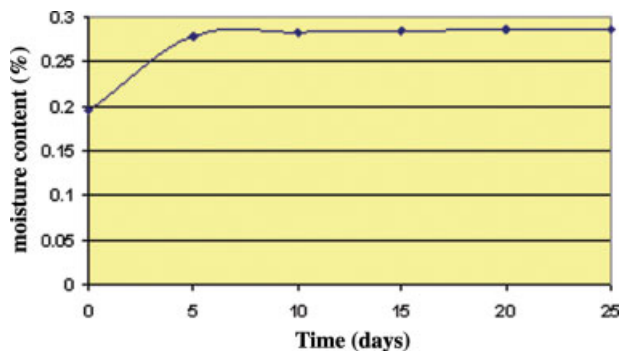**Figure 4** Scheme of a hydrolysis act in a chain fold.[39]

Figure 5 Variations of moisture content with retention time. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]
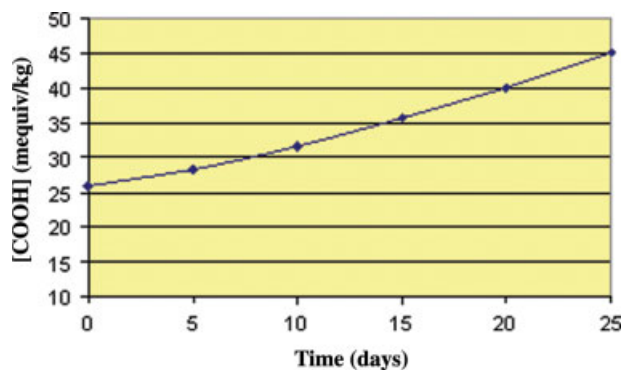

Figure 6 Plot of [COOH] versus retention time in water for PET samples. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

which the lamella thickness is indicated by L_C. On the basis of this model, the PET structure is comprised of segments including crystalline and amorphous regions. In regular sections of segments, ester linkages present in these areas are inaccessible to water molecules. Water can only reach ester linkages at amorphous regions, and chain folds of the crystalline section border and break down the bonds. Generally, it is assumed that water diffusion proceeds first in the amorphous regions of PET, and hydrolysis should be limited to this part of the samples. This issue limits the degradation reactions that occur in PET. Consequently, [IV] and molecular weight decrease toward an asymptotic value. The changes in molecular weight (in the range of 9300–24,000) with [IV] follow a simple and linear relationship, which can be expressed by the following equation:

$$M_v = 69,186 \times [IV] - 11,390 \qquad (4)$$

where [IV] is the intrinsic viscosity (dL/g). This equation can be used as a rapid and direct method for the estimation of the molecular weight by [IV] data.

The amount of moisture content in the samples increased with the time of retention (Fig. 5). However, it was interesting that there were no significant changes in moisture content for the samples after 5 days. This means with the saturation of PET, the penetration of water was stopped. Therefore, the hydrolysis continued as a result of time and temperature during the next 20 days. We concluded that during the first 5 days, degradation occurred simultaneously with the penetration of water molecules. Then, after saturation was reached, no more water penetrated to the polymer, and degradation reactions were continued by water molecules present in the polymer media.

At moderate temperatures, the PET structure is stable against water penetration. However, at elevated temperatures, especially above T_g, intermolecular motions in amorphous regions are started. This provides

the conditions for the diffusion of water molecules to this area. Furthermore, these intermolecular motions provide a good opportunity for macromolecules to rearrange. It is expected that these rearrangements will lead to an increase in crystallinity. Experimental results reported by some researchers confirm this process, that is, an increase in crystallinity during hydrolysis.[5–7] Changes in carboxyl end groups were similar to changes in [IV] but in reverse behavior (Fig. 6). As shown, the concentration of COOH groups increased gradually with the time of exposure. However, as time passes, there were smaller changes in end-group concentrations.

Variations in M_V against COOH group content are plotted in Figure 7. By measurement of either molecular weight or COOH group concentration one can make a good estimation for the other one through an equation. This equation is as follow:

$$M_v = 24.526 \times [COOH]^2 - 2350.9 \times [COOH] + 71,887 \qquad (5)$$

CONCLUSIONS

The hydrolytic degradation of PET above T_g was studied. The extent of degradation and its dependence on
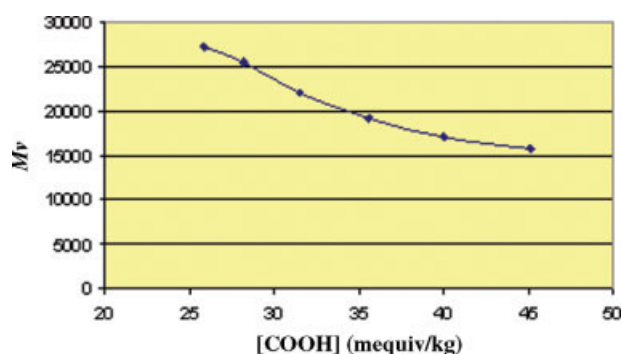

Figure 7 Changes of M_V versus [COOH] for hydrolytically degraded PET. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

the time of exposure were investigated with viscometry and end-group analysis. Experimental data obtained for the carboxyl end groups were in good agreement with [IV] and other experiments. The results show that humidity or wet conditions at high temperatures induced a strong hydrolytic degradation. This issue consequently increased carboxyl-terminated polyester chains. Furthermore, this feature had a sensible effect on the molecular weight. Careful control of these key variables is essential to produce the best processibility and physical and mechanical properties of the product in end-use applications. Predrying to very low moisture levels (<50 ppm) is required before processing. This minimizes the hydrolytic degradation of the chain ester groups. This is the common source of MW reduction in PET. On the basis of solution viscosity and end-group analyses results, two predictive analytical equations were created for the estimation of the extent of degradation.

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