

Hydrolytic and Thermal Degradation of PET Fibers and PET Granule: The Effects of Crystallization, Temperature, and Humidity

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Received 10 May 2007; accepted 16 May 2007

DOI 10.1002/app.26788

Published online 16 July 2007 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: The main purpose of this research work was to illustrate the extent of hydrolytic degradation of PET caused by warm water and also to separate the influence of moisture, temperature, and orientation in the degradation process. To achieve this purpose, thermal and hydrolytic degradation of PET (Partly Oriented Yarn (POY), Fully Drawn Yarn (FDY) and granule) at temperatures above and below glass transition temperature (T_g) were carried out using a water bath and an electrical oven. Technical methods such as determination of the moisture content, viscometric analysis, carboxylic end group titration, and X-ray diffraction were used to analyze the degradation of PET. The results obtained from different analysis show that the major portion of degradation is carried out by both moisture and heat mutually rather than their entirely individual

that have a minor effect. Degradation at lower temperatures from T_g were less prominent and was increased noticeably above T_g . Crystallinity plays a significant role in preventing hydrolytic degradation as the extent of degradation was increased from FDY to granule to POY. X-ray diffraction analysis showed that crystallinity was increased from POY to granule to FDY. Determination of intrinsic viscosity, molecular weight based on viscosity (M_v), chain scissions, and carboxylic end group analysis were the main quantities for the degradation measurement. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 106: 1544–1549, 2007

Key words: poly(ethylene terephthalate); hydrolytic/thermal degradation; moisture content; crystallinity; chain scission

INTRODUCTION

Poly(ethylene terephthalate) (PET) is a thermoplastic polymer resin of the polyester family that is used in synthetic fibers; beverage, food and other liquid containers; thermoforming applications; and engineering resins often in combination with glass fiber. It is one of the most important raw materials used in man-made fibers. Depending on its processing and thermal history, it may exist both as an amorphous (transparent) and as a semicrystalline (opaque and white) material. PET is most commonly produced by polycondensation of its monomer, which can be synthesized by the esterification reaction between terephthalic acid (TPA) and ethylene glycol (EG) with water as a byproduct or the transesterification reaction between EG and dimethyl terephthalate (DMT) with methanol as a byproduct (Fig. 1).

PET undergoes several types of degradation under different conditions, with the absence of light, reactive ions, and chemical reagents. The considered degradation types in the processing of PET are thermal, thermal-oxidative, and hydrolytic degradation.

Significant hydrolysis of PET is known to occur in moist, wet, or humid conditions at temperatures above glass transition temperature (T_g).^{1–11} The hydrolytic degradation of PET is an important problem associated with many of its commercial applications. For example, in the form of fibers, sheet, and film under conditions of high humidity, the ester functionality is most compromising to degradation. In fact, polyester is known to undergo significant hydrolysis above its T_g resulting in an increase in the number of carboxyl end groups and reduction in the molecular weight. Furthermore, under acidic and basic conditions the rate is enhanced. For example, under acidic conditions the accelerated hydrolysis involves protonation of the in-chain oxygen atom of the ester group followed by reaction with water to produce equivalent amounts of hydroxyl and carboxyl end groups. Under alkaline conditions, the hydroxide anion attacks the carboxyl oxygen atoms to produce equivalent amounts of hydroxyl and carboxyl end groups.² The hydrolytic degradation of polyesters involves the chemical scission of an ester linkage in the main chain by water (Fig. 2).³ Each chain scission uses up one water molecule and creates one carboxyl and one hydroxyl end groups.^{1–5} Hence the reaction can be followed by measuring the increase in the number of carboxyl ends with

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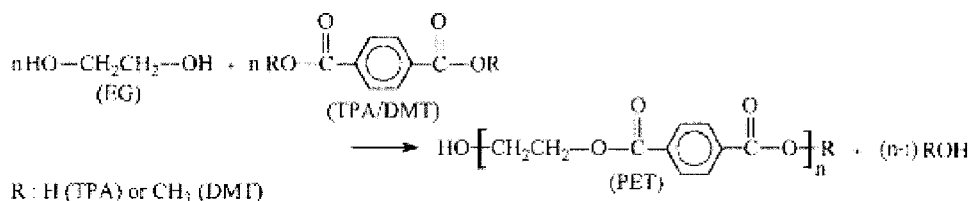


Figure 1 Polycondensation reaction for the preparation of PET.¹

time by using routinely end group analysis. Some authors^{2,3} have considered that the role of end groups is not significant and thus ignored its effect, while others reasoned that the effects of the autocatalytic and the hydrophilicity increasing of the acid must be significant.

In PET hydrolysis, it is assumed that water diffuses into the amorphous regions of the polymer where hydrolysis occurs at a rate which also depends upon the shape, morphology, degree of crystallinity, relative humidity, and temperature.^{2,3} The strong influence of crystallinity on the rate of hydrolytic degradation of PET is believed to be due to the fact that crystallites act as barriers to moisture and oxygen diffusion.¹ A higher degree of crystallinity hinders the hydrolysis reaction because the crystalline phase is inaccessible to water. Thus, initial degradation is restricted to the amorphous regions and crystallite edges.¹⁻³

Several researchers^{2,3} have reported that density changes have been attributed to a so-called "chemi-crystallization" process during the degradation process. The idea is that the chain scission will only occur in the amorphous regions, leading to small chain segments with enough mobility to realign and therefore crystallize.³ The increase in crystallinity may be caused by the extraction of low molecular weight compounds and/or chemi-crystallization. The effect of chemi-crystallization were calculated and estimated to incorporate 5-6 monomer units into the crystalline phase per chain scission.³

Thermal degradation of PET was investigated by researchers.^{2,4,6,11-14} Thermal degradation was found to follow a chain scission mechanism that results in the formation of carboxyl end groups and a progressive reduction in molecular weight.

Relationship between the initial and the final number average molecular weights of the polymer and the amount of water reacting in the system is of the form:⁴

$$n_R = \frac{M_{n0}}{M_{nf}} - 1$$

where n_R is the number of moles of water reacting per mole of PET, M_{n0} is the initial number average molecular weight (g/mol), and M_{nf} is the final num-

ber average molecular weight (g/mol). n_R (chain scission) also indicates the number of chains subjected to scissions per each mole of PET.^{2,4}

The rate of hydrolysis of ester links has been reported to be several orders of magnitude higher than thermal breakdown rate.¹¹

Many techniques have been used to study the degradation of PET, including Fourier transform infrared spectroscopy (FTIR), viscometric analysis, end group analysis, X-ray diffraction, densitometry, differential scanning calorimetry (DSC), gel permeation chromatography (GPC), and NMR.^{2-6,12,13,15,16}

This publication is concerned with the thermal and hydrolytic degradation of PET and especially the effect of the molecular chains orientation and crystallinity on the degradation by choosing proper materials with different orientation and crystallinity characteristics. Viscometric analysis, carboxyl end group analysis and X-ray diffraction were used and the number of chain scissions has been evaluated on both thermal and hydrolytic degradation.

EXPERIMENTAL

Materials

The PET fiber grade granule or chips (intrinsic viscosity = 0.672 dL/g, T_g = 80-85°C, COOH group = 24 Meq/Kg, melting point = 255.3°C) and partly oriented yarn (POY) (265dt/48f, T_g = 82°C, tenacity = 2.4-7.2 g/denier) were supplied by Zagrouz

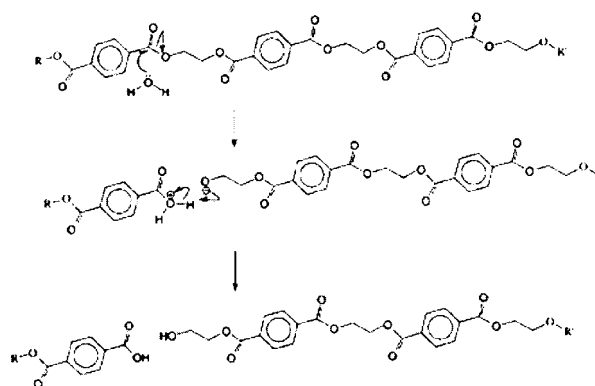


Figure 2 A proposed mechanism for hydrolysis of PET involving random in-chain scission.³

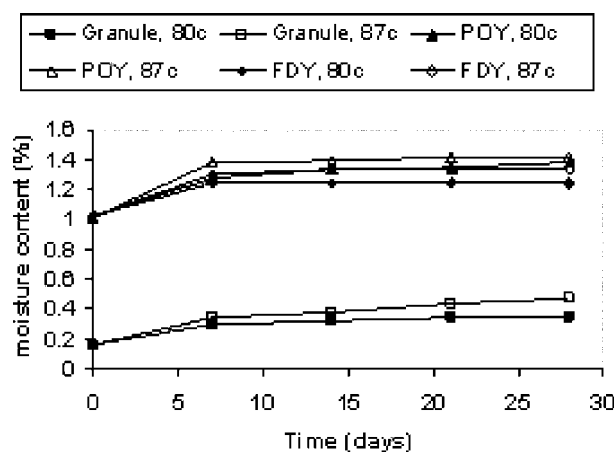


Figure 3 Moisture content (%) versus ageing time (days) for samples that exposed in water.

company, Iran. Fully drawn yarn (FDY) was supplied from drawn of POY by Tehran Fibers Company with drawn ratio of 2.065.

Phenol and 1,1,2,2-tetrachloroethane used for viscometric analysis were purchased from Merck and Fluka companies, respectively. Benzyl alcohol, chloroform, and sodium hydroxide for end group analysis were obtained from Merck.

Sample preparation

POY, FDY, and granule of PET were exposed in a bath containing demineralize water (hydrolytic degradation) and in an electrical oven (thermal degradation), at four different temperatures: 60, 70, 80, and 87°C, for a period of 7-day intervals in a final experimental period of 0–28 days. 87°C is above the T_g of PET. Samples that exposed in the water were dried with a soft cloth.

Absorbed moisture content

Sartorius water content analyzer model MA40 was used for determination of the moisture content. The

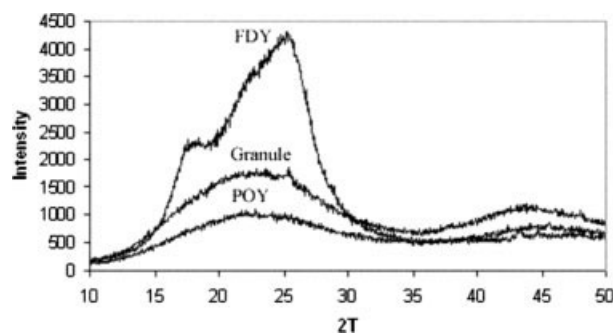


Figure 4 Intensity of X-ray versus fracture angle (the angle between the passed ray and the scattered ray) (2θ).

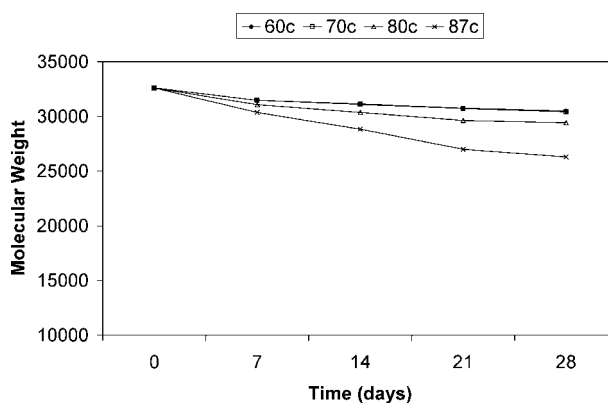


Figure 5 Changes in molecular weight of granule as a function of retention time in water.

dry temperature was set at 105°C. This temperature was selected from ASTM D 2654-76¹⁷ and the absorbed water weight was calculated for 1 g of each sample. The moisture content is calculated through the following relationship:

$$R = (W/M) \times 100$$

where R is the percentage of moisture content, W is the absorbed water weight, and M is the sample dry weight.

X-ray diffraction

To investigate the evolution of crystalline order and orientation in these samples, Philips X-ray diffraction model X'Pert-MPD was used. The start angle, the end angle, and step size were 10°, 50°, and 0.04°, respectively.

Viscometry analysis

The results could be obtained from viscometry were as follows: intrinsic viscosity, molecular weight, polydispersity index (PDI), chain scission, and total

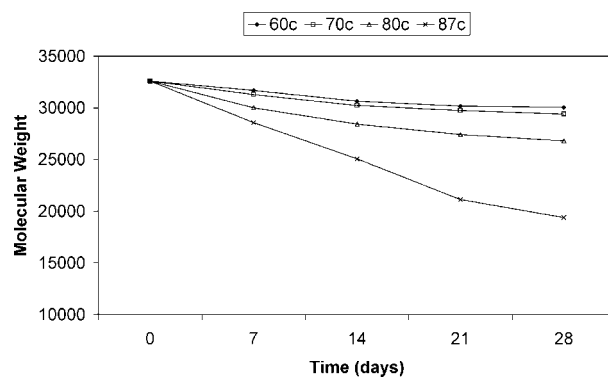


Figure 6 Changes in molecular weight of POY as a function of retention time in water.

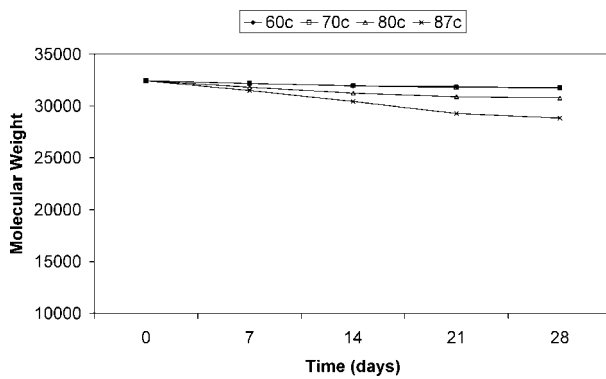


Figure 7 Changes in molecular weight of FDY as a function of retention time in water.

end group determination. In this study, the results of molecular weight and chain scission have been presented. Viscometry analysis performed using a capillary Ubbelohde viscometer (capillary diameter = 0.8 mm). PET samples dissolved in a solvent mixture with 60/40 weight ratio of phenol/1,1,2,2-tetrachloroethane at temperature of 110°C for at least 30 min. The procedure was carried out according to ASTM D 4603-96. Concentration of PET samples in solutions was adjusted to 0.5 g/dL. Temperature was set to 25°C for all samples. Intrinsic viscosity of solutions was calculated by Billmeyer relationship:¹⁸

$$\eta = 0.25(\eta_r - 1 + 3 \ln \eta_r)/C$$

Considering $\eta_r = \eta/\eta_0$, where η_0 , η , and η_r are viscosities of the solvent, polymer solution and relative viscosity, respectively. In the above equation C is concentration in g/dL. All samples were dried in an oven at temperature of 65°C for 2 h prior to test. The molecular weight is usually expressed in terms of its equivalent intrinsic viscosity. Viscosity average molecular weight of samples can be calculated based on viscosity data using Mark-Houwink equation:

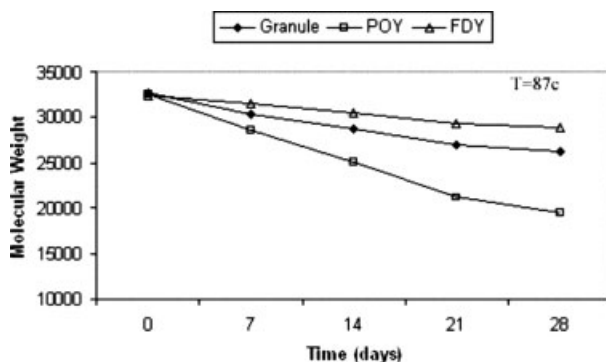


Figure 8 Changes in molecular weight of granule, POY and FDY as a function of retention time in water with temperature of 87°C.

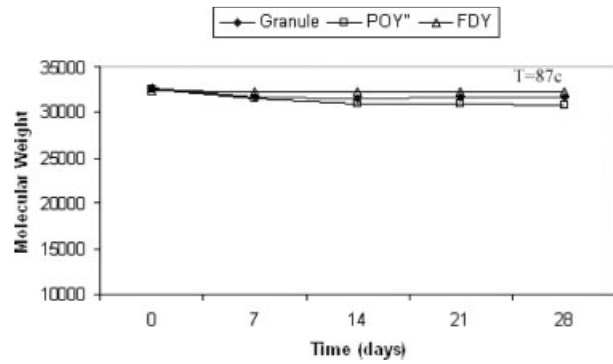


Figure 9 Changes in molecular weight of granule, POY and FDY as a function of retention time in oven with temperature of 87°C.

$$\eta = K[M_v]^a \text{ where } K = 7.44 \times 10^{-4} \text{ dL/g and } a = 0.648.^{19}$$

Titration

The titration technique was the method that used by Herbert A. Pohl²⁰ to determine carboxyl end group concentration in a solution. The sample of PET was dissolved in hot benzyl alcohol, and chloroform was added to provide the titration medium. The dissolved polymer was titrated with 0.1N sodium hydroxide in benzyl alcohol. Each titration required about 0.1 g of PET. Titration analysis was done triple for each run to relate the carboxyl end group concentration to specified processing conditions. Then the concentration of carboxyl end groups was calculated by the given formula:

$$[\text{COOH}] = (V - V_0) \times N/W_t$$

where,

- [COOH]: The amount of carboxyl end groups (Meq/Kg),
- V: The volume of consumed NaOH (μL),

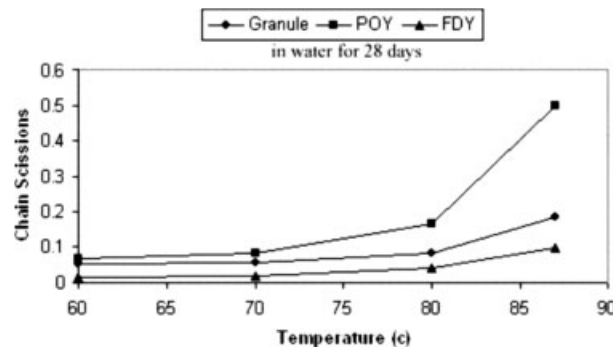


Figure 10 Chain scissions versus temperature (°C) for granule, POY and FDY with retention time of 28 days.

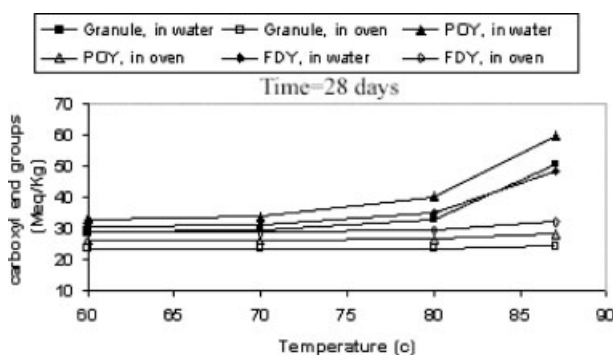


Figure 11 Carboxyl end groups versus temperature ($^{\circ}\text{C}$) for granule, POY and FDY in water and oven with retention time of 28 days.

- V_0 : The volume of consumed NaOH for blank solution (μL),
- N : Normality of NaOH,
- W_i : Weight of sample (g).

RESULTS AND DISCUSSION

The amount of the absorbed moisture content in samples that were exposed in water is increased by the time of retention (Fig. 3). These data show that the significant increase in moisture content occurred in the initial 7 days. Also, variations in moisture content were more significant in 87°C . The absorbed moisture content of POY and FDY are more than granule due to higher surface area per unit weight of yarn rather than granule. As indicated by Allen et al.,² water diffusion was made PET to hydrolyze and consequently degraded. So, degradation is more increased by the increase in moisture content of PET.

In Figure 4 the results of X-ray diffraction for granule, POY, and FDY are presented. It can be realized from Figure 4 that the crystallinity was increased from POY to granule to FDY. The crystallinity of FDY was more than the crystallinity of POY that caused by the drawn of POY. The content of the

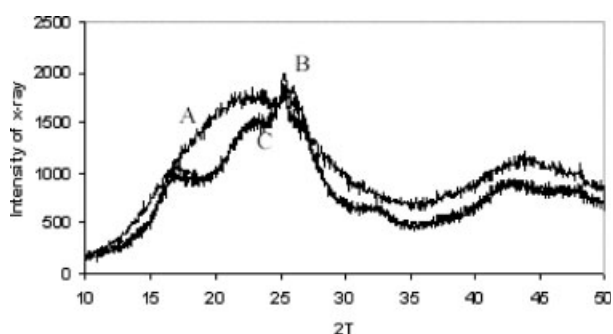


Figure 12 Intensity of X-ray versus 2θ for granule; A: not exposed, B: exposed in water (87°C , 28 days), C: exposed in oven (87°C , 28 days).

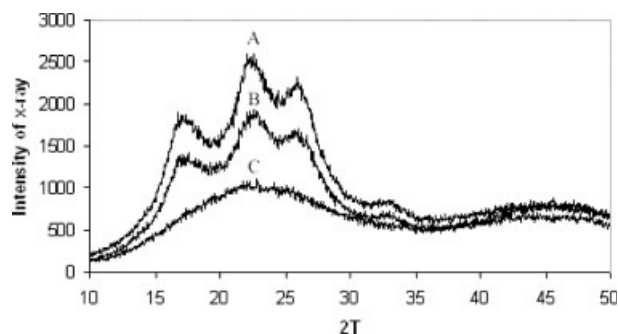


Figure 13 Intensity of X-ray versus 2θ for POY; A: exposed in water (87°C , 28 days), B: exposed in oven (87°C , 28 days), C: not exposed.

crystalline regions of granule is due to granule production conditions.

The degradation rate of the PET samples was measured by monitoring changes in the molecular weight and carboxyl end groups. The rate of hydrolytic degradation (reduction the molecular weight) increased with increasing temperature and this is illustrated by the data at 60, 70, 80, and 87°C shown in Figures 5–7 for granule, POY, and FDY, respectively.

In terms of temperature effects, degradation rates were prominent only at temperature above the T_g of PET samples. This is illustrated for the 87°C conditions in Figures 8 and 9 for thermal and hydrolytic degradation, respectively. It would be noted that crystallinity plays an important role and has a strong effect on the hydrolytic degradation. Also, the hydrolysis rate strongly depends on the moisture content, while the thermal degradation rate is insensitive to the moisture. According to the moisture absorption results, the major portion of moisture was absorbed in the first 7 days and then after this period, the role of temperature in degradation has been more important and made degradation faster in addition to the moisture.

At 60, 70, and 80°C , negligible chain scission was observed under dry condition, for all samples.

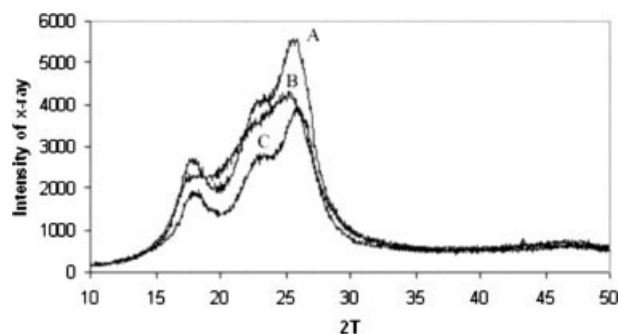


Figure 14 Intensity of X-ray versus 2θ for FDY; A: exposed in oven (87°C , 28 days), B: not exposed, C: exposed in water (87°C , 28 days).

Changes for chain scission are shown in Figure 10. These data show that hydrolysis is dominant above the T_g of PET samples.

Changes under thermal/hydrolytic ageing for carboxyl group formation are shown in Figure 11. From the data, the rates have been auto-accelerated at temperature above the T_g and under humid conditions.

In Figures 12–14 the crystallinity of the exposed samples in water bath and oven with temperature of 87°C for 28 days (the worst of the degradation conditions), are presented for granule, POY, and FDY, respectively. In the samples that were exposed in oven, the annealing process (heating and holding at an appropriate temperature below the crystalline melting point, followed by slow cooling) prepared a significant increase in crystallinity. The increase in crystallinity for the samples that were exposed in water bath may be caused by the chemi-crystallization process and/or extraction of low molecular weight compounds. While the initial crystallinity is important for impairing degradation and hydrolysis at less severe ageing conditions, hydrolysis is dominant above the T_g of PET and only under high humidity conditions.²

CONCLUSIONS

From this study, the following conclusions can be drawn:

1. The amount of the absorbed moisture content in samples that were exposed in water is increased by the time of retention.
2. Moisture absorption of POY and FDY are more than granule.
3. Crystallinity was increased from POY to granule to FDY.

4. The rate of hydrolytic degradation increased with increasing temperature.
5. Degradation rates were prominent only at temperature above the T_g of PET samples.
6. The hydrolysis rate strongly depends upon the moisture content while the thermal degradation rate is insensitive to the moisture.

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