

Investigation of Hydrolysis in Poly(ethylene terephthalate) by FTIR-ATR

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Abstract The hydrothermal aging of poly(ethylene terephthalate) (PET) was investigated at 70–95 °C. A new method to investigate the hydrolysis degree of PET by Fourier transform infrared spectroscopy (FTIR) was proposed. The spectra during the hydrothermal aging were measured using attenuated total reflection accessory (ATR). Peak resolving of carbonyl regions was performed, and the ratio of two groups of bands representing carboxylic acids and esters respectively were calculated to show the hydrolysis degree of ester groups in PET. The acid/ester ratio shows exactly the same trend as the average chain scission number per unit mass at various temperatures and thus can be used as a parameter to characterize the hydrolysis and random chain scission of PET. This method related to the hydrolysis mechanism directly, is simple, fast and convenient compared to the traditional methods such as viscometry, end-group titration and size exclusion chromatography (SEC). It may also be useful in hydrolysis characterization of other polyesters.

Keywords: Poly(ethylene terephthalate); FTIR-ATR; Hydrolysis; Acid/ester ratio.

INTRODUCTION

Poly(ethylene terephthalate) (PET) is a leading thermoplastic polyester that is widely used in applications as diverse as bottles, fibers, films and engineering plastics. Therefore, its durability is of great concern^[1]. Because of the presence of ester groups in the backbone, PET is easy to be attacked by water and undergoes hydrolytic degradation when exposed to humidity. The hydrolytic degradation of PET involves the transformation of ester groups to corresponding carboxyl acids and alcohols, with chain scissions and the decrease of the molecular weight. Therefore, the molecular weight is the most important parameter to manifest the changes during hydrolysis. There are several ways to measure the molecular weight, including intrinsic viscosity measurement, end group titration, size exclusion chromatography (SEC), *etc*^[2–6]. However, these methods often need expensive and toxic solvents and are time-consuming.

Infrared spectroscopy (IR) is a very convenient way to characterize chemical structures, and has been widely used in the investigation of crystallization and conformation of PET^[7–11]. It has also been used in the investigation of hydrolysis of PET^[5, 12, 13]. Al-Abdul Razzak *et al.*^[5] determined the hydroxyl concentration from IR spectra. The O—H absorbances from hydroxyl groups, carboxylic acids (the resultant species of hydrolysis of PET) and H₂O appear in the region 3000–4000 cm^{−1}. In order to eliminate the effect of H₂O, high purity N₂ was used to purge the compartment. Partini *et al.*^[12] studied the hydrolysis of PET in an alkaline atmosphere. The peak at about 1570 cm^{−1}, which is attributed to carboxylate formed, was used to represent the degradation. Opaparakasit *et al.*^[13] studied the hydrolysis of PET copolymer in a phosphate buffer solution. Absorbance ratio of 1760 cm^{−1} to 1720 cm^{−1} was used to show more chain scission of aliphatic part than aromatic part. Formation of carboxylic acids and carboxylates was proved by bands at 1685 and 1610 cm^{−1}.

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Carbonyl absorbance in IR spectra of PET can supply abundant information on hydrolysis since both original ester groups and hydrolysis-induced carboxylic acids have absorbances in this region. However, hydrolytic degradation is rarely studied using carbonyl region because it is often saturated even in thin films and various absorbances of carbonyl species often overlapped each other. In this paper, we used FTIR-ATR with diamond crystal to measure the IR spectra at the surface of PET, and Peak Resolve software was applied to resolve the overlapped carbonyl groups from esters and acids. The acid/ester ratio is then calculated and correlates with the average chain scission number per unit mass n_t . The results demonstrated that the change of acid/ester coincides very well with n_t and FTIR-ATR is a good and convenient method for the hydrolysis degradation characterization.

EXPERIMENTAL

Materials and Characterization

PET (BG-80, Yizheng Fiber Company, China) pellets for bottle production were directly injected to standard dog-bone tensile bars according to ASTM D638-08. PET pellets were carefully dried at about 160 °C for 4 h before injection in order to remove absorbed water as much as possible and limit the processing-induced hydrolysis.

Hydrothermal Aging of PET

PET bars were immersed in deionised water at various temperatures (70–95 °C) for different times (from a couple of days to several months). At certain time intervals, 3–5 bars were taken out, washed with deionized water and dried. Then they were conditioned at room temperature with 50% relative humidity for test.

Viscometry

The measurement of intrinsic viscosity of PET was performed at 25 °C with an Ubbelohde viscometer according to the standard ASTM D 4603. Aged PET was dissolved in the solvent mixture of phenol/1,1,2,2-tetrachloroethane (60/40) with the concentration of 0.25 g/dL. From the flow times of the pure solvent mixture and the PET solutions, the relative viscosity (η_{rel}) and the intrinsic viscosity ($[\eta]$) can be obtained with following equations:

$$\eta_{rel} = t / t_0 \quad (1)$$

$$[\eta] = \frac{0.25(\eta_{rel} - 1 + 3 \ln \eta_{rel})}{c} \quad (2)$$

where t = flow time of PET solution (s), t_0 = flow time of pure solvent mixture (s), c = PET concentration (g/dL).

The relationship between the intrinsic viscosity ($[\eta]$ in dL/g) and the number-average molecular weight (M_n in g/mol) under this condition is calculated according to the equation in the literature^[14]:

$$[\eta] = 3.72 \times 10^{-4} M_n^{0.73} \quad (3)$$

Fourier Transform Infrared Spectroscopy (FTIR)

Surface FTIR spectra of PET bars were collected from the aged PET bars. A small piece was cut from the surface and was detected with a Thermo Scientific Nicolet iS10 FTIR Spectrometer, equipped with a single-reflection Smart Performer accessory with diamond crystal for attenuated total reflection (ATR) measurements. The contact pressure was carefully adjusted to obtain spectra with same penetration depth. 32 co-added spectra were recorded for each specimen at a resolution of 4 cm⁻¹, in a wavenumber range of 650–4000 cm⁻¹ with N–B strong as the apodization function. ATR with diamond crystal helps to obtain spectra with satisfied contact and without saturated absorbances. The absorbance band of carbonyl groups in the region of 1640–1780 cm⁻¹ was resolved with the Peak-Resolve function in OMNIC 7.3 software. First, the second derivative (SD) transformation was done to show how many peaks are present and where they are (see in Fig. 1). Then a

Gaussian/Lorentzian function was chosen to fit the profile. The software automatically found candidate peaks according to SD results and given peak width (4 cm^{-1}) as initial values. The peak positions were fixed constant at the values from SD. Peak height, width and Gaussian fraction were iterated till the error reached the minimum or below permitted. 8 peaks were resolved in this region. An example is shown in Fig. 2. These peaks are attributed to esters and carboxylic acids in different physical/chemical circumstances. Among them, 1697 , 1701 and 1713 cm^{-1} may come from associated acid-terminated hydrolysis products, while 1716 , 1722 , 1729 , 1733 and 1738 cm^{-1} may be absorbances of esters in hydrolysis products and in main chain^[6]. The total areas of the former 3 peaks and the latter 5 peaks represent the total amount of acids and esters, and the area ratio of these two species (acid/ester ratio) was used as an indication of the hydrolysis degree.

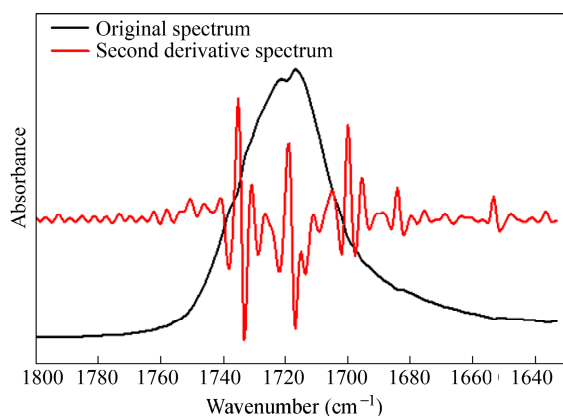


Fig. 1 Second derivative spectrum showing the overlapped peaks

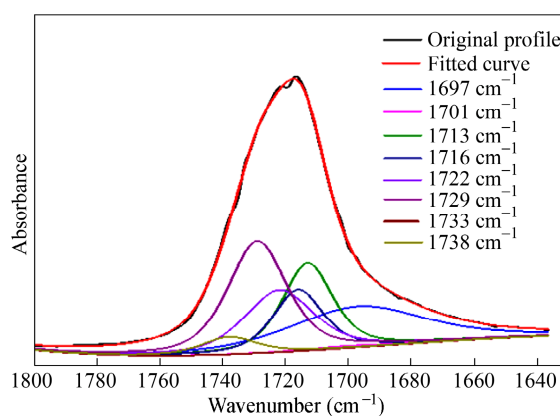


Fig. 2 Peak-resolving result in carbonyl region of PET aged at $90\text{ }^{\circ}\text{C}$ for 10 days

RESULTS AND DISCUSSION

During the hydrolysis of PET, owing to the water absorption and hydrolysis reaction with water, the weight increase did not follow the Fick's law, but showed a two-stage increase (shown in Fig. 3). The first increase was mainly attributed to the water absorption, while the second increase was mainly attributed to hydrolysis reaction with water. When the temperature does not exceed the glass transition temperature (T_g , *ca.* $85\text{ }^{\circ}\text{C}$), the water absorptions after the first stage are nearly the same. When the temperature is higher than T_g , more water can be absorbed at the end of the first stage owing to the increased free volume. Although hydrolysis resulted in the decrease of the molecular weight and the formation of oligomers, which may migrate into the water, the consequent weight loss was relatively small and could not be measured.

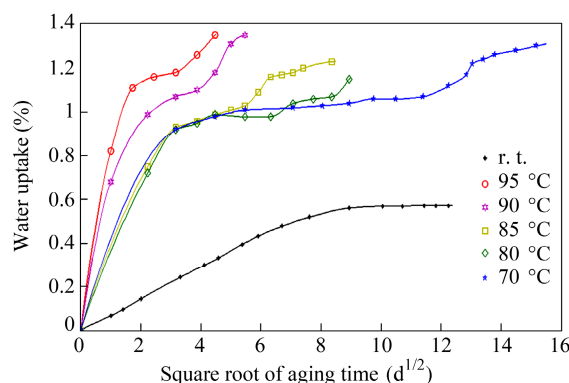


Fig. 3 Weight changes of PET during hydrothermal aging at different temperatures

In the carbonyl region of an IR spectrum of PET, there are various carbonyl species overlapped together, including mainly esters and acids (coming from the terminal carboxyl group). During the hydrothermal aging of PET, hydrolysis leads to the formation of carboxylic and hydroxyl end groups. Therefore, the concentration of carboxylic groups increased with aging time and that of ester groups decreased, with the profile changed as shown in Fig. 4. Since the peak positions of the various carboxylic acids and esters do not differ significantly, the superposition of these absorbances leads to a strong and broad band. This brings great difficulties in identification of each functional group and also studying their trends. This may be why this region has rarely been investigated in the literatures although they represent the nature of hydrolysis degradation. Peak-resolving, based on second derivative, is an effective technique to distinguish overlapped absorbances and was used in this paper to resolve various carboxylic and ester groups in carbonyl region, as shown in Figs. 1 and 2. The eight peaks at 1697, 1701, 1713, 1716, 1722, 1729, 1733 and 1738 cm^{-1} were attributed to ester groups in main chain and end carboxyl groups, as well as their hydrogen bonded associations^[15]. The changes of hydroxyl groups in the region of 3000–3500 cm^{-1} represent the formation of hydroxyl groups at the chain end. However, the hydroxyl groups are not used to study the hydrolysis because they are strongly influenced by water absorbance, and drying samples takes long time and may cause further changes^[5].

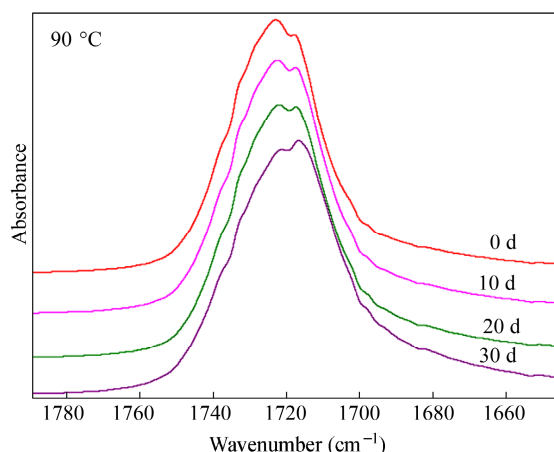


Fig. 4 Carbonyl region of unaged and aged PET at 90 °C for up to 30 days

By viscometry, the intrinsic viscosity and the number-average molecular weight (M_n) of PET was determined according to Eqs. (1)–(3). M_n change with time at 90 °C is shown in Fig. 5 as an example. The molecular weight decreased greatly from the very beginning, and the trend slowed down after 15 days of exposure in water. M_n changes at other temperatures show similar trends, with different speeds at different temperatures. The decrease of molecular weight represents the random chain scission of PET, and the average chain scission number per unit mass, n_t , is given by:

$$n_t = \frac{1}{M_n} - \frac{1}{M_{n0}} \quad (4)$$

in which, M_{n0} and M_n (g/mol) are the number-average molecular weight of PET before and at time t during hydrothermal aging.

Since both the acid/ester ratio and n_t represent the hydrolysis degree, they should change in a similar way. Therefore, the acid/ester ratio and n_t with aging time at different temperatures were plotted in Figs. 6 and 7. All the curves showed the auto-accelerated character, which could be related to an increase of hydrophilicity or autocatalysis during the hydrolysis by carboxylic acid end groups^[16]. At all temperatures, acid/ester ratio by IR showed nearly the same trend with n_t by viscometry. When plotting acid/ester ratio versus n_t , a good linear relationship can be obtained and an example is shown in Fig. 8. The perfect coincidence of these two parameters

with relative coefficients of 0.956 at 95 °C, 0.995 at 90 °C, 0.992 at 85 °C, 0.918 at 80 °C and 0.989 at 70 °C demonstrated their strong inter-correlation. Therefore, IR is a convenient and concise method in characterizing the hydrolysis degree, and acid/ester ratio can be a good indicator of chain scission of PET by hydrolysis.

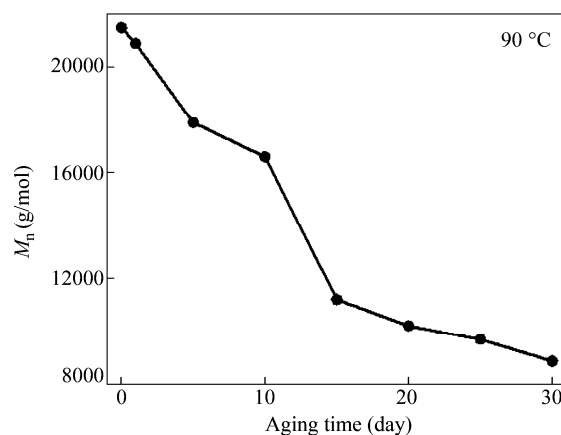


Fig. 5 Evolution of molecular weight of PET with aging time at 90 °C

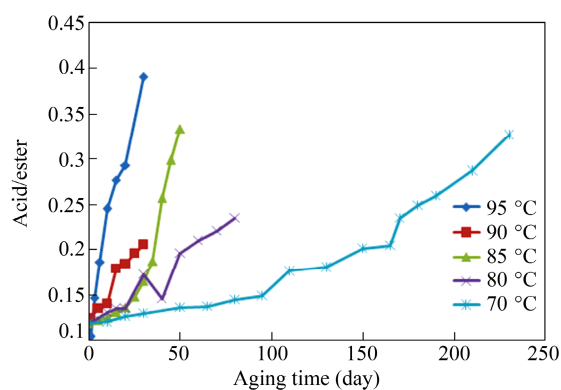


Fig. 6 Acid/ester ratio with aging time at different temperatures

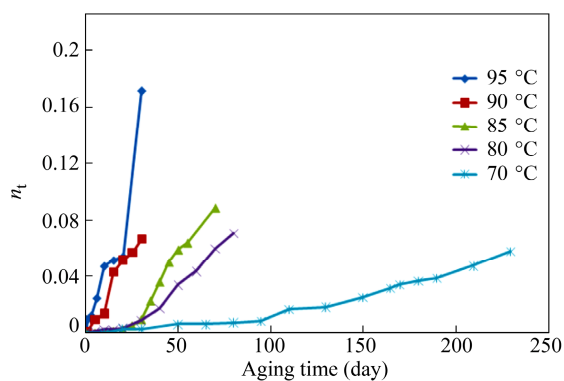


Fig. 7 n_t with aging time at different temperatures

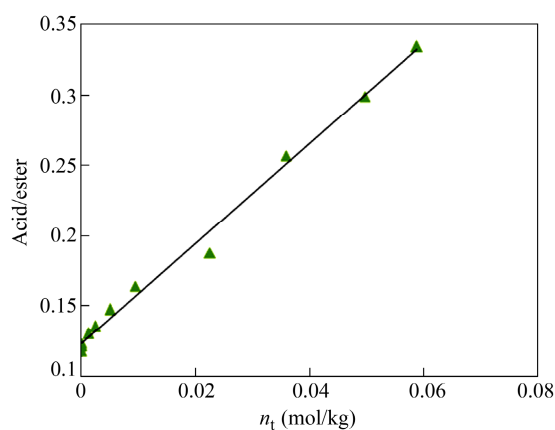


Fig. 8 Correlation between acid/ester ratio and n_t at 85 °C

CONCLUSIONS

In this paper, a new characterization method of hydrolysis degradation of PET by FTIR-ATR has been proposed and verified by the viscometry at various temperatures. The carbonyl region in IR spectra was peak-resolved and the acid/ester ratio was calculated. It represents the decrease of ester groups and the corresponding increase of acid groups and has very good correspondence with the average chain scission number per unit mass, n_t . Therefore, the acid/ester ratio from IR spectra is proved to be a good indicative parameter of the chain scission during hydrolysis. In addition, as well as n_t , it demonstrated an auto-acceleration process of PET during hydrothermal aging. Furthermore, this method is fast and convenient and can be used in the hydrolysis degradation of other polyesters.

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