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Characterization of Polyesters: Thermo-Oxidative Degradation

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The thermo-oxidative degradation of *PET* was investigated. Using turbidimetric titration the distribution of molecular mass at different degradation steps was determined. Chemical and molecular transformations of the polymers during degradation were also analyzed. It is shown that vinylic end groups are involved in radical reactions and determine the increase of the molecular mass.

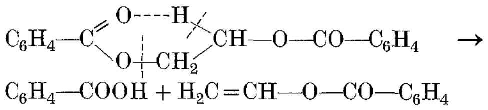
[Keywords: Fractionation; Poly(ethylene terephthalate); Thermo-oxidative degradation]

Characterisierung von Polyestern: Thermo-oxidativer Abbau

Es wird der thermo-oxidative Abbau von *PET* untersucht. Mit Hilfe der turbidimetrischen Titration wurde die Molekulargewichtsverteilung in unterschiedlichen Stufen des Abbaus bestimmt. Die chemischen und molekularen Umwandlungen des Polymers während der Abbauzeit wurden ebenfalls untersucht. Es wurde festgestellt, daß Vinylester-Endgruppen an Radikal-Reaktionen beteiligt sind und eine Molekulargewichtserhöhung verursachen.

Introduction

The thermo-oxidative degradation, TOD, of poly(ethylene terephthalate), *PET*, was rather intensively investigated both from the point of view of the kinetics and the nature of low molecular species which appear in this process[1–6]. This interest is partly justified by the fact that during synthesis and processing of *PET* favourable conditions for TOD are provided. In the first steps of the destructive process some ester links are broken and new species having terminal —COOH and —CH = CH_2 groups are subsequently formed[3], according to the following reactions:



$$C_6H_4{-}C\begin{matrix}\nearrow O{\cdots}H\\ \searrow O{-}CH_2\end{matrix}CH{-}O{-}CO{-}C_6H_4 \rightarrow$$

$$C_6H_4{-}COOH + H_2C{=}CH{-}O{-}CO{-}C_6H_4 \qquad (1)$$

The next steps are marked by the formation of both certain low molecular derivatives which are non-homogeneous in chemical composition, and much longer chain fragments which give rise to the subsequent formation of branched and/or crosslinked structures. In the present paper a correlation between chemical transformations occurring during the TOD process and the magnitude and distribution of the molecular weight of *PET* is shown.

Experimental

Thermo-oxidative degradation. A known amount of wet *PET* granules (Ţerom ^{R}, Romania) was heated at 300 °C in a circular aluminum tray of 15 cm^2 cross area for varying periods of time (Table 1) in the apparatus shown in Fig. 1. The apparatus was provided with a flow-meter for circulating air (1 l/min), an air preheater (250 °C) and a hot plate thermostated at 300 °C.

Intrinsic viscosity. Both initial and degraded samples were dissolved in phenol/1,1,2,2-tetrachloroethane (3/2, *v/v*) as solvent and filtered. The relative viscosities of the resulting solutions were measured at 25 °C, using an *Ubbelohde* viscometer provided internally with a fritted glass plate and dilution bulb. The intrinsic viscosity, $[\eta]$, was determined graphically by extrapolation. The concentration of the initial solution was determined by weighing the dried polymer obtained after precipitation with acetone.

Molecular mass. The number average molecular mass, $\bar{M}_n$, was determined by titration of end groups according to *Conix*[6]. Carboxyl groups were titrated potentiometrically[7].

Fractionation. The distribution of molecular mass of both initial and degraded *PET* samples was determined by turbidimetric titration[8]. The calibration of the apparatus (SPEKOL-DDR) was made with *PET* fractions separated by coacervate extraction[9,10]. A detailed description of this fractionation was reported recently[11]. The initial samples (i.e., wet industrial granules) and some fractions separated by coacervations were characterized by gel permeation chromatography in the system 1,1,2,2-tetrachloroethane/nitrobenzene (95/5, *v/v*) at 100 °C in order to attest the efficiency of the preparative fractionation method. The obtained data are listed in Table 2. All samples were dissolved in phenol/tetrachloroethane mixture (3/2, *v/v*) at room temperature before GPC analysis. These experimental conditions for GPC characterization were chosen in order to avoid on the one hand the high instability of the *PET*-nitrobenzene system and, on the other hand, the relative high viscosity of the phenol/tetrachloroethane mixture if used as eluent.

Determination of diethylene glycol. Polymer degradation: 1 g *PET*, 2.5 g benzyl alcohol and 50 ml KOH solution (1 *N* in methanol) were introduced in a flat bottom flask provided with a condenser and magnetic stirrer. The reaction mixture was refluxed for 2 h on a hotplate stirrer. Subsequently, it was neutralized with concentrated HCl solution, filtered, and the liquid was concentrated on a water bath to 1/5 of the initial volume. Three standard samples of known diethylene glycol (*DEG*) concentration were treated similarly in order to get the calibration ratio, i. e. peak area: concentration, by gas chromatography. The concentrated samples were analyzed using a Hewlett-Packard 5750 GC fitted with a glass column (2,5 m × 0.005 m) filled with 5% Carbowax 20 M/95% Chromosorb GAW-DMCS 30/60 mesh.

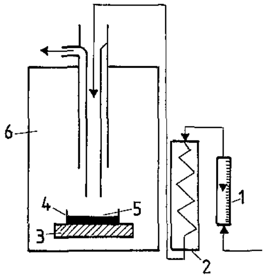


Fig. 1. Thermo-oxidative degradation of *PET*. *1* flow-meter; *2* preheater; *3* support; *4* aluminum tray; *5* polymer sample; *6* oven

Results and Discussion

By TOD of *PET* three categories of compounds are formed: (1) low molecular species which leave the system as gases due to the high reaction temperature, (2) macromolecular species which can be solubilized and extracted, and (3) an insoluble material of polymeric nature. The present paper deals with the soluble part only.

The Influence of TOD on the Magnitude and Distribution of Molecular Mass of PET

The data presented in Fig. 2 show the variation of $[\eta]$ and weight loss during TOD of *PET*. It can be seen that most of the weight loss occurs during the first 90 min of the process, after which time it levels at about 12.5%. Therefore it is reasonable to assume that branched and/or crosslinked macromolecular species are formed from the parent polyester towards the end of the process. Regarding the change of $[\eta]$, our data are similar to those reported by *Yoda*[1] (Fig. 2, dotted line). One can notice that $[\eta]$ of the thermally treated *PET* decreases only in the

Table 1. *Characterization of thermally treated PET samples*

Run No.	Amount g	Heating Time (min)	Weight loss g	Weight loss %	$[\eta]$ dl/g	COOH (eq/g) 10^6	$\bar{M}_n$ Dalton	*DEG* %
1	4.31	10	0.021	0.48	0.64	64	17 800	11.5
2	4.39	20	0.023	0.52	0.63	66	17 300	12.9
3	4.20	30	0.051	1.21	0.53	144	14 000	16.3
4	3.93	60	0.184	4.69	0.26	174	6 100	17.0
5	4.69	75	0.501	10.58	0.20	296	4 300	17.1
6	4.41	90	0.535	12.13	0.26	358	6 400	16.8
7	3.90	150	0.470	12.20	0.23	494	5 100	17.5
8	3.72	180	0.461	12.40	0.25	510	5 600	18.1
9	4.06	210	0.514	12.67	0.22	570	4 800	19.2
10	3.90	240	0.490	12.60	0.18	574	3 800	20.5
Initial	polymer	—	—	—	0.68	35	22 000	1.0

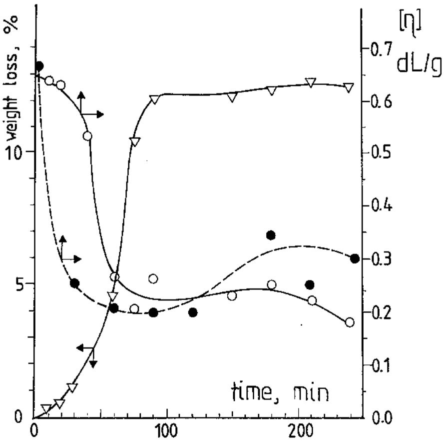


Fig. 2. Variation of weight loss (▽) and intrinsic viscosity (○) with degradation time; data reported by *Yoda*[1] are plotted on the broken line (○)

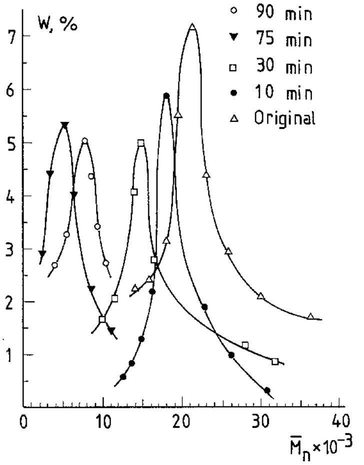


Fig. 3. Differential distribution curves of molecular mass at different degradation times obtained by turbidimetric titration

first stages of degradation and that towards the end of the process, i.e. after 75 min, it starts to increase again. We confirmed this increase by determining the distribution of molecular mass of degraded samples and of the initial polymer (parent *PET* granules and samples 1, 3, 4, and 5 from Table 1).

Indeed, the differential distribution curves obtained by turbidimetric titration (Fig. 3) indicate that during the first 75 min TOD causes a decrease of the molecular mass of the initial sample. Consequently, the maximum of molecular mass distribution is shifted to the domain of low molecular weight species. For example, the sample treated for 90 min has $\bar{M}_n$ higher than that of the polymer treated for 75 min (see Table 1 and Fig. 3).

Even though only the soluble fraction has been taken into consideration in this study, we think that the increase of molecular mass in the final stages of TOD is due to a radical process in which the vinyl groups (formed in the early stages of degradation) play an important role. The divinyl species of rather low molecular weight, which can be formed in addition to monovinyl compounds, may act—even in very low concentrations—as crosslinking agents. This assumption is supported by the identification of vinyl groups only in the IR spectra of samples 1-4 from Table 1 (very weak bands at ca. 3 150 cm^{-1}).

The Influence of TOD upon the Structure of PET Main Chains

Data listed in Table 1 indicate that the concentration of carboxyl end groups and the content of *DEG* increased after the thermooxidative treatment. The variation of —COOH concentration is presented in Fig. 4. The same Fig. shows the change of the *DEG* content with the time of thermal treatment. Several reactions can account for the formation of 2,2′-oxydiethylene structures[12–16], of which the most probable are:

I — intermolecular dehydration of ethylene glycol
II — addition to hydroxy ester end groups of the transition radical CH_2—CH_2—O
III — disproportionation of two hydroxy ester end groups
IV — thermal decomposition of the main chains or of hydroxy ester end groups
V — thermal scission of acetaldehyde from linear acetal structures.

However, under the present degradation conditions, the role of catalysts in the formation of —COOH groups at chain ends also has to be taken into consideration. It has been established that the metal from the catalytic system determines the polarity of the ester linkage and the formation of an intermediary transition complex from which, by chain breaking, two new species terminated by —COOH and —CH$=$$CH_2$ groups, respectively, are formed[13]. It has been shown also that the *DEG* content in *PET* is dependent upon the nature and amount of catalyst used[15]. In our experiments the free ethylene glycol has a low probability of appearance and consequently the reaction I can not be representative for the increase of *DEG* in the degraded samples.

Table 2. *GPC analysis of original PET sample and of fractions separated by coacervate extraction*

Sample	$\bar{M}_n$	$\bar{M}_w$	$\bar{M}_w/\bar{M}_n$
Original	21 200	47 000	2.24
Fraction 2	11 300	16 700	1.22
Fraction 4	14 800	22 000	1.55
Fraction 6	23 800	32 100	1.34

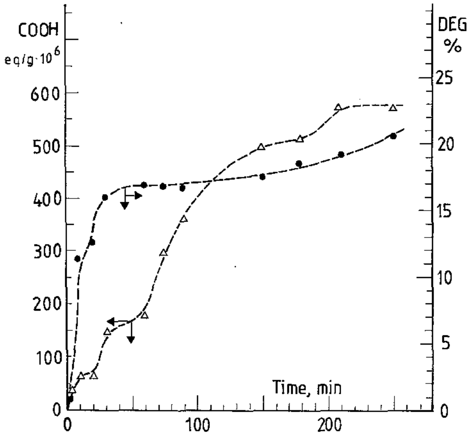


Fig. 4. Variation of concentration of carboxyl groups and *DEG* content in polyester samples at different degradation times: COOH (○); DEG (Δ)

Formation of *DEG* during TOD of *PET* is an intricate process based on a complex mechanism. From the examination of data given in Table 1 one can only affirm that in the early stages of thermal treatment *DEG* can have a high rate of formation through the consumption of hydroxy ester end groups according to reaction II and III. In the last moments of degradation this process proceeds perhaps mianly through reactions IV and V.

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