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Thermal degradation and melt viscosity of ultra-high-molecular-weight poly(ethylene terephthalate)

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The thermal degradation and melt viscosity of ultra-high-molecular-weight poly(ethylene terephthalate) (UHMW-PET) with an intrinsic viscosity exceeding 2 dl g^{-1} were studied in the melt phase under a nitrogen atmosphere. The degradation rate increased with the molecular weight of the polymer. The high degradation rate of UHMW-PET could be interpreted by the differences in the terminal-end-group concentrations. The activation energy for the degradation of UHMW-PET with an intrinsic viscosity (*IV*) of 2.3 dl g^{-1} was 41 kcal mol^{-1}. The effect of molecular-weight change on the thermal degradation of UHMW-PET could be simulated by an empirical formula. The melt viscosity of UHMW-PET with $M_w = 2.3 \times 10^5$ at 300°C under zero shear was 8×10^5 P and the empirical formula for calculation of the melt viscosity was $\eta_0 = 1.45 \times 10^{-17} M_w^{4.23}$. Copyright © 1996. Published by Elsevier Science Ltd.

(Keywords: poly(ethylene terephthalate); thermal degradation; melt viscosity)

INTRODUCTION

Much work on the degradation of poly(ethylene terephthalate) (PET) has been carried out and it has been considered that the degradation of PET proceeds by a random scission of ester linkages[1]. Gooding[2] showed that the rate of thermal degradation was affected by the content of by-products such as acetaldehydes and by the stirring conditions of the molten PET. Zimmermann and coworkers[3,4] reported that the terminal carboxyl group had a catalytic effect on the degradation. Jabarin and Lofgren[5] reported the kinetics for degradation of PET and also calculated the activation energy for degradation under a dry nitrogen atmosphere to be 28 kcal mol^{-1}. Kamatani and Kuze[6] pointed out by analysis of the electron spin resonance spectra of degraded materials that the degradation of PET proceeded by a radical reaction. Sugimura and Tsuge[7] studied the thermal degradation of aromatic polyesters by pyrolysis gas chromatography. Additionally, Ito *et al.*[8] prepared high-tensile-strength fibre from UHMW-PET with an intrinsic viscosity (*IV*) of 3.6 dl g^{-1} by solution spinning and reported that the *IV* retention of the UHMW-PET after heat treatment was smaller than that of conventional PET with a *IV* of 0.6 dl g^{-1}.

Ultra-high-molecular-weight poly(ethylene terephthalate (UHMW-PET) with an intrinsic viscosity exceeding 2 dl g^{-1} ($M_w = 2.2 \times 10^5$) was obtained by the swollen-state polymerization technique in specific solvents[9–11]. It is considered that UHMW-PET has an extremely high melt viscosity on account of its high molecular weight. Consequently, the processing of UHMW-PET must be conducted under a high temperature in order to reduce its melt viscosity. However, high temperatures may induce serious degradation of UHMW-PET during processing to fibres, films, etc. Therefore, evaluation of these parameters is very significant for the processing of UHMW-PET. Gregory and coworkers[12–14] measured the melt viscosity of PET under various conditions. However, in these previous studies, the molecular weight M_w of the PET used for the thermal degradation experiments and for the measurement of melt viscosity was $3–7 \times 10^4$ ($IV = 0.6–1$ dl g^{-1}). Therefore, in order to clarify the effect of molecular weight, we studied the thermal degradation and melt viscosity behaviour of UHMW-PET with an intrinsic viscosity exceeding 2 dl g^{-1}.

EXPERIMENTAL

Preparation of UHMW-PET

UHMW-PET with $IV > 2$ dl g^{-1} was prepared from conventional PET with $IV = 0.6$ dl g^{-1} by the swollen-state polymerization technique using hydrogenated terphenyl as the solvent[9].

The important characteristics of UHMW-PET and conventional PET are shown in *Table 1*. The measurement methods used for *IV* (dl g^{-1}), carboxyl end-group content (equivalents per 10^6 g), diethylene glycol content (mol% per total glycol content), and molecular-weight distribution (M_w/M_n) are described elsewhere[15].

Thermal degradation

UHMW-PET was pulverized by a freezer mill in liquid nitrogen and dried at 130°C under vacuum for 16 h. Dry UHMW-PET (1 g) was charged into the glass tube and

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*To whom correspondence should be addressed. Present address: Japan U-pica Technical Research Institute, Japan U-pica Co. Ltd, 5-3-3 Higashiyawata Hiratsuka, Kanagawa 254, Japan sealed by fusing under a nitrogen atmosphere. The glass tube was immersed in a salt bath at a specific temperature for a set period of time and was then cooled in liquid nitrogen. After grinding the treated samples to a powder, they were finally dried at 50°C under vacuum, and the *IV* and carboxyl content were then measured.

Measurement of melt viscosity

The melt viscosity of UHMW-PET was measured by a cone and plate viscometer (MR-3, Reology Co. Ltd); the diameter of the cone was 1.8 cm with an angle of 5°; the diameter of the wire was 1.6 mm. Pulverized UHMW-PET (0.2 g) was placed on the plate, and the temperature was then raised up to 300°C under a nitrogen atmosphere. After melting the polymer, the melt viscosity was measured under a specific shear rate.

RESULTS AND DISCUSSION

Degradation rate of UHMW-PET

The degradation rate of a polymer is affected by the degradation condition chosen and the characteristics of the polymer itself. The degradation conditions described in the Experimental section were selected by considering the processing of UHMW-PET. The characteristics of the PET samples are listed in *Table 1*. As UHMW-PET ($IV = 2.3$) did not have a high content of either carboxyl end-groups or diethylene glycol moieties, these effects on the degradation may therefore be neglected[4]. The molecular-weight distribution of UHMW-PET was greater than that of conventional PET. The polydispersity of UHMW-PET ($IV = 2.3\,\mathrm{dl\,g^{-1}}$) was 2.3, and decreased to 2.0 by heat treatment in the melt phase due to rapid ester interchange. If the polydispersity is taken into account, the relationship[5] between IV and weight-average molecular weight can be expressed as follows:

$$IV = 4.68 \times 10^{-4}(M_w/M_n)^{0.68}(M_n)^{0.68} \qquad (1)$$

Equation (1) indicates that *IV* decreases from 2.3 to $2.1\,\mathrm{dl\,g^{-1}}$, when the polydispersity of UHMW-PET changes from 2.3 to 2.0 during the melting process.

The changes in intrinsic viscosity as a result of heat treatment are represented in *Figure 1*. UHMW-PET with an initial intrinsic viscosity (IV_i) of 2.3 or $2.7\,\mathrm{dl\,g^{-1}}$ shows a smaller *IV* retention than conventional PET with $IV_i = 0.6$. After 2 h of degradation at 300°C, the *IV* of all of the PET samples was reduced to $\sim 0.6\,\mathrm{dl\,g^{-1}}$. It was considered that the degradation of PET proceeded by a random scission of the ester linkages[1,16]. Therefore, according to the concept of probability, the number of molecules increases with time and degradation rate. Thus, the degree of polymerization (*DP*) before and after the degradation can be expressed by the following equation:

$$\frac{1}{DP_f} - \frac{1}{DP_i} = K_d t \qquad (2)$$

Where DP_i and DP_f are the degree of polymerization before and after the degradation, respectively, K_d is the degradation rate and *t* is time (h). Thus, the reciprocal of DP_f against degradation time gives a straight line, as shown in *Figure 2*; the slope of this line represents the degradation rate (K_d) in equation (2). The relationship between K_d and DP_i is shown in *Table 2*. It is clear that the degradation rate of UHMW-PET is twice as great as that of conventional PET (with $IV = 0.6\,\mathrm{dl\,g^{-1}}$) at 300°C.

Table 1 Characteristics of the materials used in the thermal degradation studies

	UHMW-PET	Conventional PET	
$IV\,(\mathrm{dl\,g^{-1}})$	2.3	1.0	0.6
M_w/M_n	2.3	2.1	2.0
COOH content[a]	5	12	10
Diethylene glycol content (mol %)	0.8	1.2	1.2
Polymerization process[b]	Swollen state	Solid state	Melt phase

[a] Expressed as number of equivalents per 10^6 g
[b] Sb was used as the catalyst in each process

Relationship between degradation rate and molecular weight

Isothermal degradation at 300°C was carried out for

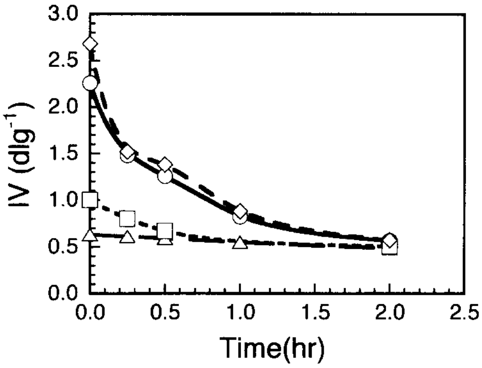

Figure 1 Intrinsic viscosity of PET as a function of degradation time at 300°C: (◇) $IV_i = 2.7$; (○) $IV_i = 2.3$; (□) $IV_i = 1.0$; (△) $IV_i = 0.6\,\mathrm{dl\,g^{-1}}$

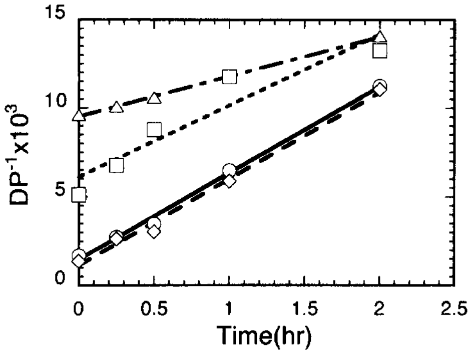

Figure 2 Relationship between reciprocal of degree of polymerization of PET after thermal degradation and degradation time at 300°C: (◇) $IV_i = 2.7$; (○) $IV_i = 2.3$; (□) $IV_i = 1.0$; (△) $IV_i = 0.6\,\mathrm{dl\,g^{-1}}$

Table 2 Effect of initial degree of polymerization of PET (DP_i) on the degradation rate at 300°C

DP_i	$K_d \times 10^{-3}\,(\mathrm{h^{-1}})$
104	2.257
196	4.044
591	4.869
730	4.871

PET samples with a wide range of molecular weights. *Figure 3* shows the correlation between the degradation rate and the degree of polymerization before degradation takes place. An empirical formula (obtained by the least-squares method) for this relationship was given by the following:

$$K_d \times 10^3 = -4.197 + 3.135\log(DP_i) \qquad (3)$$

The content of carboxyl end-groups in thermally degraded PET was then measured. *Figure 4* shows the relationship between the content and thermal degradation treatment time. The slope of each line in *Figure 4* represents the increase in content rate with time, and these are all nearly equal to each other, i.e. the rate does not depend on the molecular weight. This suggests that the degradation mechanism for the UHMW-PET is similar to that of conventional PET. The main reaction in PET degradation is the cleavage of ester linkages and the formation of vinyl ester and carboxyl groups[4]. If hydroxyethyl end-groups remain at a high concentration in the polymer, these functional groups may react with each other or with the carboxyl end-groups. These propagation reactions can contribute towards keeping the *IV* at a high level.

As the results show, propagation of low-molecular-weight PET overcomes the degradation reaction. In fact, the difference in terminal-end-group concentration is very large. Conventional PET with $IV = 0.6\,\mathrm{dl\,g^{-1}}$ has 108 equivalent terminal end-groups per 10^6 g of PET, while on the other hand, UHMW-PET with $IV = 2.3\,\mathrm{dl\,g^{-1}}$ has only 15 equivalent end-groups.

Effect of degradation temperature

The effect of temperature on the degradation is shown in *Figure 5*, with higher temperatures causing the largest degradation of PET as expected. In addition, the Arrhenius plot given in *Figure 6* shows that the degradation rate of PET increases with temperature; the activation energy for the degradation of UHMW-PET was $E_a = 41\,\mathrm{kcal\,mol^{-1}}$, similar to that found in previous work. Zimmerman and coworkers[3,4] reported that the activation energy of degradation of PET was 29–41 $\mathrm{kcal\,mol^{-1}}$. Thus, an empirical formula for the degradation of PET was obtained from a multivariable regression analysis of the change in *IV* (i.e. before and after thermal degradation) and is given as follows:

$$\ln(K_d) = 34.86 + 0.5879\ln(IV_i) - 23260T^{-1} \qquad (4)$$

where IV_i is the intrinsic viscosity of PET before degradation and T is the degradation temperature (K). The intrinsic viscosity after degradation (IV_f) can be calculated by the combination of equations (1), (2) and (4). The values of IV_f calculated by using these equations were in reasonable agreement with the experimental data. The IV_f results for the UHMW-PET are simulated in *Figure 7*. These results reveal that the *IV* value decreases from 2.0 to 1.1 $\mathrm{dl\,g^{-1}}$ after heat treatment at 300°C for 30 min. Thus, in order to maintain a retention of 80% *IV*, the processing temperature of UHMW-PET must be below 280°C and the processing time must be less than 30 min. In conclusion, processing of UHMW-PET must be conducted with as lower temperatures and with as shorter time as possible in order to maintain the molecular weight during the processing.

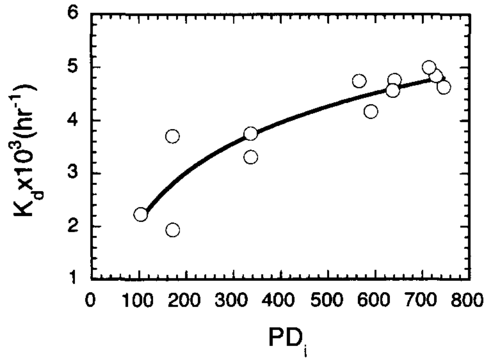

Figure 3 Relationship between degradation rate and initial degree of polymerization of PET

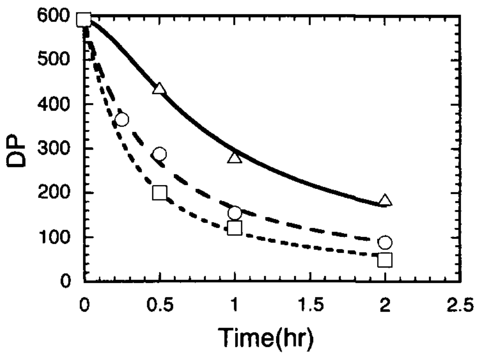

Figure 5 Degree of polymerization of PET at various temperatures as a function of degradation time: (○) 300; (□) 310; (△) 290°C

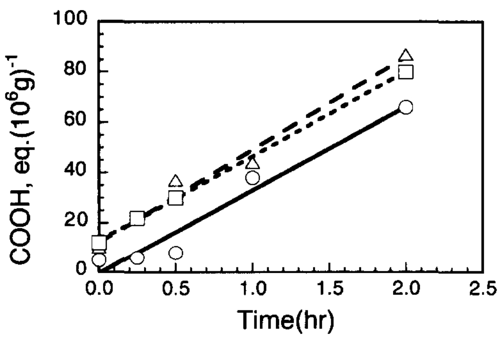

Figure 4 Carboxyl end-group content of PET as a function of degradation time at 300°C: (○) $IV_i = 2.3$; (□) $IV_i = 1.0$; (△) $IV_i = 0.6\,\mathrm{dl\,g^{-1}}$

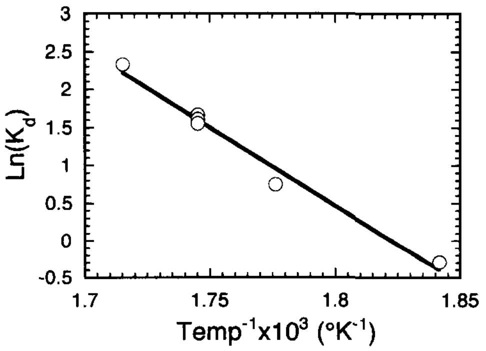

Figure 6 Arrhenius plot of the degradation rate of UHMW-PET with $IV = 2.3\,\mathrm{dl\,g^{-1}}$

Melt viscosity of UHMW-PET

It is well known that the melt viscosity of a polymer at zero shear rate is proportional to the weight-average molecular weight of the polymer raised to the power of 3.4. Gregory and coworkers[12–14] developed a rheology equation for molten PET and showed that the zero-shear viscosity of PET with $M_w = 2\text{–}7 \times 10^4$ is proportional to its weight-average molecular weight raised to the power of 3.5. *Figure 8* represents the melt viscosity of UHMW-PET with $M_w = 1.6\text{–}2.3 \times 10^5$ measured at various temperatures. Newtonian plateaux are clearly observed in these samples, except for the PET sample which shows the highest melt viscosity; this higher-*IV* sample shows shear thinning at lower shear rates[12]. One can assume that the zero-shear viscosity is almost the same as the viscosity at $0.1\,\mathrm{s}^{-1}$. *Figure 9* shows the relationship between weight-average molecular weight and zero-shear melt viscosity at 300°C. From this linear correlation, the following equation can be obtained:

$$\log(\eta_0) = -16.8 + 4.23\log(M_w) \quad (5)$$

The exponent of the molecular weight is higher than that reported by Gregory and coworkers[12]. The temperature dependence of the melt viscosity at zero shear of UHMW-PET with $IV = 2.1\,\mathrm{dl\,g^{-1}}$ is shown in *Figure 10*; the activation energy for fluidity is $27\,\mathrm{kcal\,mol^{-1}}$ at around 300°C.

According to equation (5), the melt viscosity of UHMW-PET with $IV = 2\,\mathrm{dl\,g^{-1}}$ at 300°C will be 6.1×10^5 P. Such a value for the melt viscosity thus anticipates difficulty in melt processing of UHMW-PET.

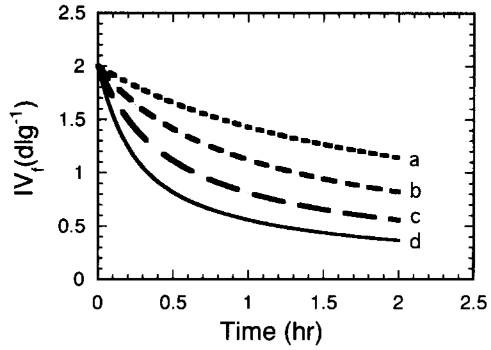

Figure 7 Simulation results obtained for the degree of polymerization of UHMW-PET with $IV = 2\,\mathrm{dl\,g^{-1}}$ at various temperatures: (a) 280; (b) 290; (c) 300; (d) 310°C

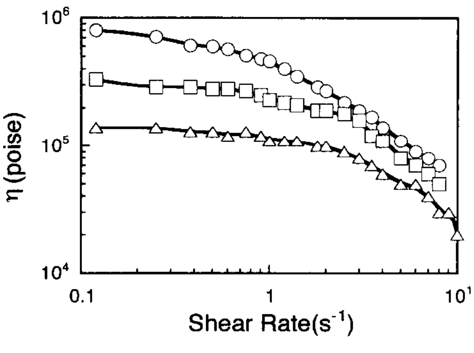

Figure 8 Melt viscosity of UHMW-PET with $IV = 2.1\,\mathrm{dl\,g^{-1}}$ as a function of shear rate at various temperatures: (○) 300; (□) 310; (△) 320°C

From the results in the preceding section, the processing temperature of UHMW-PET must be below 280°C in order to avoid any serious degradation. However, at 280°C, the melt viscosity under zero shear may be greater than 10^6 P. In order to reduce the melt viscosity, processing must therefore be conducted at a high temperature; however, a high temperature may induce serious degradation of the UHMW-PET. Therefore, reduced-viscosity processing of UHMW-PET at low temperatures will be required. A new approach for such reduced-viscosity processing of UHMW-PET will be presented in a subsequent paper.

CONCLUSIONS

The thermal degradation of UHMW-PET with an intrinsic viscosity exceeding $2\,\mathrm{dl\,g^{-1}}$ was carried out in the melt phase under a nitrogen atmosphere. It was found that UHMW-PET had a greater degradation rate than that of conventional PET with $IV = 0.6\,\mathrm{dl\,g^{-1}}$. The degradation rate calculated from *IV* changes was increased with the molecular weight of the PET that was used. The high degradation rate of UHMW-PET could be interpreted by the differences in the terminal-end-group concentrations. The degradation mechanism appeared to be the same as that of conventional PET, as deduced from the similar trends observed for the terminal carboxyl group content. The activation energy for the degradation of UHMW-PET with $IV = 2.3$ was $41\,\mathrm{kcal\,mol^{-1}}$. The molecular-weight change after thermal degradation of UHMW-PET could be simulated by an empirical formula. This simulation showed that *IV* decreased from 2.0 to $1.1\,\mathrm{dl\,g^{-1}}$ after treatment at 300°C for 30 min. The melt

Figure 9 Relationship between weight-average molecular weight of UHMW-PET and melt viscosity at zero shear

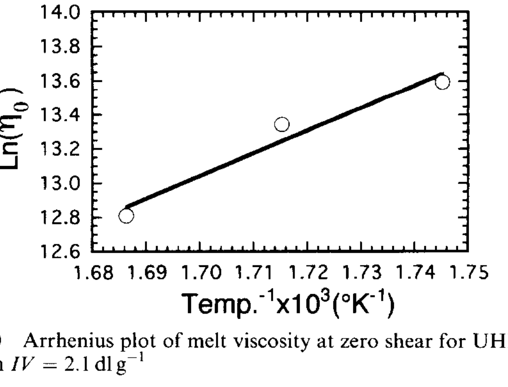

Figure 10 Arrhenius plot of melt viscosity at zero shear for UHMW-PET with $IV = 2.1\,\mathrm{dl\,g^{-1}}$

viscosity of UHMW-PET with a weight-average molecular weight of 2.3×10^5 was estimated to be 8×10^5 P at 300°C under zero shear. In conclusion, the processing of UHMW-PET must be conducted with as lower temperatures and with as shorter times as possible in order to maintain a high retention of the molecular weight during the processing treatment.

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