

THERMAL DEGRADATION OF UHMWPE

E. Rudnik and Z. Dobkowski

Industrial Chemistry Research Institute, Rydygiera 8, 01-793 Warsaw, Poland

Abstract

The thermal behaviour of ultra-high molecular weight polyethylene (UHMWPE) of different molecular weights was examined by thermal analysis methods. The melting temperature T_m and the heat of melting ΔH were measured by the DSC method. The thermooxidative degradation process was investigated by using a MOM Q-1500 D derivatograph at various heating rates in air atmosphere. The initial decomposition temperature T_i was determined from the TG curves, and other characteristic temperatures of decomposition were calculated. It was found that T_m and ΔH are higher for UHMWPE than those for HDPE, i.e. 146°C and 195 J g⁻¹ for UHMWPE as compared with 133°C and 166 J g⁻¹ for HDPE. The thermal behaviour of the investigated UHMWPE samples is not significantly influenced by molecular weight.

Keywords: thermal analysis, thermooxidative degradation, ultra-high molecular weight polyethylene

Introduction

Ultra-high molecular weight polyethylene (UHMWPE) is a thermoplastic material with an excellent set of properties, such as good abrasion resistance, the highest impact toughness of any plastic at cryogenic temperature, good corrosion resistance and environmental stress-crack resistance, a low coefficient of surface friction, and noise- and shock-abatement properties [1, 2]. Many applications in different areas, e.g. in mining, foundries and transportation, have been found for UHMWPE, due to its unique properties. Moreover, UHMWPE is used in medicine for the manufacture of artificial joints in most orthopaedic replacements, especially for hips and knees.

Extensive studies were recently carried out on high-strength and high-modulus UHMWPE fibres obtained by various methods, usually the solution-crystallization method [3-5] or the gel spinning technique [6-10]. Morphological [11] and surface [12] modifications of UHMWPE fibres have been reported. The influence of the molecular weight of UHMWPE on its microstructure and mechanical properties has been studied [13]. Thermal analysis methods have been used to study the melting and crystallization behaviour of UHMWPE fibres and gels [9, 14-17]. However, no data have been found in the available literature on the thermal decomposition of UHMWPE.

In the present work, the thermooxidative degradation of UHMWPE of different molecular weights was investigated. High-density polyethylene (HDPE) was studied for comparison.

Experimental

Materials

Hizex UHMWPE (Mitsui Petrochemical Industries) in powder form and HF210 HDPE (Idemitsu) as pellets were investigated. The molecular characteristics of the samples are listed in Table 1.

Table 1 Molecular characteristics of polyethylene (PE) samples

No.	Sample	$\eta/\text{dl g}^{-1}$	$M_v \times 10^{-4}$
1	HF 210	3.2	26.4
2	Hizex 145 M	7.8	89.6
3	Hizex 240 M	16.8	256
4	Hizex 340 M	25.6	456

Note: Intrinsic viscosity in decalin at 135°C, and molecular weight of UHMWPE according to literature data [13]; that of HF 210 according to our measurements.

Measurements

The melting behaviour of the investigated PEs was characterized by the DSC method. Measurements were performed with a Perkin-Elmer DSC 7 instrument. Samples were heated at a rate of 20°C min⁻¹ from room temperature up to 200°C in nitrogen atmosphere, and then cooled at a rate of 20°C min⁻¹; the second heating cycle was performed at the same heating rate. The sample size was about 10 mg. The melting point and the heat of fusion measurements were calibrated with indium and zinc as standard materials.

The TG method was applied to study the thermooxidative process with a MOM Budapest Q 1500D derivatograph. PE samples of about 40 mg were heated from room temperature to 1000°C at various heating rates in the range from 1.25 to 20°C min⁻¹. All measurements were performed in environmental air atmosphere without induced circulation.

Results and discussion

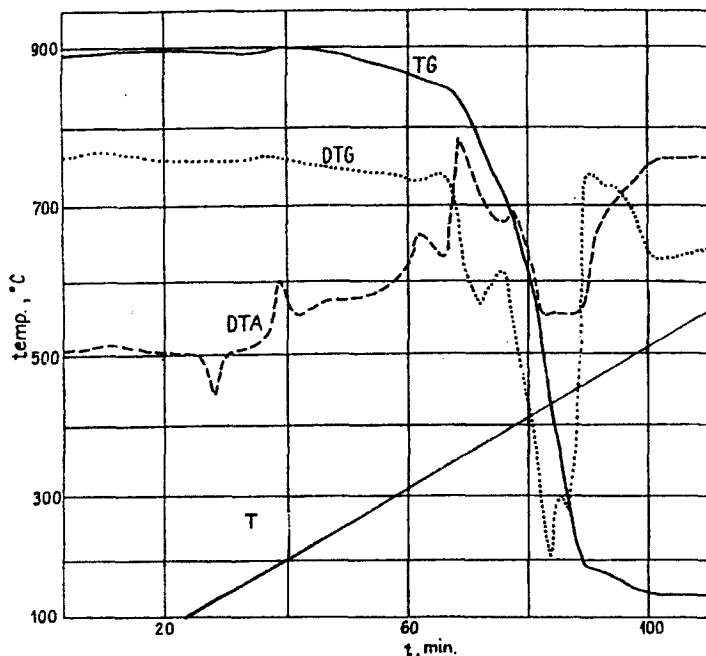
Details on the melting behaviour of the investigated PEs are given in Table 2. It has been reported by many authors [11, 15, 17] that two peaks, corresponding to the orthorhombic/hexagonal and hexagonal/melting transitions, are observed in the typical DSC curves for UHMWPE fibres. One melting peak is found for UHMWPE powders.

In our experiments, one melting peak was observed and the melting temperatures T_m were in the range 145–150°C. The melting temperatures were higher for UHMWPE than for HDPE. It was also observed that the peak values of T_m increased with increasing molecular weight of the PE. This is in agreement with the IUPAC report [13]. The T_m values of UHMWPE were 6–7°C lower on the second heating (Table 2).

Table 2 Melting behaviour of PEs revealed by DSC

No.	Sample	First heating			Second heating		
		$T_m/^\circ\text{C}$	$\Delta H/J\text{ g}^{-1}$	Crystallinity/%	$T_m/^\circ\text{C}$	$\Delta H/J\text{ g}^{-1}$	Crystallinity/%
1	HF 210	130	166	57	134.7	178	61
2	PE 125 M	145	221	75	139.0	157	53
3	PE 240 M	146	195	67	139.0	148	50
4	PE 340 M	150	197	67	140.5	141	48

The crystallinity of the PE samples was estimated by the DSC method, using a value of 293 J g^{-1} [18] as the heat of fusion of the PE crystal. The crystallinity on the first heating was higher for all UHMWPE samples than for HDPE, while on the second heating it decreased to approximately the same values for all investigated UHMWPE samples.

**Fig. 1** TG, DTG and DTA curves of PE 240 M (heating rate: 5°C min^{-1})

TG, DTG and DTA curves obtained at a heating rate of 5°C min^{-1} are given in Figs 1 and 2 for PE 240 M and PE HF 210, respectively. The thermooxidative degradation proceeds in one stage for both types of PE. It seems that the thermal behaviour of UHMWPE does not depend on molecular weight.

In order to determine the thermal stability of the PEs, the following temperatures were determined (Table 3):

→ from the TG curves:

T_i temperature of initial decomposition, °C;

$T_{x\%}$ temperature corresponding to $x\%$ mass loss, °C;

W_T mass loss at a given temperature T , in wt%;

→ from the DTA curves:

T_{peak} temperature of the first exothermic peak in the DTA curves, °C (cf. Fig. 1).

This distinct peak may be ascribed to some oxidation process since a slight mass increase in also observed in the TG curve (cf. Fig. 1) for UHMWPE. Such a peak is not observed for the HF 210 sample (cf. Fig. 2).

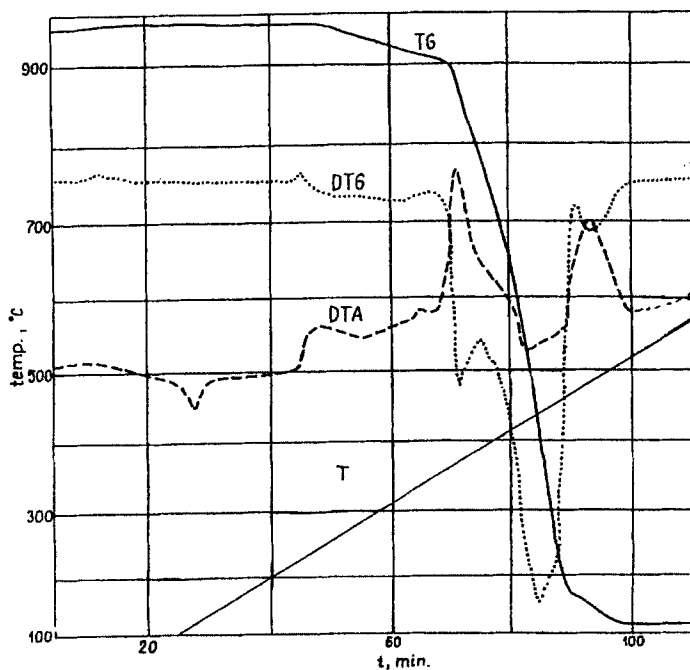


Fig. 2 TG, DTG and DTA curves of PE HF 210 (heating rate: $5^{\circ}\text{C min}^{-1}$)

Table 3 Characteristics of thermooxidative decomposition of PE samples (heating rate: $5^{\circ}\text{C min}^{-1}$)

No.	Sample	$T_i/^{\circ}\text{C}$	$T_{3\%}/^{\circ}\text{C}$	$T_{10\%}/^{\circ}\text{C}$	$T_{20\%}/^{\circ}\text{C}$	$W_{300^{\circ}\text{C}}/\%$	$W_{350^{\circ}\text{C}}/\%$	$T_{\text{peak}}/^{\circ}\text{C}$
1	HF 210	240	341	370	382	2.4	5.5	—
2	PE 145 M	240	320	362	384	2.9	8.5	195
3	PE 240 M	242	330	367	387	2.7	6.8	195
4	PE 340 M	248	318	358	380	3.4	8.4	200

Similar characteristic decomposition temperatures were observed for all the investigated UHMWPE samples. Hence, it seems that the thermal stability of

UHMWPE is not influenced significantly by the molecular weight. However, there is a small difference between UHMWPE and HDPE. The temperatures $T_{x\%}$ are slightly higher and the mass losses W_T are smaller for HF210 than for UHMWPE.

Conclusions

Overall, the thermal behaviour of the investigated UHMWPE samples is not significantly influenced by the molecular weight.

However, a difference does exist between UHMWPE and HDPE. T_m and ΔH were found to be higher for UHMWPE than for HDPE, i.e. 146°C and 195 J g⁻¹ for UHMWPE as compared with 133°C and 166 J g⁻¹ for HDPE.

References

- 1 H. F. Mark, N. M. Bikales, Ch. G. Overberger, G. Menges, *Encyclopedia of Polymer Science and Technology*, A Wiley-Interscience Publication, New York 1986, Vol. 6, p. 490.
- 2 R. Juran (Ed.), *Modern Plastics Encyclopedia '91*, Mc Graw-Hill, Inc., New York 1991, p. 66.
- 3 A. Zwiijnenburg and A. Pennings, *Colloid. Polym. Sci.*, 254 (1976) 868.
- 4 J. Smook, J. C. Torfs, P. F. Hutten and A. Pennings, *J. Polym. Bull.*, 2 (1980) 293.
- 5 P. J. Barham and A. Keller, *J. Mat. Sci.*, 15 (1980) 2229.
- 6 P. Smith and P. J. Lemstra, *J. Mat. Sci.*, 15 (1980) 505.
- 7 D. J. Dijkstra and A. J. Pennings, *Polymer Bull.*, 19 (1988) 481.
- 8 N. S. Murthy, S. T. Correale and S. Kavesh, *Polym. Commun.*, 31 (1990) 50.
- 9 Ch. Xiao, Y. Zhang, S. An and G. Jia, *J. Appl. Polym. Sci.*, 59 (1966) 931.
- 10 Y. Sakai and K. Miyasaka, *Polymer*, 29 (1988) 1608.
- 11 J. Economy and A. G. Andreopoulos, *Polym. Adv. Tech.*, 5 (1994) 349.
- 12 M. S. Silverstein, O. Breurer and H. Dodiuk, *J. Appl. Polym. Sci.*, 52 (1994) 1785.
- 13 K. Nakayama, A. Furumiya, T. Okamoto, A. Kaito, C. R. Choe, L. Wu, G. Zhang, L. Xiu, D. Liu, T. Masuda and A. Nakajima, *Pure & Appl. Chem.*, 63 (1991) 1793.
- 14 W. Hoogsteen, G. ten Brinke and A. J. Pennings, *Coll. Polym. Sci.*, 266 (1988) 1003.
- 15 H. Phuong-Nguyen and G. Delmas, *Macromolecules*, 25 (1992) 408.
- 16 H. Phuong-Nguyen and G. Delmas, *Macromolecules*, 25 (1992) 414.
- 17 Y. Hsieh and J. Ju, *Appl. Polym. Sci.*, 53 (1994) 347.
- 18 G. Cappaccio, J. Clements, P. J. Hine and I. M. Ward, *J. Polym. Sci., Polym. Phys. Edn.*, 19 (1981) 1435.