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INVESTIGATIONS AND MOLECULAR MODELING OF SOME THERMOPHYSICAL PROPERTIES OF POLYSULFONES

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Abstract

Degradation of commercial polysulfones (PSF) was investigated in air and in inert atmosphere (nitrogen) using thermogravimetric (TG) method. It has been found that the degradation of Udel P-1800 PSF is initiated about 400°C, both in air and in nitrogen. The activation energy of degradation of PSF, (E_a), has been calculated by the Kissinger and Ozawa methods. The value of E_a about 200 kJ·mol^{-1} has been found for both air and nitrogen atmosphere. Experimental results concerning thermal properties of PSF (T_g and $T_{d,1/2}$) were compared with those obtained by the computer modeling technique, and a good agreement has been found.

Keywords: computer modeling, degradation, polysulfones

Introduction

Recently the use of computer-aided modeling technique in studies of polymer properties is of considerable interest, including computer-aided investigations of polymer thermal properties, such as glass transition temperature T_g, as well as polymer thermal stability. Calculations of T_g and the temperature of half decomposition $T_{d,1/2}$, as well as other polymer properties, have been described by Bicerano [1, 2]. This method has been used in our investigations of some thermophysical properties of polysulfone, i.e. bisphenol A polysulfone (PSF).

PSF is known as an engineering material having an excellent hydrolytic and thermal stability [3–5]. Its T_g has been reported as 190°C [6]. A few experimental works on thermal degradation of PSF has recently been found [7, 8]. It has been reported that the degradation of PSF proceeds at temperature above 380°C to sulphur dioxide, methane, oxides of carbon, hydrogen, and phenol or its derivatives [7]. Thermal stability of PSF has been investigated by Blumenfeld *et al.* [8] in the presence of aromatic phosphates and phosphites as stabilisers. There is also a few works published on the computer modeling investigations of properties of PSF [9, 10].

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Thermal degradation of PSF has recently been studied in our Institute using thermoanalytical methods such as differential scanning calorimetry (DSC) and thermogravimetry (TG). The aim of this work was to compare our experimental results with those calculated using computer modeling technique.

Experimental

Materials

The materials used in this work were commercial Udel polysulfones (Amoco Chemical): the general purpose P-1800 for either injection molding or extrusion (melt index range: 5–9 g/10 min), and P-3500 for extrusion with a higher molecular weight (melt index range: 1–5 g/min).

Measurements

A Perkin Elmer TGA-7 Thermogravimetric Analyser was used to study the degradation process of polysulfones in both air and nitrogen atmosphere at heating rate range from 1.5 to 20 deg·cm^{-1}. Samples of approximately 10 mg were used.

Glass transition temperature (T_g) of polysulfones was measured using a Perkin Elmer DSC 7 differential scanning calorimeter.

Molecular modeling and computer calculation were performed at the Interdisciplinary Computer Modeling Center (ICM) of the Warsaw University, using the CRAY EL 98 computer and the Insight II software of BIOSYM Technologies Inc.

Results and discussion

Thermograms of polysulfones (PSF) in air and nitrogen atmosphere are shown in Fig. 1 and thermal decomposition characteristics of PSF in Table 1.

Table 1 Thermal decomposition of polysulfones. (Heating rate: 5 deg·min^{-1})

Polysulfone	Atmosphere	T_o /	T_5 /	T_{10} /	T_{max} /
		°C			
Udel P-1800	air	394	506	514	528
	nitrogen	411	497	505	515
Udel P-3500	air	336	506	514	532

T_o - temperature at which decomposition initiates; T_5 - temperature corresponding to 5% weight loss; T_{10} - temperature corresponding to 10% weight loss; T_{max} - the peak temperature in DTG plot

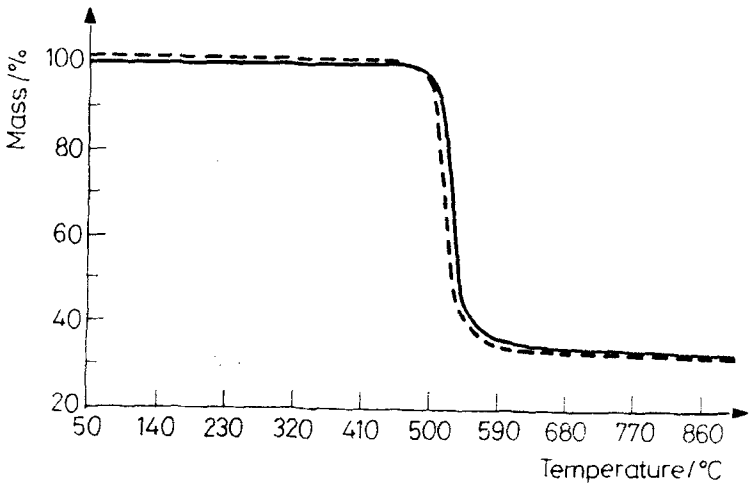

Fig. 1 TG curves of Udel P-1800 polysulfone — air; --- nitrogen

Investigated polysulfones exhibit a single stage decomposition. A rapid loss of mass is observed during the degradation of PSF, either in air or nitrogen atmosphere, over the range 490–550°C due to C–S bond scission, followed by elimination of SO_2 and formation of two phenyl radicals [11]. There is not a significant difference between the thermal and thermooxidative degradation of PSF, e.g. in nitrogen and in air atmosphere, respectively. This observation is confirmed by similar values of apparent activation energy of decomposition of PSF calculated by the Kissinger's method (Table 2). Similar effect of atmosphere on the degradation of PSF was found by Yamashita *et al.* [12] during photodegradation study of PESF and PSF.

The activation energy E_a *vs.* conversion degree α for the decomposition of PSF, calculated by the Ozawa method, is shown in Fig. 2. The values of E_a for the conversion degree up to 50% have not been changed significantly.

Table 2 Kinetic parameters of thermal decomposition of polysulfones according to Kissinger's method

Polysulfone	Atmosphere	Activation energy E_a /kJ·mol^{-1}	Pre-exponential factor /min^{-1}	Correlation / r^2
Udel P-1800	air	205	5.00×10^5	0.9348
	nitrogen	195	4.18×10^5	0.9109
Udel P-3500	air	189	4.09×10^5	0.9964

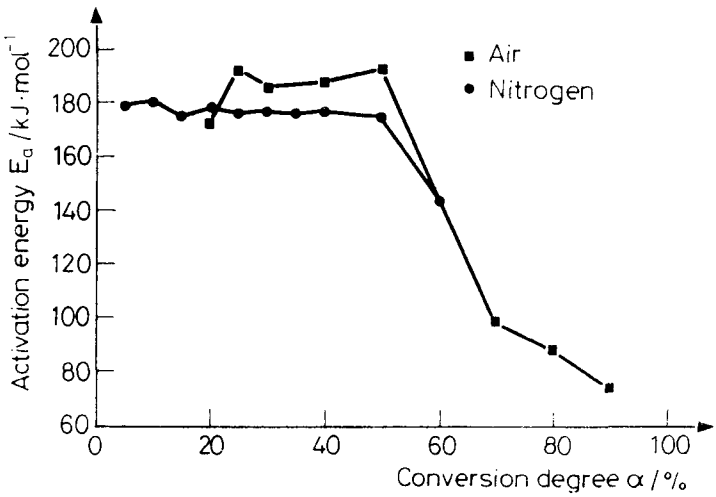

Fig 2 Activation energy *vs.* conversion degree for Udel P-1800 polysulfone — air; --- nitrogen

Molecular modeling

Modelled structure of PSF has been generated and minimised by the steepest descent and BFGS quasi Newton iteration techniques to obtain lowest energy conformations. The properties of PSF were calculated using the Synthia Module of BIOSYM Technologies software [13].

Results of experimental and calculated values of some properties of PSF are presented in Table 3. A good agreement between experimental DSC and computer modeling values of T_g has been found.

Table 3 Experimental and computer modeling data

Property	Experimental	Computer modeling
Glass transition, T_g /	190 /Udel P-1800/	189
°C	190 /Udel P-3500/	
Temp. of half decomposition, $T_{d,1/2}$·		470
heating rate / deg·min^{-1}:		
20	577°C	
15	550°C	
10	547°C	
5	528°C	
1.5	495°C	
Density at 25°C / g·cm^{-3}:	1.24*	1.23

*producer's data

Polymer thermal stability is characterized by the temperature of half decomposition, $T_{d,1/2}$, defined as 'the temperature at which the loss of weight during pyrolysis (at a constant rate of temperature rise) reaches 50% of its final value' [1, 6].

The experimental values of $T_{d,1/2}$ depend on the heating rate (Table 3). Extrapolation of temperature of half decomposition $T_{d,1/2}=f(\beta)$ to $\beta=0$ (where β is the heating rate), gives value of $T_{d,1/2}=499°C$ (Fig. 3). A reasonable agreement between experimental and calculated values of $T_{d,1/2}$ has been found.

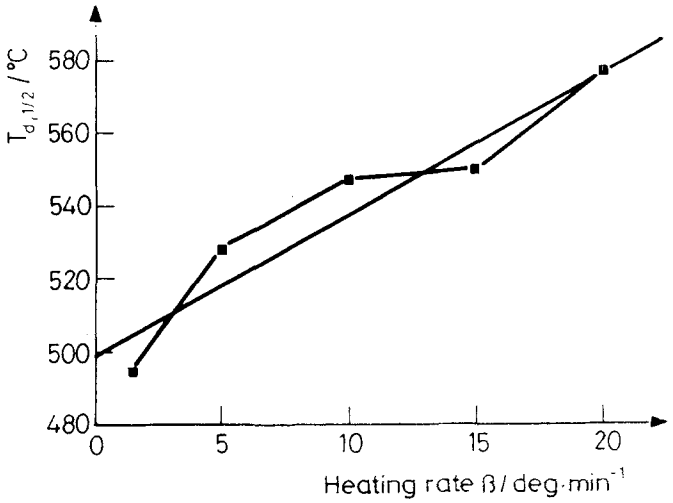

Fig. 3 Temperature of Half Decomposition $T_{d,½}$ *vs.* heating rate β

It should also be noted that there is an excellent agreement between density of PSF given by the producer and the computer modeling calculated value.

Conclusions

It has been found that the activation energy of degradation of PSF, both in air and in inert atmosphere, calculated by the Kissinger and Ozawa methods, has a similar value.

Experimental results related to thermal properties of PSF are consistent with those obtained using the Synthia Module of BIOSYM Technologies software.

Further work on computer-aided investigations of thermal properties of polymers will be continued.

* * *

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References

1 J. Bicerano, Predictions of the Properties of Polymers from their Structures, Marcel Dekker, New York, 1993.
2 J. Bicerano, Computational modeling of polymers, Marcel Dekker, New York 1992.
3 H. Mark, W. Bikales, Ch. Overberger and G. Menges, Eds, Encyclopedia of Polymer Science and Engineering, 2nd Ed., John Wiley and Sons, Inc., New York 1985, Vol. 13, p. 196.
4 L. M. Robeson, B. L. Dickinson and S. T. Crisafulli, Hydrolytic stability of high T_g engineering polymers: Relevance to steam sterilization, Union Carbide Corporation publication.
5 M. I. Robeson and S. T. Crisafulli, J. Appl. Polym. Sci., 28 (1983) 2925.
6 D. W. Van Krevelen, Properties of polymers, 3rd Ed., Elsevier, Amsterdam 1991.
7 J. Troitzsch, International Plastics Flammability Handbook, Hanser, Munchen 1990.
8 A. B. Blumenfeld, E. V. Kalugina, L. M. Bolotina and M. E. Sawina, Plast, Massy, 2 (1993) 21.
9 A. Letton, Secondary relaxation processes in bisphenol A polysulfone, in Ref. [2], Ch. 12.
10 C. F. Fan and S. L. Hsu, mc^2, 1 (1994) 19.
11 M. T. Bryk, Degradation of filled polymers, Ellis Horwood, New York 1991, p. 57.
12 T. Yamashita, H. Tomitaka, T. Kudo, K. Horie and I. Mita, Polym. Deg & Stab., 39 (1993) 47.
13 Insight II, User Guide, version 2.3.0, BIOSYM Technologies, San Diego, 1993.

Zusammenfassung — Mittels Thermogravimetrie wurde der Abbau handelsüblicher Poly- sulfone (PSF) in Luft und in inerter Atmosphäre (Stickstoff) untersucht. Es wurde gezeigt, daß der Abbau von Udel P-1800 PSF bei etwa 400°C einsetzt, sowohl in Luft als auch in Stickstoff. Die Aktivierungsenergie E_a des Abbaues von PSF wurde nach der Methode von Kissinger und von Ozawa berechnet. Sowohl für Luft als auch für Stickstoff wurde ein E_a-Wert von etwa 200 kJ/mol gefunden. Die experimentellen Ergebnisse bezüglich der thermischen Eigenschaften von PSF (T_g und $T_{d,1/2}$) wurden mit denen aus einer Computermodelltechnik verglichen, was eine gute Übereinstimmung ergab.