Journal of Thermal Analysis and Calorimetry, Vol. 63 (2001) 317–321

Short Communication

APPLICATION OF DSC METHOD FOR THERMAL STABILITY AND FLAMMABILITY ASSESSMENT OF MODIFIED POLYURETHANES

K. Pielichowski, D. Słotwińska and J. Pielichowski

Department of Chemistry and Technology of Polymers, Technical University, ul. Warszawska 24, 31-155 Cracow, Poland

(Received November 25, 1999)

Abstract

Differential scanning calorimetry (DSC) was applied to investigate the thermal behaviour of a series of segmented polyurethanes based on diphenylmethane-4,4'-diisocyanate (MDI), polyoxypropylenediol (POPD) and 3-chloro-1,2-propanediol (CPD)/1,2-propanediol (PD).

It has been found that the heat of thermal transition in the range of 250–300°C increases with the amount of CPD, which also causes a decrease of polyurethanes' flammability, characterised by its Limited Oxygen Index (LOI) value. On the basis of obtained results it can be concluded that DSC may be applied for flammability evaluation of segmented polyurethanes.

Keywords: chlorinated polyurethanes, DSC, flammability

Introduction

Thermal analysis methods such as thermogravimetry (TG) and differential scanning calorimetry (DSC) have found a growing application for the evaluation of flammability of polymeric materials [1–3]. Since the flammability of polymers becomes a major issue due to safety regulations and environmental risks, the thermal analysis techniques gain more attention through their display of the thermal degradation profile of minute samples that makes it possible to describe, even quantitatively, the combustibility of a polymer. Mainly DSC method was used so far to observe the changes in the polymers prior to and during decomposition, where, in a conventional diffusion flame, the oxygen is completely consumed in the high temperature zone of

1418–2874/2001/ $ 5.00

Akadémiai Kiadó, Budapest
Kluwer Academic Publishers, Dordrecht

the flame [4, 5], and in a conventional ‘pre-mixture’ flame the fuel is provided to the burning front at an arbitrary rate. A polymer in a stable state of destruction is self-fed by the fuel at a rate which must satisfy the equilibrium conditions of the burning process, that is the rate of production of the inflammable products should be equal to the rate of their consumption; both may be measured in a calibrated heat flux DSC cell.

In this work we present first results of DSC studies on the thermal decomposition and flammability of novel chemically-modified polyurethanes with enhanced thermal properties.

Experimental

Materials

Polyurethanes used in the course of this work were prepared according to the method described in [6, 7]. 3-Chloro-1,2-propanediol (Aldrich), 1,2-propanediol (POCh Gliwice) and polyoxypropylenediol (M_n=750; Rokita S.A.) were used as received. Diphenylmethane-4,4’-diisocyanate was produced by Zaklady Chemiczne Zachem in Bydgoszcz. MDI/sum of diols ratio was determined equivalently.

The composition of the samples is given in Table 1.

Table 1 Composition of the samples*

Sample No.	CPD/mass%	PD/mass%
1	80	0
2	60	20
3	40	40
4	20	60
5	0	80

*Amount of POPD is constant and equal to 20 mass%

Techniques

Differential scanning calorimetry

For the DSC measurements a Netzsch DSC 200, operating in a dynamic mode under air atmosphere, was employed. Sample of ~4 mg mass was placed in sealed aluminum pan. The heating rate of 10 K min^{-1} was applied as the best choice to ensure high resolution of the DSC curves. Prior to use the calorimeter was calibrated with an indium standard; an empty aluminum pan was used as a reference.

Oxygen index

Oxygen index measurements were performed on a standard flammability test apparatus, according to the procedure described in [8].

Results and discussion

From the DSC traces of samples 1–5, depicted in Fig. 1, one can see for each thermal curve a small endothermic peak in the range of 200°C (except of sample 2) and, at 250–300°C, a broader, exothermic transition (Fig. 1).

The first thermal effect may be attributed to melting of hard segments, the local distribution of which depends on the synthesis conditions, particularly temperature

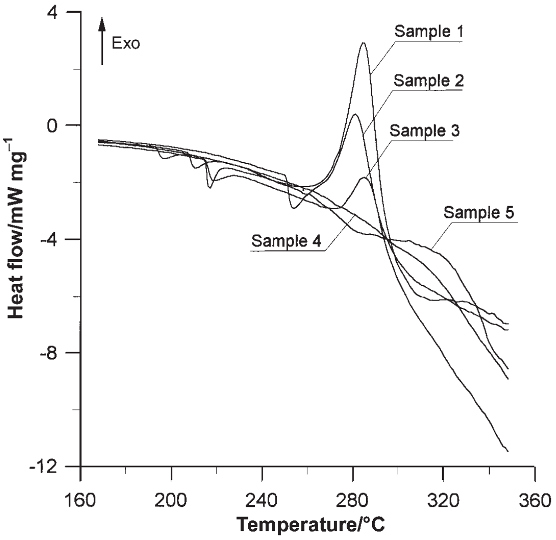

Fig. 1 DSC traces at 10 K min^{-1} of samples 1–5

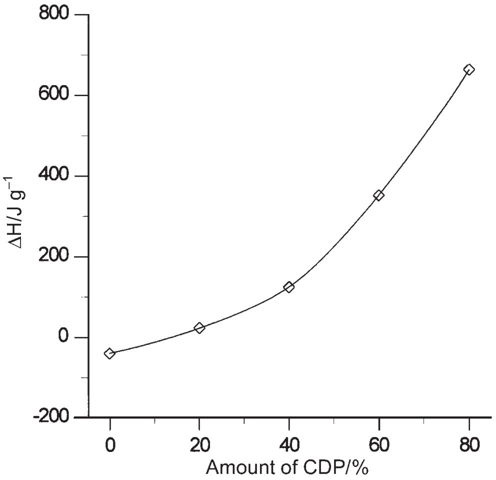

Fig. 2 Heat of transition *vs*. amount of CPD for samples 1–5

[9]. The melting temperature depends on mixing of hard and soft segments which may segregate to form microphase separated domain structure, the amount and degree of which are dependent upon their structure and the processing conditions, whereby every kind of attractive forces (e.g. H-bonding) between hard and soft segments makes phase segregation more difficult. Hydrogen bonding between the hard segments enhances the thermal stability of the hard segment microdomains; at elevated temperature, however, dissociation of hydrogen bonding between the segments and disordering of various kinds of short-range order within the hard-segment region usually occur.

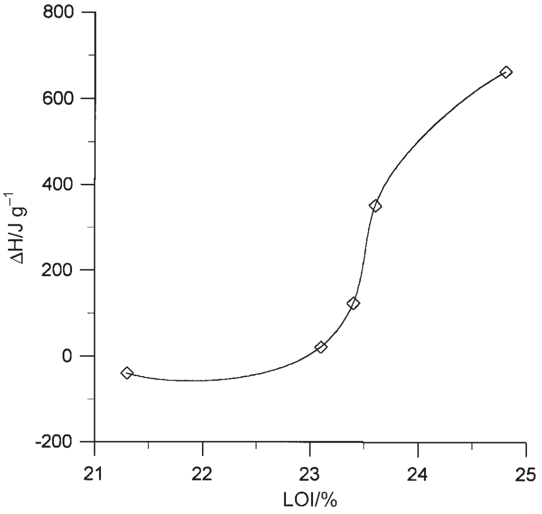

Fig. 3 Heat of transition *vs*. LOI for samples 1–5

The second effect, connected with the onset of decomposition process, show a distinct dependence of the heat of transition *vs*. amount of CPD (Fig. 2). Heats of transition were determined by using a proportional baseline.

This observation would indicate that chlorinated diols play a decisive role in the first phase of combustion, namely pre-heating, which, in turn, governs the flammability process itself, as it can be seen from the relationship between the heat of transition and LOI (Fig. 3).

Organochlorine compounds formed during decomposition can react with $H^{\cdot}$ and $HO^{\cdot}$ radicals, dissipating thus their energy and lowering vapour-phase activity by replacement the major propagating species with those that do not propagate the flame as readily.

The effects described may be utilised for characterisation of flammability by DSC method – detailed studies towards better understanding of this phenomena are now in progress and will be published in a full paper.

Conclusions

For a series of segmented polyurethanes, prepared from diphenylmethane-4,4’-diisocyanate, polyoxypropylenediol and 3-chloro-1,2-propanediol/1,2-propanediol, it has been found that there is a correlation between the heat of thermal transition (as measured by differential scanning calorimetry (DSC) method) and the Limited Oxygen Index (LOI) value, making thus possible to apply DSC technique for flammability assessment of segmented polyurethanes.

References

1 D. W. Van Krevelen, Polymer, 16 (1975) 615.
2 T. D. Gracik and G. L. Long, Thermochim. Acta, 212 (1992) 163.
3 E. A. Turi, Ed., Thermal Characterization of Polymeric Materials, Academic Press, New York 1981.
4 J. Brossas, Polym. Degr. Stab., 23 (1989) 313.
5 S. J. Burge and C. F. H. Tipper, Combustion and Flame, 13 (1969) 495.
6 K. Pielichowski, J. Pielichowski, H. Altenburg and M. Wiegmann, Angew. Makromol. Chem., 224 (1995) 89.
7 K. Pielichowski, J. Pielichowski, H. Altenburg and H.-J. Balloff, Thermochim. Acta, 284 (1996) 419.
8 ASTM D2863-87
9 W. P. Yang, C. W. Macosko and S. T. Wellinghof, Polymer, 27 (1986) 1235.