Journal of Thermal Analysis, Vol. 36 (1990) 2249-2252

APPLICATION OF THE DSC ANALYSIS OF THERMOPLASTIC POLYURETHANE ELASTOMERS TO A COMPARATIVE STUDY OF THEIR TECHNOLOGICAL PROPERTIES

J. T. Haponiuk, A. Balas and *T. Kawka**

TECHNICAL UNIVERSITY, INSTITUTE OF ORGANIC AND FOOD CHEMISTRY AND TECHNOLOGY, 80-952 GDANSK;
*INSTITUTE OF LEATHER INDUSTRY, 91-463 LODZ, POLAND

The fusion and crystallization enthalpies, dynamic viscosity of melts and tensile properties of a series of commercially available thermoplastic polyurethane elastomers (TPU) were estimated. The DSC analysis has been proved as useful to prediction of the processability and tensile properties of TPU's with a similiar hard segment content.

Thermoplastic polyurethane elastomers (TPU), as segmented copolymers, exhibit two-phase microstructure, resulting from thermodynamic incompability of soft segments, based on polyesters or polyethers, and of hard segments, based on isocyanates, usually diphenylomethanediisocyanate, and aliphatic diols, acting as chain extenders.

A balanced combination of soft segment and hard segment components yields the unique, high performance properties of these polymers. Each phase may be characterized by its glass transition temperature and a melting endotherm. The occurrence of a phase transition in a DSC investigation depends mainly on chemical composition, segment type and ability of the segments to crystallize [1-4].

The purpose of this work was to investigate structure-property relationships of some commercially available thermoplastic polyurethane elastomers, selected for their high hard segment content and excellent to temperature properties.

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Experimental

Materials

In this work samples of commercially available thermoplastic polyurethanes have been used. These were: Desmopan 356 (DS 356) and Desmopan VP PU 01144 (DS VP) from Bayer A. G., Gethane J-96 (G-96) from Gethis Co., Mellioplast SP 4934 (M4934) from Quinn and Polur N-55 (N-55.1 and N-55.2) from Zaklady Chemiczne "Zachem" Bydgoszcz. TPU's labeled as "Polur" have been developed by Institute of Organic and Food Chemistry and Technology of Gdansk Technical University.

Methods

DSC measurements have been carried out on Perkin-Elmer DSC 7 thermal analyser with the 3700 data station at a heating rate of 20 deg/min and at a cooling rate of 10 deg/min.

Dynamic viscosities have been measured using the Brabender Plastograph PLD 651. Tensile properties have been estimated at Instron tensile tester. The brittle points have been estimated on LEAS-Torino apparatus using 2 mm thick samples.

Results and discussion

The results of the measurements are summarized in Table 1. Crystallization exotherms are shown in Fig. 1. Glass transitions occured between -35.9° and -10°, except for the samples DS VP and G-96, for which a glass transition has not been observed down to - 60°. On cooling, the sample DS VP, which in fact is a composite material, exhibits a double peak. Lower T_g generally means lower brittle point. It is clearly seen for the samples N-55.1 and N-55.2, which differ only in the [NCO]/[OH] ratio. Introducing of allophanate crosslinking (Polur N-55.2) decreases T_g and the brittle point and increases the dynamic viscosity of the melt.

For polymer processing the dynamic viscosity of the melt is of primary importance. Its optimal value for injection molding of TPU is of 2000-3000 Pa·s. From TPUs of the same chemical constitution of hard and soft segments, like Polur N-55.1 and Polur N-55.2, the sample, which more easily crystallizes from melt, exhibits lower dynamic viscosity, despite of having higher melting point. Therefore the method of Lawandy and Hepburn [5, 6]

Table 1 Thermal, tensile and rheological properties of investigated thermoplastic polyurethane elastomers

Sample	T_g,	T_m,	ΔH_m	T_c	ΔH_c	Tensile at break,	Elongation at break,	Hardness,	Brittle point,	Dynamic viscosity			
										190°C	200°C	210°C	220°C
	°C	°C	J/g	°C	J/g	MPa	%	°ShD	°C	(Pa·s)			
DS 356	–35.9	220.2	12.84	180.2	15.38	43.4	527	52	–50		4062	1480	635
DS VP		223.9	12.40	115.1	18.65	45.7	400	54	<–50		5714	2530	978
G-96		223.3	18.27	160.6	22.66	50.7	383	52	–20	6742	1152		
M 4934	–21.9	174.5	7.18	131.2	15.41	29.2	572	38	–64		5297	4675	2354
N-55.1	–10.3	203.7	12.50	172.7	12.62	33.7	528	51	–21	4883	2893	1206	
N-55.2	–30.0	177.6	16.24	158.3	10.02	38.2	493	49	–47	6373	3977	2285	

of prediction ofthe best injection molding temperature for thermoplastic polyurethane elastomers is limited to polyurethanes of strictly linear structure.

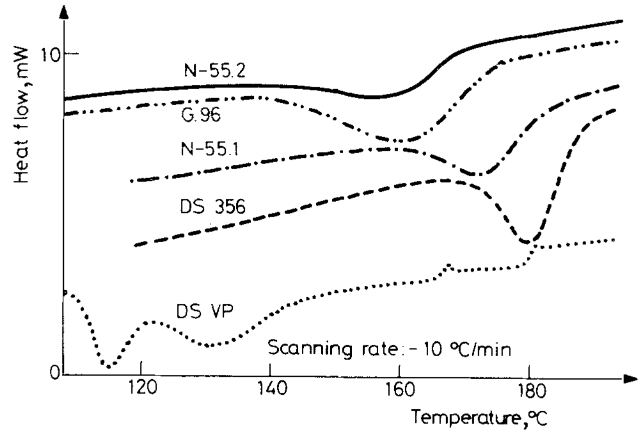

Fig. 1 DSC cooling curves of the investigated thermoplastic polyurethane elastomers

The estimated crystallization enthalpies correlate very well with the tensile at break. The correlation for samples of the same hardness range (M 4934 excluded) is linear with the coefficient of correlation of 0.95.

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Zusammenfassung — Schmelz- und Erstarrungsenthalpie, die dynamische Viskosität der Schmelze und Zugdehnungseigenschaften bei einer Reihe von im Handel erhältlichen thermoplastischen Polyurethanelastomere (TPU) wurden ermittelt. DSC-Analyse erwies sich als ein geeignetes Mittel zur Vorhersage der Verarbeitungsfähigkeit und der Zugdehnungseigenschaften von TPU mit ähnlichem Hartsegmentanteil.