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Thermoanalytical investigations of polyurethanes for medical purposes[1]

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Abstract

Two types of laboratory synthesized polyurethanes (PU), for medical application, were investigated using the DSC method. Each PU was tested with, and without, additional purification. Commercial polyurethanes were also studied for comparison. It was found that the applied purification process influences the morphology of the polyurethanes. Changes were especially observed in the short- and long-order regions of the polymer matrix. © 1998 Elsevier Science B.V.

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1. Introduction

Polyetherurethanes (PU), used in implantation medical devices, are multiblock copolymers with hard segments based on aromatic urethanes or urethane ureas and soft segments consisting of aliphatic polyethers [1–4]. Segmented polyurethane elastomers are materials that possess a good blood compatibility and excellent mechanical properties. They are commonly used in implantation medical devices, such as cardiac pacemaker-leads insulation, ventricular assist bladders, heart valves, vascular prostheses, catheters and artificial hearts.

Commercially available polyurethanes contain antioxidants, catalysts, solvents, processing aids and trace impurities. It is supposed that, in the course of implantation, the leacheability of these constituents and the possible enzymatic degradation products negatively influence biocompatibility of PU [5,6].

A method of purification of medical-purpose PU based on forced diffusion has been proposed [7]. It was confirmed by in-vitro studies that the purification enhances nontoxicity and biocompatibility of polyurethanes [8]. For example, alkalinity and acidity of water extracts from PU, as well as the content of reducing compounds in the extracts, were substantially diminished after purification. The content of impurities, which may be observed in the UV-spectrometer, was also reduced. Contamination with Cl^-, NH_4^+ and heavy metal was negligible. The toxicity tests with *Lebistes reticulatus* and bull sperm were negative. No biodegradation of three-month old intramuscular implants from the purified PU in rabbits, when tested by measuring tensile stress for 100% elongation, tensile strength and relative elongation at break, was found [8].

The aim of our work was to investigate the influence of the purification on thermal behaviour of the polyurethanes for medical purpose using thermoanalytical

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[1] Dedicated to Prof. A. Kettrup on the occasion of his 60th birthday.

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methods, e.g. differential scanning calorimetry (DSC). Laboratory-made PUs, prepared without any additives, as pure polymers and additionally purified with a method developed in our laboratory were studied. For comparison, commercial medical-grade polyurethanes were also investigated.

2. Experimental

2.1. Materials

Two types of PU (PU-47 and PU-90) containing different amounts of hard segment, e.g. 59 and 37%, respectively, were synthesized in our laboratory.

The novel segmented poly(ether)urethanes (PU) were prepared in one-shot process which were carried out without use of solvents. Both PUs were prepared from 4,4'-diisocyanatodiphenylmethane (MDI) (BASF), poly(oxytetramethylene)diol of molecular mass MW=1000 (PTMO) (Commercial Products DuPont, USA) and as short-chain extender 1,4-butanediol (BD)(BASF). Polyol PTMO was carefully dried (24 h; 70°C in vacuum) in order to decrease the water content below 0.2% (measured by the Fischer method). BD was distilled under vacuum at 2.5×10^{-6} MPA. PU-90 reaction stoichiometry is MDI/PTMO/BD 2 :1 : 1 and PU-47 MDI/PTMO/BD 4.5 : 1 : 3.5. These two polymers do not contain any stabilizer or other additives.

In order to eliminate the effect of any residual monomer in polymers and antioxidants, which may have been present in the monomer and/or raw materials, polymers were purified by extraction method developed in our laboratory.

Commercial polyurethanes of the Pellethane series 2363-80A and 2363-55D were obtained from Dow Chemicals. These materials were used as received.

The physicomechanical characteristics of the polyurethanes are given in Table 1.

2.2. Procedure

DSC measurements were performed on a Perkin–Elmer differential scanning calorimeter DSC 7. The instrument was calibrated using acetanilide and indium as standards. Polyurethanes were dried under vacuum (70°C, 4 h) prior to testing, and a sample weight of ca. 8 mg was used. Samples were heated from −100° to 200°C at a rate of 20°C/min.

3. Results and discussion

Typical thermal transitions observed in polyurethanes may include glass transitions of either the 'hard' or 'soft' microphases, a short-range order endotherm of the hard phase attributable to storage or annealing effects, endotherms associated with long-range order of crystalline portions of either soft or hard segments, and microcrystalline hard segment domain melting [9–11].

Figs. 1–3 show the DSC curves for polyurethanes PU-47, PU-90 and Pellethanes, respectively. Results from DSC curves are summarized in Table 2.

For unpurified polyurethane PU-47, containing 59% of hard segment, the following thermal events were observed: glass-transition temperature of the soft microphase, T_g and three multiple melting endotherms labelled T_1, T_2 and T_3. The T_1 and T_2 peaks can be attributed to the disruption of short- and long-range order, respectively (due to the distribution in hard segment length) [9–12]. The T_3 endotherm may be ascribed to melting of the microcrystalline region in the hard segment-rich microphase.

After purification, the glass-transition temperature, T_g, for PU-47 is shifted to a higher temperature. The

Table 1
Some physicomechanical properties of the polyurethanes

Property	PU-47	PU-90	Pellethane 2363-55D	Pellethane 2363-80A
Hardness, Sh	95A	81A	55D	83A
Tensile strength, MPa	38	24	45	42
Tensile modulus at 100% elongation, MPa	16	5	17	6
Elongation at break, %	440	700	430	550

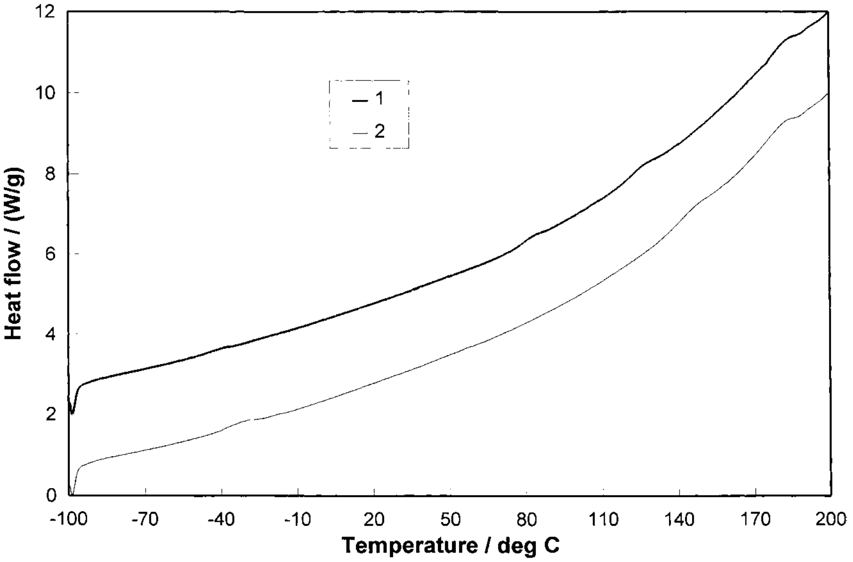

Fig. 1. DSC curves of polyurethane PU-47: curve 1, before purification; and curve 2, after purification.

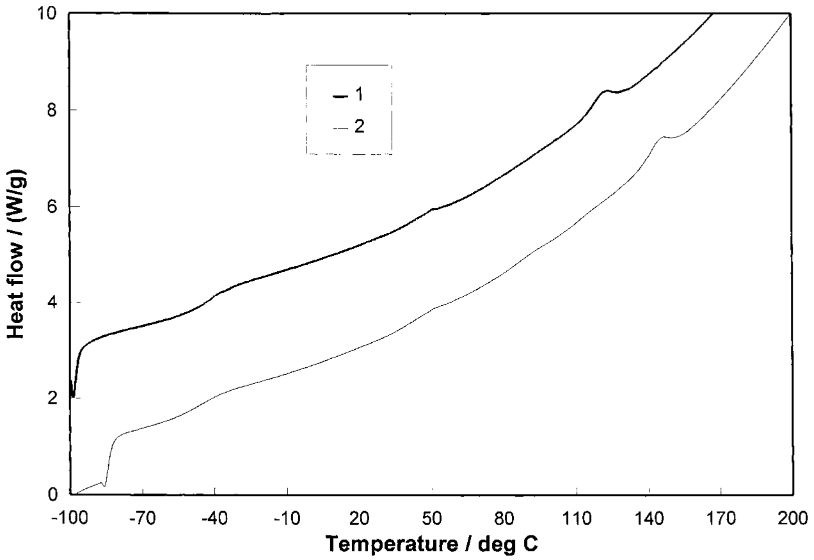

Fig. 2. DSC curves of polyurethane PU-90: curve 1, before purification; and curve 2, after purification.

disappearance of the T_1 endotherm and a shift of the T_2 peak by about 20°C for purified than for unpurified PU-47 is observed (see Fig. 1). The T_2 peak shows a slight increase in size. These changes may be explained by the achievement of better short-range order. A hard segment melt transition (T_3) remains for PU-47 after purification. However, the T_3 peak is slightly lower after purification than before, and the enthalpy ΔH_3 increases, indicating that the purification process may also influence hard segment packing.

Unpurified PU-90 has approximately the same T_g value as unpurified PU-47. In comparison with PU-47,

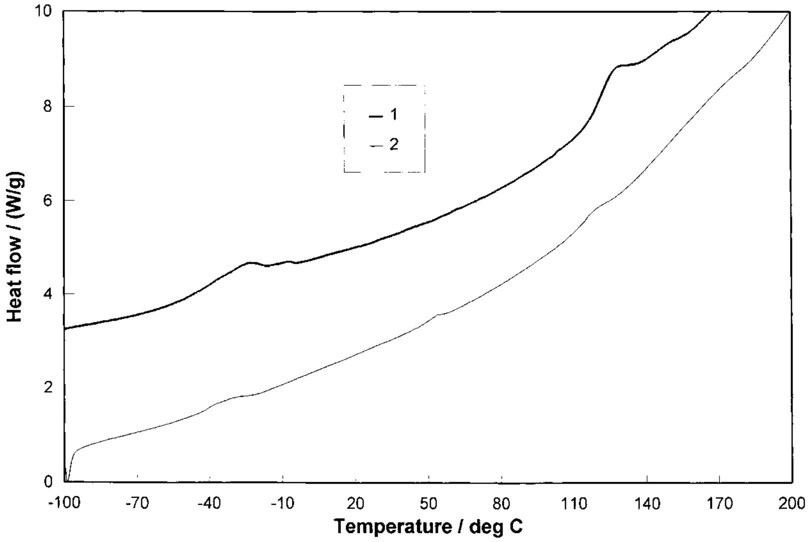

Fig. 3. DSC curves of medical grade polyurethanes: curve 1, Pellethane 2363-80A; and curve 2, Pellethane 2363-55D.

Table 2
DSC results of polyurethanes

Polyurethane		First heating							
		Tg/°C	ΔC_p/(J/g K)	T_1/°C	ΔH_1/(J/g)	T_2/°C	ΔH_2/(J/g)	T_3/°C	ΔH_3/(J/g)
PU-47	before purification	−40.9	0.03	82.3	0.27	125.9	0.72	182.35	1.16
	after purification	−35.8	0.13	—	—	146.3	1.0	180.9	1.63
PU-90	before purification	−41.5	0.09	50.0	0.32	121.4	1.84	—	—
	after purification	−44.4	0.13	50.6	0.46	144.70	2.10	—	—
Pellethane-55D		−39.9	0.11	53.7	0.45	118.6	1.07	—	—
Pellethane-80A		−38.9	0.38	—	—	126.8	5.46	—	—

there is no observable transition in the hard segment melt temperature range for PU-90. The presence of the T_1 peak at about 50°C in the temperature range corresponding to short-order disruption is observed. After purification, as opposed to PU-47, the T_g value of PU-90 is lower than that for unpurified PU, suggesting a greater degree of microphase separation. However, a similar behaviour is observed in the long-order region, e.g. the shift of the T_2 melting endotherm and a small increase in ΔH_2 enthalpy (cf. Figs. 1 and 2).

The T_g values of Pellethanes are similar to those for both the laboratory-made PUs before purification. Transition in the hard segment temperature range up to 200°C is not observed . The peak temperature depends on the sample composition which is unknown for commercial polyurethanes.

4. Conclusions

It was found that the purification process influences the morphology of polyurethanes. The similar effect is observed for both the PUs, differing only in hard segment content, i.e. the shift of the T_1 and T_2 endotherms.The observed changes may be explained by better ordering in short- and long-order transition region due to the purification process. However, the difference exists in the glass-transition region. In the case of PU-47, having a greater amount of hard segment after purification, the glass-transition temperature is shifted to higher temperatures than in the case of unpurified PU, suggesting better phase mixing. On the contrary, a decrease in T_g value is observed for purified PU-90 as compared to the unpurified PU-90.

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