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Thermochimica Acta 304/305 (1997) 347–352

thermochimica
acta

Investigation of an engineering thermoplastic polyurethane by MDSC

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Received 21 July 1996; accepted 7 April 1997

Abstract

A commercial engineering thermoplastic polyurethane (ETPU) resin was investigated by modulated-temperature DSC (MDSC). Use of this recently developed technique provided an accurate measurement of the changes in heat capacity resulting from crystallization and depolymerization processes. The former process was examined in a pseudo-isothermal experiment and the latter in a dynamic one.

The ETPU resin investigated in this work is crystallizable but at such a slow rate that no crystalline regions are expected to be formed under normal processing conditions. Significant amounts of crystalline material are not formed until after 150 min at 160°C and the crystallization process is not completely finished even after 700 min. It is shown that the endothermic activity observed upon heating is not a true melting process but is caused by a breakup of the crystalline regions by depolymerization.

Heat capacity (C_p) traces obtained from a heat–cool–heat sequence of the amorphous material indicate that no significant irreversible changes to the resin have occurred during the time frame of the experiment. Starting from ca. 175°C, a positive deviation in the linearity of the C_p vs. temperature relationship is observed. It is believed that this deviation is the result of a reversible depolymerization/repolymerization process. Number-average molecular weights, in line with expectations, have been calculated from the observed C_p changes using literature data for polystyrene. © 1997 Elsevier Science B.V.

Keywords: Crystallinity; DSC; Engineering thermoplastic polyurethane (ETPU); Molecular weight; Modulated-temperature DSC (MDSC)

1. Introduction

The Dow Chemical Company markets an engineering thermoplastic polyurethane (ETPU) resin family, prepared from diisocyanatodiphenylmethane (MDI) and a low molecular weight aliphatic diol, for engineering applications under the trademark ISOPLAST[1] [1]. These materials are available in transparent grades, opaque impact-modified grades and long glass fibre reinforced grades. This resin family has good abrasion properties, excellent chemical resistance (especially to gasoline and fuel oils), toughness and dimensional stability. Fields of application include medical, oil- and gas-field industry, and a wide variety of other engineering applications

A key element in the processing of these materials is reversible depolymerization which occurs at the melt temperatures (225–240°C) normally employed. The depolymerization process causes a further decrease in melt viscosity at high temperatures and facilitates the filling of thin-walled mouldings and the use of high glass-fibre loadings.

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PII S0040-6031(97)00178-0

Like the polycarbonate family of engineering resins [2], this ETPU resin family is expected to be crystallizable. Although of no commercial interest at present, it is worthwhile to determine the conditions under which these materials can be stimulated to assume the more thermodynamically stable crystalline form.

Modulated-temperature differential scanning calorimetry (hereafter referred to as MDSC) has been employed to investigate the depolymerization/repolymerization and crystallization/melting processes. In particular, we were interested in the possibility of determining the change in molecular weight with temperature, the rate of the crystallization process and the nature of the subsequent melting phenomenon.

2. Experimental section

The ETPU material was dried at 85°C at a dew point of −50°C for 24 h in order to remove absorbed water. The final water content was < 200 ppm. All calorimetry experiments were performed via a TA Instruments model 2920 DSC equipped with a liquid-nitrogen cooling unit. Temperature (*N*-octadecane, indium and zinc) and heat capacity (HDPE at 140°C and periods of 40 and 100 s) calibrations were performed using the same Al pans employed for the analyses. A helium flow of 30 ml/min was employed throughout.

Specimen heat capacity was monitored at a temperature of 160°C using an amplitude of 1°C and a period of 100 s. The heat flow properties of the starting resin and after pseudo-isothermal treatment were measured over a (50–270)°C temperature range at a ramp rate of 4°C/min, amplitudes of 0.425°C (heating only conditions) and 1°C and a period of 40 s. The following heat–cool–heat was employed for the ramp rate of 4°C/min. Specimens were initially heated to 50°C, held isothermally for 10 min, ramped to 270°C, held isothermally for 2 min, ramped to 50°C, held isothermally for 2 min and ramped to 270°C. Some experiments were performed at a much slower scan rate (0.5°C/min, 0.053°C amplitude and 40 s period) in order to obtain additional information about the crystallization and melting phenomena. Sample weights of (8–10) mg were employed for all experiments and care was taken to ensure that the Al pan weights were the same, i.e. within 0.1 mg. Specimens (sample + pan) were weighed before and after analysis to check for loss of material.

3. Results and discussion

3.1. *Crystallization and melting processes*

The results of the pseudo-isothermal experiment at 160°C (see Fig. 1) clearly indicate that there is a significant change in the specimen heat capacity with time. There is no appreciable weight loss during the experiment so that this change must be due to a change in the physical state of the material. The most likely explanation is formation of a crystalline phase and this has indeed been confirmed by microscopic analysis (data not presented here). The heat capacity vs. time data indicate that the crystallization process starts after only a few minutes at 160°C but that the rate does not become appreciable until after 150 min. Even after 700 min, the crystallization process is not complete.

The melting phenomenon was examined for three samples which had been allowed to crystallize for 150, 300 and 700 min at 160°C. Results are illustrated in Figs. 2–4, respectively. A T_g is observed at temperatures ranging from 99 to 87°C and the step change in C_p at this transition decreases (−0.024 to −0.009 W/gm) as does the sharpness of the transition with increasing time at 160°C. An increase in the endotherm peak area (8.2 to 50.0 J/gm) with time at

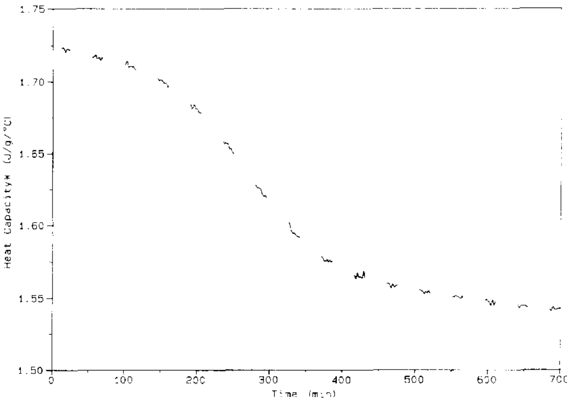

Fig. 1. Heat capacity (C_p) vs. time for a pseudo-isothermal experiment at 160°C. Note that the data were not recorded continuously but at regular intervals during the experiment.

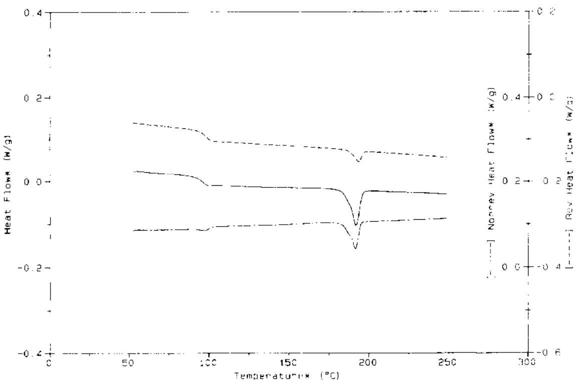

Fig. 2. Heat flow signals (total, reversible and nonreversible) vs. temperature for an ETPU specimen held pseudo-isothermally at 160°C for 150 min.

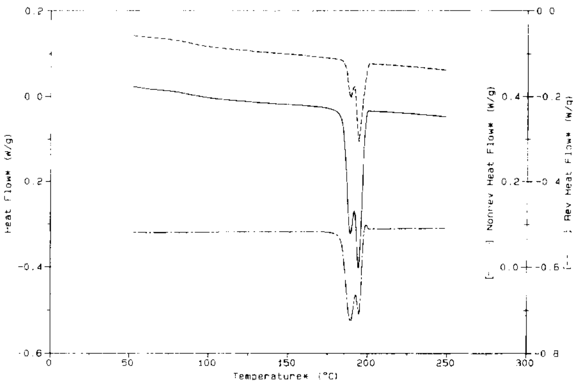

Fig. 4. Heat flow signals (total, reversible and nonreversible) vs. temperature for an ETPU specimen held pseudo-isothermally at 160°C for 700 min.

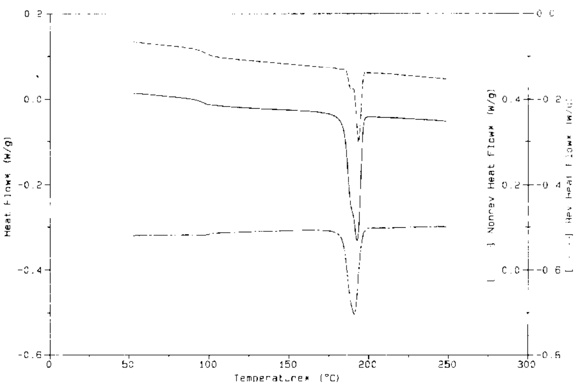

Fig. 3. Heat flow signals (total, reversible and nonreversible) vs. temperature for an ETPU specimen held pseudo-isothermally at 160°C for 300 min.

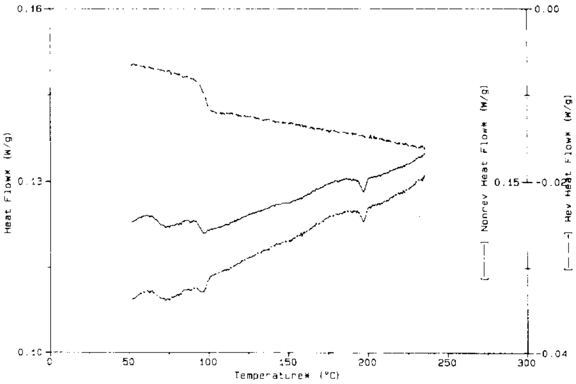

Fig. 5. Heat flow signals (total, reversible and nonreversible) vs. temperature for first heating of an amorphous ETPU specimen at a scanning rate of 0.5°C/min.

160°C is also observed. All of these observations are consistent with the formation of a semicrystalline morphology. However, there are a number of features of these endotherms which need to be examined in closer detail before we can be certain that a melting process is involved.

Interestingly, there is no exothermic activity in the nonreversing or kinetic signal as has been observed for other semicrystalline polymeric materials [3–6]. Since the crystallization process for this material is slow, it is possible that no crystallization can occur on the experimental time scale and thus the melting process becomes irreversible. We have indeed observed this behaviour for solvent crystallized polycarbonate. In order to examine this possibility in more detail, we performed some experiments at a reduced scan rate. Fig. 5 illustrates the results of an initially amorphous sample scanned at a rate of 0.5°C/min. Exothermic activity is observed above ca. 150°C followed by a small endotherm at a temperature very similar to the high-temperature shoulder/peak observed at the faster scan rate. The endothermic activity is completely absent from the reversing signal as expected from a system which maintains steady-state conditions [7]. The initially crystalline samples show some apparent endothermic activity in the reversing signal although much less than that observed at the higher scan rate. The crystallization exotherm is also much stronger except for the most highly crystalline sample, where it is completely absent.

The results in Fig. 5 indicate that the material is capable of crystallizing during the slow scan rate and yet once endothermic activity commences the crystallization process ceases. This is not consistent with the expected melting behaviour of a polymeric material crystallized under these conditions. The breadth of the crystallization peak implies that the crystals formed are of an imperfect nature and so should continue to recrystallize throughout the melting process. The sharpness of the endothermic peak also raises suspicion. Owing to the low degree of crystalline perfection, a much broader melting peak is expected. Indeed, we have observed a broad melting peak in crystalline polycarbonate materials. It is also suspicious that the endotherm remains at essentially the same temperature at the slower scan rate. Now that the crystals have time to reorganize a significantly higher melting temperature would be expected if a melting process were involved.

The onset temperature (ca. 175°C) of endothermic activity at the higher scan rate and the highly crystalline sample at the slow scan rate corresponds to the stability limit of the polyurethane bond [8] so that another explanation of the endothermic activity is a breakup of the crystalline phase by depolymerization. FTIR results (not reported here) show that detectable amounts of free isocyanate are present at temperatures of 180°C and above. This information combined with the anomalies revealed by the MDSC results leads the author to the conclusion that the observed endothermic activity is caused by a breakup of the crystalline phase due to a depolymerisation and not a true melting process.

Still to be explained is the observed bimodality of the endothermic peaks which is even more pronounced the slower scan rate. One possible explanation is the presence of two distinct crystallite populations, either in terms of size or structure, and another is the presence of rigid amorphous (i.e. interfacial) material. The author favours the latter explanation since it could explain why the additional peak/shoulder only appears at higher levels of crystallinity and why it occurs at a lower temperature. Other techniques such as x-ray diffraction (XRD), combined DSC-XRD and solid-state NMR might be able to shed more light on this matter. Unfortunately, such a study was beyond the scope of the work reported here.

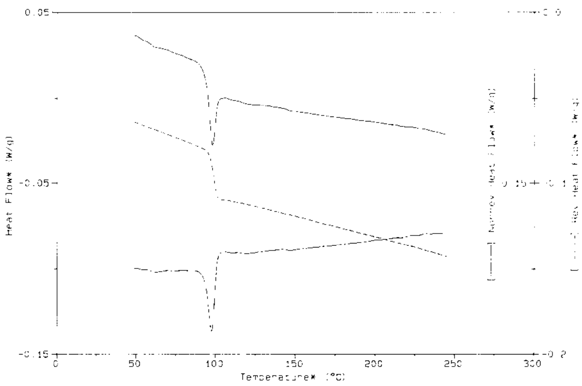

Fig. 6. Heat flow signals (total, reversible and nonreversible) vs. temperature for first heating of an amorphous ETPU specimen.

3.2. Thermal properties of the amorphous form

A typical first heating curve of the ETPU resin investigated here is illustrated in Fig. 6. The most obvious feature is the T_g at 99°C, although some very weak irreversible exothermic activity is evident starting at ≈140°C. The exothermic activity may be caused by reaction of residual water with free isocyanate groups. A weight loss of ca. 150 μg was typically found. An overlay of the heat capacities measured for the heat–cool–heat sequence (see Fig. 7) indicates that there are no significant changes in the specimen during the experiment. The observed shift of the first heating

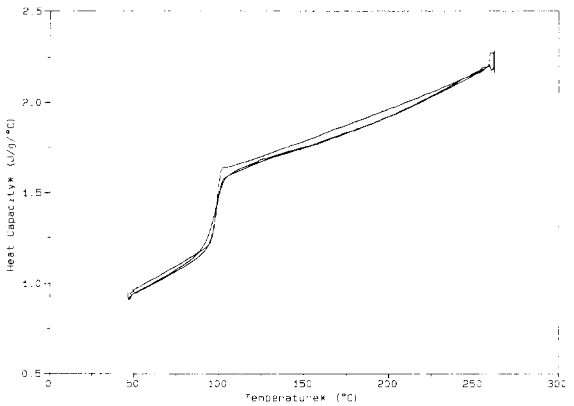

Fig. 7. Heat capacity (C_p) vs. temperature traces for a heat–cool–heat sequence of an amorphous ETPU specimen. Note that the first heating trace differs from the other two owing to a difference in thermal contact.

data set with respect to the cooling and second heating data sets can be attributed to an improved thermal contact during the latter two stages.

Close examination of the heat capacity traces in Fig. 7 indicates that, above T_g, C_p initially increases linearly with temperature but that starting at ≈175°C a positive deviation is observed. This deviation, which was repeatedly observed, may be due to some chemical or physical change to the sample since many polymeric materials in the melt obey a linear C_p vs. T relationship over broad temperature ranges [9]. The observed weight loss cannot account for this phenomenon as it would cause a negative deviation in C_p. Depolymerization is a possible cause of the deviation. The lower molecular weight (M_n) species produced would have a higher mobility owing to an increase in the number of end groups which would result in an increase in C_p. It is known that the change in C_p at T_g is strongly dependent on M_n below values of ca. 10 000 daltons [10,11]. Since the true M_n value for the material investigated here is about 20 000 daltons [12] values below 10 000 daltons should be readily obtainable.

We would like to relate the observed C_p deviation to a change in M_n. In the absence of experimental data for ETPU materials, literature data for polystyrene have been employed [10]. The dependence of T_g on M_n and the change in C_p (ΔC_p) at T_g are given by Eqs. (1) and (2) respectively.

$$T_g = T_{g\infty} - C_1/M_n \tag{1}$$

$$\Delta C_p T_g \approx C_2 \tag{2}$$

where, for polystyrene, $T_{g\infty}$ is 373 K, C_1 1.05×10^5 K g and C_2 is 107 J/g. If one assumes that the difference in C_p observed at T_g is maintained at higher temperatures, then Eqs. (1) and (2) can be employed to relate the observed C_p deviation to a change in M_n. The measured deviation (D) has been referenced to the starting M_n value (20 000 daltons) at which the value of C_p is 0.291 J/K/g. Eq. (3) relates M_n to D and the other above-mentioned constants:

$$M_n = (D + 0.291)C_1/(T_{g\infty}D + 0.291T_{g\infty} - C_2) \tag{3}$$

Calculated M_n values are summarized in Table 1. The values are qualitatively in line with expectations despite the assumptions made and the use of polystyrene data. It is possible that the M_n values at higher temperatures have been overestimated since Eq. (1) is known to underestimate T_g at low molecular weights [12]. However, it must be remembered that M_n is very sensitive to the presence of small weight fractions of low molecular weight species such as monomers or oligomers. Unfortunately, experimental confirmation of the C_p vs. M_n relationship found here would require the synthesis of model compounds. Perhaps, theoretical calculations would provide a simpler way of confirming the correctness of the model proposed here.

Table 1
Temperature, C_p deviation and M_n

Temperature (°C)	C_p Deviation (J/C/g)	Calculated M_n (daltons)
190	0.019	3770
200	0.033	2460
210	0.048	1830
220	0.067	1420
230	0.086	1180
240	0.11	990
250	0.13	880

4. Conclusions

The ETPU resin investigated in this work is crystallizable but at such a slow rate that no crystalline regions are expected to be formed under normal processing conditions. Significant amounts of crystalline material are not formed until after 150 min at 160°C and the crystallization process is not completely finished even after 700 min. The endothermic activity observed upon heating is not a true melting process but is caused by a breakup of the crystalline regions by depolymerization.

Heat capacity (C_p) traces obtained from a heat–cool–heat sequence show no significant changes during the time frame of the experiment. Starting from about 175°C a positive deviation in the linearity of the C_p vs. temperature relationship is observed. It is believed that this deviation is the result of a reversible depolymerization/repolymerization process. Number-average molecular weights, in line with expectations, have been calculated from the observed C_p changes using literature data for polystyrene.

Acknowledgements

The author would like to thank The Dow Chemical Company for permission to publish this work.

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