NOTES

A Recording Differential Dilatometer for the Investigation of Polymer Crystallization Rates and Melting Temperatures

INTRODUCTION

One common method of studying phase transformation in polymers is that of dilatometry. The basic designs of Bekkedahl[1] and Kovacs[2] have been used extensively. Sample sizes of approximately 1 ml are widely used with these dilatometers. The use of dilatometers for measuring rates of phase transformations does, however, depend on the ability to establish rapid thermal equilibrium of the entire sample with its surroundings. Banks et al.[3] have described a microdilatometer which is capable of fast thermal equilibration. A recording microdilatometer designed for a few milligrams of sample and ca. 1 ml confining liquid has been described by Tung.[4] The sensitivity, and thus also the reproducibility of a dilatometer, does, however, decrease as the volume of the confining liquid increases in relation to the sample volume. This drawback has been overcome by compensating for the volume of the confining liquid with a second dilatometer. This novel method, which is called differential dilatometry (in this paper), is described, and its application in measuring crystallization rates and melting temperatures is outlined for a polyacetal copolymer.

THE DIFFERENTIAL DILATOMETER

The principle of the recording differential dilatometer is shown in Figure 1. The dilatometers are made of precision-bore glass tubings with an inside diameter of 5.0 mm. A close-fitting precision-ground plunger senses changes in volume of the sample and the confining liquid in dilatometer A. The displacement of the plunger is converted to an elec-
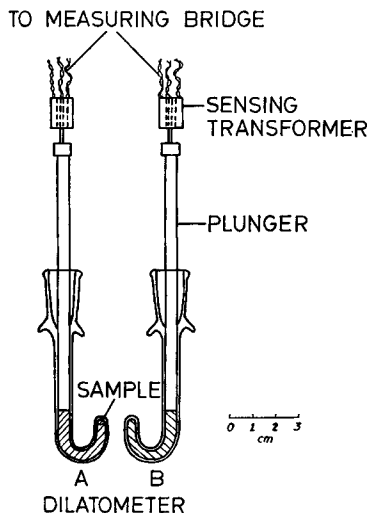

Fig. 1. Diagram of the recording differential dilatometer.

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trical output by a linear variable differential transformer.   Dilatometer B is identical to dilatometer A, except that it does not contain any sample.   The difference between the electrical outputs from the two transformers is registered by a recorder.

The dilatometers used in the system were made by Laboratorietjänst AB, Stockholm; the differential transformers are two matched Daytronic 27-5c units; and the measuring bridge is a Daytronic 300 D/72.   The volume of the confining liquid is about 1.0 ml, and sample sizes of about 1 μl to 100 μl may be used.   The dilatometers are filled by standard vacuum technique.

EXPERIMENTAL

The differential dilatometer has been tested on a polyoxymethylene copolymer, Kematal M 90-01, marketed by I.C.I.   The experiments were performed on 25-mg samples, with mercury used as the confining liquid.

Prior to the initiation of crystallization, the samples were melted by immersion of the dilatometers in a constant temperature bath at 185°C for 3 min.   The dilatometers were quickly transferred to another bath, with temperature controlled to ±0.04°C.   It was found that the crystallization rate of the sample is not dependent on the temperature of premelting, since melting between 2 and 10 min at any temperature between 172° and 195°C resulted in the same crystallization isotherm.   The time to reach thermal equilibrium after transfer to the low temperature bath was never greater than 2 min.

The reproducibility of the differential dilatometer is shown in Figure 2 for the crystallization of 25-mg samples.   All runs have been performed with fresh polymer specimens. In Figure 2, h_t is the height of the plunger at time t, and h_0 and h_∞ are the heights at the beginning and end of the crystallization process.
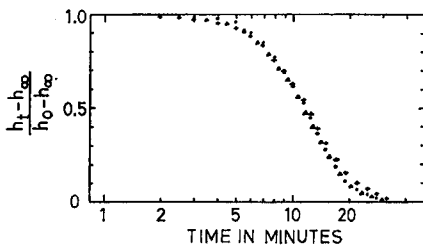

Fig. 2. Reproducibility of crystallization at 154.6°C for a 25-mg polyoxymethylene sample of Kematal M 90-01.
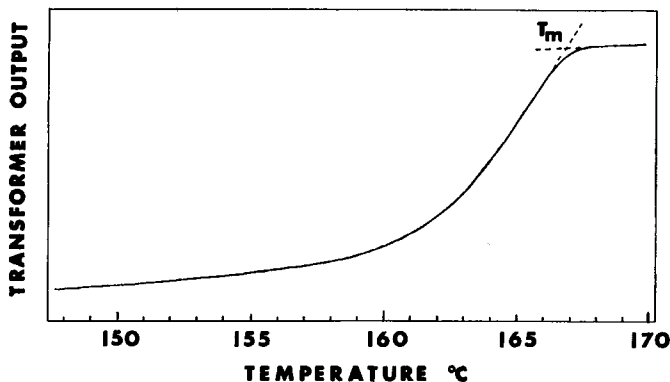

Fig. 3. Determination of melting temperature of Kematal 90-01 by differential dilatometry.   Heating rate, 0.5°C/min; sample size, 25 mg.

The half-time $t_{1/2}$ for crystallization of 25.0 mg Kematal M 90-01 at 154.6°C was calculated from ten determinations.   The differential dilatometer resulted in $t_{1/2}$ = 11.3 ± 0.6 min, while the result with a single dilatometer was 11.3 ± 1.1 min at a 95% confidence level.   The lower reproducibility with a single dilatometer is mainly due to temperature variations.

The differential dilatometer was also used to determine the melting temperatures. Figure 3 shows a typical melting curve for a sample of Kematal M 90-01, which was precrystallized isothermally at 154.6°C.   Using a rate of 0.5°C/min, the melting temperature was determined from the intersection of the extrapolated linear portions of the curve in Figure 3.   Under these conditions, the melting temperature of the Kematal M 90-01 sample was 166.8 ± 0.3°C, which represents an average of ten runs with a confidence level of 95%.

References

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