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DILATOMETRIC STUDIES OF PHYSICAL AGING OF POLYETHERIMIDE

J. W. Sobieski, S. L. Simon and D. J. Plazek*

University of Pittsburgh, School of Engineering, Pittsburgh, PA 15261, USA

Abstract

Physical aging of polyetherimide (PEI) was studied using a bellows dilatometer based on Zoller's design. A linear variable differential transformer (LVDT) is used to measure the displacement of the bellows. The voltage output of the LVDT is interfaced to a computer for automated data collection. Isothermal aging experiments were carried out at temperatures near the glass temperature (206–209°C) using a constant temperature oil bath maintained at the desired aging temperature. The time required to reach equilibrium and the reduced curve produced by aging time-temperature superposition are given. The results compare well with data obtained by capillary dilatometry for the same material.

Keywords: glass, physical aging, polyetherimide, volume recovery

Introduction

Physical aging occurs in amorphous substances at temperatures below the glass temperature (T_g). As the material is cooled from the liquid state to the glass state it departs from equilibrium at T_g due to its decreasing molecular mobility relative to the rate of cooling. A glass is, therefore, not in thermodynamic equilibrium and its properties including volume, entropy and creep compliance, change as it moves towards equilibrium. Understanding of the kinetics of physical aging is important in the prediction of long term performance of glassy materials. The interest in this behavior has caused it to be the subject of several reviews [1–4].

This paper reports volume recovery measurements carried out on polyetherimide (PEI) using a stainless steel dilatometer with automated data acquisition capability. Automation is valuable when conducting volume recovery experiments which may last a week or more. The experimental design is described and the results of dilatometric aging experiments near T_g are presented. The data is compared to results for physical aging experiments obtained by traditional capillary dilatometry.

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* Author to whom all correspondence should be addressed.

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Experimental

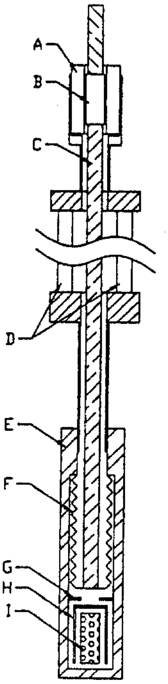
Material

General Electric polyetherimide (PEI), Ultem 1000 was used in this study. The material is reported by the manufacture to have a number average molecular weight of 30 (kg mol^{-1}). Polyetherimide is completely amorphous and its T_g is approximately 207°C determined by cooling experiments at 1°C min^{-1} [5].

Dilatometer

Volume recovery studies were carried out in a stainless steel bellows dilatometer designed by Norman Wachenhut [6] as a modification of that of Paul Zoller's [7]. Figure 1 is a diagram of the dilatometer used. The dilatometer consists of a stainless steel chamber fitted with a stainless steel bellows. The bellows move in response to volume changes of the chamber and its contents. The chamber contains the sample of PEI in an inverted stainless steel cup. The remaining volume of the chamber is filled with mercury. The sample and the bellows are separated by a washer that allows the Hg to move freely but prevents the sample and inverted cup from interfering with the movement of the bellows.

The displacement of the bellows is measured by a Linear Variable Differential Transformer (LVDT) supported above the chamber by invar rods. Invar was chosen



A - LVDT coil
B - LVDT core
C - invar core rod
D - invar support rods
E - sample chamber
F - stainless steel bellows
G - washer
H - stainless steel sample cup
I - sample

Fig. 1 Schematic drawing of the dilatometer because of its low thermal expansion coefficient and strength. The LVDT consists of a coaxial transformer with opposing outputs from the secondary coils and a ferro magnetic core that couples the primary and secondary coils. The core is attached to the bellows by another invar rod. Displacement of the LVDT core results in a linear change in the voltage across the differential output of the secondary coils. A digital transducer readout (DTR) provides the excitation voltage across the primary coil and reads the output voltage across the secondary coils. The DTR is connected to a 286 computer that monitors and records the resulting output voltage. It was necessary to thermostat the DTR because changes in the DTR temperature due to room temperature variations caused significant changes in the output voltage.

Experimental setup

The aging studies were carried out using the previously described dilatometer, two temperature controlled oil baths, and a computer with the proper interfaces to monitor the LVDT voltage and the temperatures of the baths. The bath oil is DC 210H Fluid, a polydimethyl siloxane based oil for use at temperatures exceeding 200°C. Both baths include a stirrer, a large constant heater and a small control heater. The large heaters are controlled by variacs. They are necessary to maintain the high temperatures required, but are not used as control heaters because of their large time constants. Bath A is maintained at a temperature above the T_g, where the sample can be maintained at equilibrium volume. The temperature of this bath is controlled by an on/off controller. The other bath, Bath B, is maintained at the desired aging temperature, controlled by a proportional controller. The temperatures of each bath is monitored by platinum resistance thermometers (PRT) interfaced with the computer. The resolution of the PRTs are 0.01 °C.

Aging studies

Aging experiments were conducted by allowing the dilatometer and sample to come to thermal and volumetric equilibrium at 216°C in Bath A. The data acquisition program is then started and shortly there after (~2 min) the dilatometer is quenched by transferring it to Bath B controlled at the desired aging temperature (T_a). The isothermal aging time is assumed to start after thermal equilibrium is reached. The time to reach thermal equilibrium was found to be 200 s for a 10°C jump between two temperatures above T_g.

Results

The normalized volume relaxation curves for PEI at aging various temperatures are presented in Fig. 2. For comparison, aging curves for PEI using a capillary dilatometer from previous work [5] is included.The data is normalized in order to compare the volume relaxation data at different aging temperatures. The normalized volume, δ_v, is determined using the following formula:

$$\delta_v = (v(t) - v_\infty)/(v_0 - v_\infty) \qquad (1)$$

where $v(t)$ is the specific volume at given time, v_∞ is the specific volume at equilibrium, and v_0 is the initial specific volume. Hence, the normalized volumes goes from unity when $v(t)=v_0$ (at very short times) and to zero when $v(t)=v_\infty$ (at equilibrium). The specific volume at equilibrium, v_∞, is determined experimentally as the steady state value after aging has ceased. The initial specific volume, v_0, is assumed to be the specific volume after a perfect quench in which the sample follows the glass line. Because no quench is instantaneous, there is a systematic error in v_0.

For aging experiments, the LVDT voltages can be substituted directly into Eq. (1) for the specific volume since the experiment is isothermal and the data is normalized. It can be assumed that the linear displacement of the bellows relates only to the volume change of the sample under isothermal conditions. It should be noted

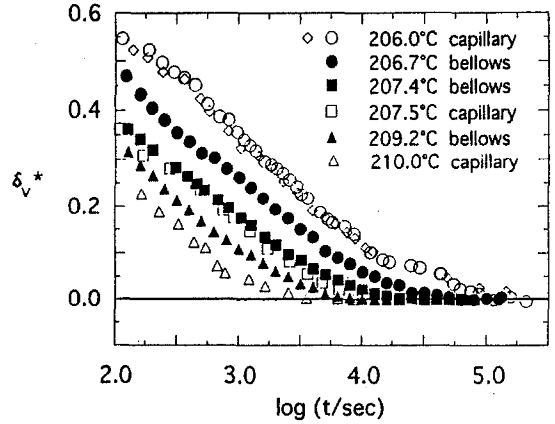


Fig. 2 Normalized specific volume *vs.* log time for PEI at three aging temperatures

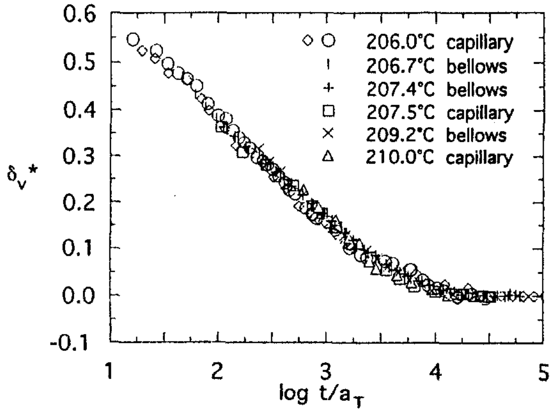


Fig. 3 Reduced curve of the normalized specific volume *vs.* log time for PEI. The reference temperature is 207.43°C

that the data has been corrected to account for a drift in the LVDT voltage output over long times.

Figure 2 shows that at lower aging temperatures the time to reach equilibrium increases. This is expected due to the kinetic nature of the aging process. As the temperature decreases the molecular mobility decreases causing the approach to equilibrium to decrease. The shapes of the curves on the log time scale are similar and aging time-temperature superposition of the data can be applied. Figure 3 is the reduced curve, obtained by a horizontal shift of both the bellows and capillary dilatometric data to the reference curve at 207.43°C.

The degree to which the curves are shifted is characterized by $\log a_T$, where $\log a_T$ is the shift factor required to superimpose each curve on the reference curve. The temperature dependence of the shift factors and of the times to reach equilibrium volume are shown in Fig. 4. The same temperature dependence is observed for both sets of data.

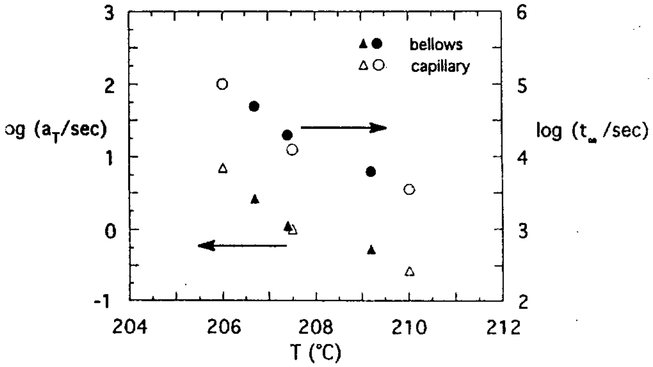


Fig. 4 Temperature dependence of the shift factor and the time required to reach equilibrium volume for bellows and capillary dilatometric data

The agreement in the results obtained by the bellows and capillary dilatometers can be seen in Figs 2 to 4. The reduction of all data on a single curve indicates that the two techniques are comparable and subtracting the long-term drift from the bellows dilatometer data is appropriate.

Conclusion

Volume recovery measurements on PEI using a bellows dilatometer have been made. The results of the volume recovery data have been reduced by aging time-temperature superposition. The data compare well to data obtained by capillary dilatometry, a proven technique, on the same material. The bellows dilatometer allows automated data collection, which is an improvement over capillary dilatometry. This is useful in physical aging experiments that can take up to a week or more.

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