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The Rigid Amorphous Fraction in Semicrystalline Polymers: Investigating Open Questions with Volume Dilatometry

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The objective of this study is to use volume dilatometry to examine the structural relaxation process of poly(ethylene terephthalate), a semi-crystalline polymer, with a particular focus on the rigid amorphous fraction (RAF). An estimate of the glass transition temperature (T_g) of the RAF and its breadth, and the impact of crystallization on structural recovery, will be investigated. Prior to starting these experiments, in the past year, a required modification of the capillary dilatometric setup was completed.

The capillary dilatometer, itself, consists of a metal sample holder connected to a precision capillary tube using a KOVAR glass-to-metal joint following the design of Plazek [1]. The dilatometer, in use, contains the sample in the sample holder surrounded by mercury; the height of mercury in the capillary column allows calculation of volumetric changes and the sample volume as a function of temperature, time, and thermal history. A capacitance-based measurement system has been constructed to follow the height of mercury in the column following the work of Frey and Richert [2]. The exterior of the capillary tube is coated with a metallic silver layer (DuPont 7713) such that it can serve as the outer electrode in the circuit and the mercury column itself is used as the inner electrode. An ultra-precision capacitance (Andeen-Hagerling 2550A 1 kHz) bridge is used for precision capacitance measurements. Noise in the capacitance data that originated from magnetic interference of the temperature bath motors has been eliminated by constructing a new bath for the dilatometer, shown in Fig. 1. Stainless steel is used to construct this dilatometer bath, the outer surface of which is wrapped in fiberglass for thermal insulation. Vibrations of the dilatometer are minimized by installing two stainless steel parallel bars at the bottom of the bath. Short circuits between the dilatometer and the bath surfaces are eliminated using thin teflon sheets within the bath as electrical insulators. The entire system is electrically shielded using an aluminum tube connected to the grounds of the electrodes and the bridge. The level control in the dilatometer bath is performed by installing a level gauge to the side of the bath, shown schematically in Fig. 1. The level gauge contains a glass tube viewing window. A Keyence LS-7600 series LED micrometer is used to measure the oil level, and a Watlow EZ ZONE PM controller controls a Swagelok KONE actuated needle valve to maintain the oil level in the dilatometer within ± 0.5 mm using PID control. The noise resulting from the level fluctuation during tests is thus completely eliminated.

The overall setup, shown in Fig. 2, is designed for heating/cooling ramps and isothermal temperature tests. Two Hart Scientific precision baths (Models 6025 & 6330) are used with Rhodorsil silicone oil (47V50) which is circulated through the system using a magnetic-drive, close coupled centrifugal pump (Liqioflo Century Series, Model No. 620-MC). In addition to the in-built heating system of the mother bath, a Watlow screw plug immersion heater has been installed in the mother bath, and heating tapes (HTS/AMPTEK Silicone Extruded Duo-tapes, ASR series) are wrapped around the whole piping circuit to compensate for the heat loss during circulation. A Fisherbrand Isotemp cooler equipped with a solenoid valve flow control (GRANZOW) is used to control the circulating oil temperature during the cooling ramps. All three heating sources (the internal bath heaters, the external heater, and the heating tapes) and the cooler are controlled using PID control using a Watlow EZ ZONE PM temperature controller coupled with a Hart Scientific 1560 Black Stack equipped with a Hart Scientific 5699 precision PRT probe placed in the dilatometer bath to get accurate temperature readings in the vicinity of the sample holder. Temperature control is better than ± 0.1 K in the dilatometer. Data acquisition from the AH 2550 capacitance bridge and the Hart Scientific 1560 Black Stack are obtained using a National Instrument data acquisition system. LabVIEW is used to filter, bin, and plot the data.

The behavior of the dilatometer filled with mercury shows a stability in capacitance of better than ±1 fF ($\pm 1\times10^{-15}$ F), equivalent to a stability in volume of $\pm 2\times10^{-5}$ cm^3. The stability of the modified setup compares well to our previous system in which the long-term was estimated to be $\pm 5.0\times10^{-5}$ cm^3 for a 5 g sample. Experiments are planned in the coming year to study the rigid amorphous fraction of the semi-crystalline polymer poly(ethyleen terephtahalate) with varying crystallization history and morphology to understand the volume recovery of the rigid amorphous fraction in this material, as well as the interplay between crystallization and structural recovery.

References:

1. Craig A. Bero and Donald J. Plazek. "Volume-dependent rate processes in an epoxy resin." *Journal of Polymer Science Part B: Polymer Physics* 29.1 (1991): 39-47.
2. Sarah Frey and Ranko Richert. "Capacitive measurement of mercury column heights in capillaries." *Review of Scientific Instruments* 81.3 (2010): 034702.

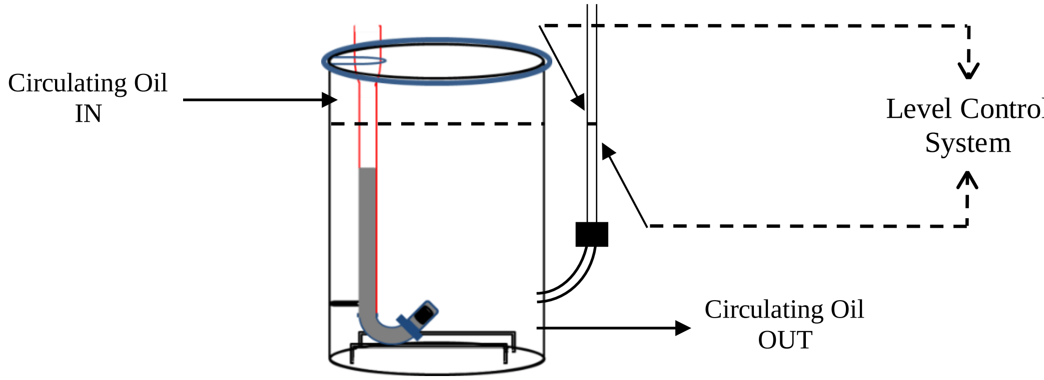

Figure 1: New custom-built bath for the dilatometer

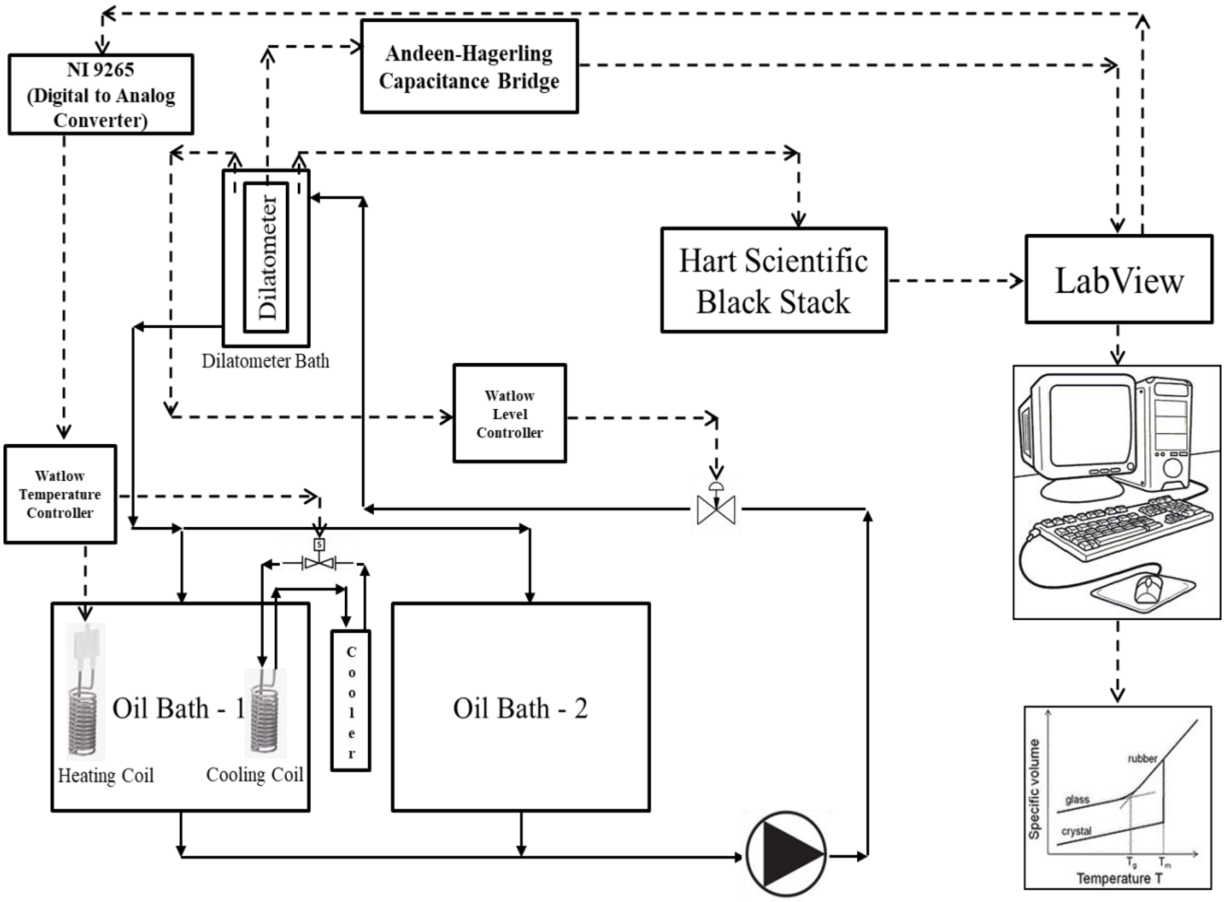

Figure 2: Operational Scheme of the New Setup