Effects of moisture on the thermal expansion of poly(methylmethacrylate)

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The effects of moisture on the thermal expansion of compression-moulded poly(methylmethacrylate) (PMMA, Plexiglas V811) were investigated by pushrod dilatometry. Moisture conditioning at high relative humidity, immersion in water, or vacuum drying were used to prepare PMMA specimens at different moisture contents. Weight and length change measurements were used to indicate water uptake. A substantial, reversible effect of moisture content on the coefficient of thermal expansion of PMMA was demonstrated. At 50°C, the expansion coefficient was observed to increase 32% (from 70.4 to 92.8 × 10⁻⁶ K⁻¹) for a 2% gain in weight. A significant correlation was observed between Tg and moisture content, of approximately -1°C per 0.1% weight increase. Increases in weight and length of the PMMA with time were suggestive of the dual mode kinetic sorption process advanced by others, and indicated that a significant fraction of water was accommodated in microvoids.

1. Introduction
Poly(methylmethacrylate) (PMMA) is a potential material for use in making flat-plate Fresnel concentrator lenses for solar energy systems. In this application, it is important to consider thermal expansion effects in the modeling of the dimensional behaviour of this material, since the focussing performance of the lens must be understood as the material cycles through wide temperature excursions. In addition, hygroscopic expansion of the material can significantly affect the lens dimensions, and is particularly important where hot, wet environments are anticipated. While the separate thermal and hygroscopic expansion properties of PMMA have been documented for some time [1], the effects of moisture absorption on the thermal expansion behaviour of PMMA have received little attention. Brand [2] showed that absorbed moisture could significantly, and reversibly, affect the thermal expansion properties of epoxy-glass laminates used in printed wiring board materials. Adamson [3] found that saturation with water more than doubled the thermal expansion of cured epoxy resins. He suggested that the increased volume of the resin due to swelling caused by moisture absorption tended to weaken the overall interchain hydrogen bonding, which would be expected to result in an increase in thermal expansion.

In this report, we describe the results of thermal expansion measurements on compression-moulded PMMA (“Plexiglas” V811), measured by pushrod dilatometry, as a function of absorbed moisture content of the PMMA. Additional thermal analyses (DSC and TGA) were performed to characterize the effects of moisture on the specimens.

2. Material
Specimens were obtained from a compression-moulded sheet, nominally 3 mm thick, of Rohm and Haas “Plexiglas” V811. For thermal expansion measurements, test samples 25 × 6 mm² were cut from the sheet and measured along the long dimension; no in-plane orientation dependence on the thermal expansion was observed.
polynomial. This deviation polynomial was then applied at each temperature data point to the values obtained from a specimen run. Thermal expansion coefficients determined by this technique have been found to be accurate to within ±5%.

For the thermal expansion results reported here, specimens were heated and cooled in air in the dilatometer at 2°C min⁻¹ over the range −40 to 60°C while length change data were obtained. Weight and length measurements were obtained at 20°C before and after the thermal cycling of the expansion measurements. Typically, the highest moisture content materials lost no more than 0.15% of their weight due to the thermal cycling in the dilatometer. Drier specimens lost even less. Some of the driest samples gained weight (+0.02%) due to ambient exposure in the dilatometer. TGA measurements (Perkin-Elmer Series 7 Thermogravimetric Analyzer) on high moisture content PMMA verified these weight loss results. Approximately twenty thermal expansion measurements were made on eight samples.

4. Results and discussion
The linear thermal expansion (LTE) data, corrected as described above, displayed a significant quadratic dependence on temperature, as shown in the representative data displayed in Fig. 1. The LTE data from the cooling portion of a cycle were least-squares fit to a quadratic polynomial, with a typical r.m.s. deviation of the fit of less than 0.001%. Coefficient of thermal expansion (CTE) functions were determined by differentiation of the LTE fits, yielding a linear dependence of CTE on temperature over the range studied.

The curves in Fig. 1 also demonstrate the significant dependence between moisture content and thermal expansion. In this case, data are shown from a single sample, after vacuum drying and after a 2.0% weight gain due to moisture conditioning. To quantify this dependence on moisture content, the CTE functions were evaluated at specific temperatures and compared as a function of moisture content.

Fig. 2 shows this dependence, where the CTE of PMMA is displayed, evaluated at 20 and 50°C for a number of specimens with different moisture contents. For each, the abscissa indicates the specimen weight prior to the expansion measurement, relative to its original weight (prior to humidity exposure). After machining for measurement in the dilatometer, some of the specimens were dried, while others were conditioned at high relative humidity (85% RH, 30°C) for different time periods. The resultant suite of samples yielded a variety of different moisture contents.