JOURNAL OF MATERIALS SCIENCE 24 (1989) 3137–3140

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

W. D. DROTNING, E. P. ROTH
Thermophysical Properties Division, Sandia National Laboratories, Albuquerque, New Mexico 87185, USA

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 $92.8 \times 10^{-6}\,K^{-1}$) for a 2% gain in weight. A significant correlation was observed between T_g 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 $25 \times 6\,mm^2$ were cut from the sheet and measured along the long dimension; no in-plane orientation dependence on the thermal expansion was observed.

3. Experimental procedure

Specimens were moisture conditioned by either equilibration in air at 30° C and 85% relative humidity (RH), or by immersion in water at 20° C. Drying of samples was performed by heating to 50° C in dry air for prolonged periods or by vacuum drying at 50° C. Periodic weight and length measurements were obtained, following surface drying, to monitor moisture absorption or loss. No distinction among the conditioning methods was observed in the results.

Thermal expansion measurements were performed using a Harrop Model TDA-H2-SP fused silica, single pushrod dilatometer. This device was modified to allow data acquisition, analysis and control by a Hewlett-Packard 1000 minicomputer system operating in a real-time multi-tasking environment. Primary voltage signals from the LVDT length change sensor and the type K thermocouple are scanned and digitized at the dilatometer site and sent to the computer via the IEEE-488 bus for disc storage and subsequent analysis.

The data analysis procedure is as follows: after calibration of the LVDT over an appropriate range, a standard run was made with the dilatometer using a thermal cycle similar to that used for measurement of each specimen. For the current measurements, an NBS-referenced platinum thermal expansion standard was used [4]. The standard run was least-squares fit to a fourth-order polynomial; deviations between the fit to the standard run and the standard reference data were then obtained, and subsequently fit to another

0022–2461/89 $03.00 + .12

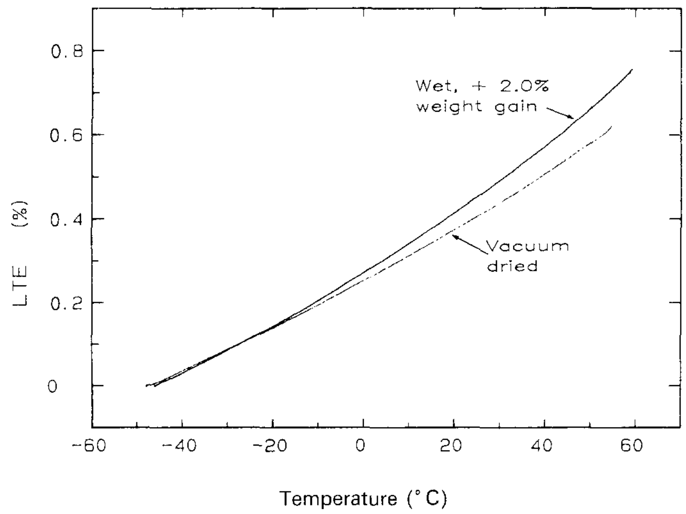

Figure 1 Linear thermal expansion (LTE) expressed in per cent, plotted against temperature, for two representative Plexiglas V811 specimens of different moisture content. Data were obtained at 2° C min^{-1}.

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

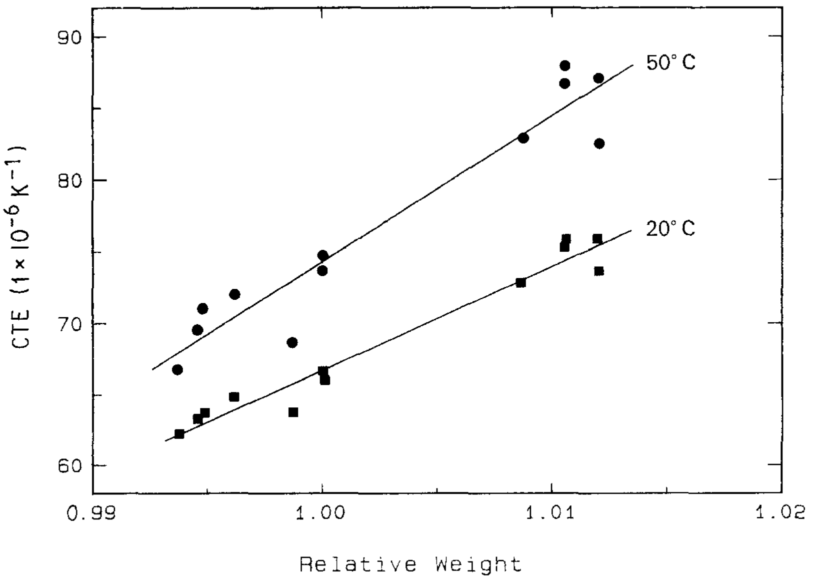

Figure 2 Coefficient of thermal expansion (CTE) of Plexiglas V811 for several specimens conditioned to different moisture contents, as a function of weight at time of measurement relative to the original weight. CTEs were determined from quadratic least-squares fits to LTE data; the fits were differentiated and evaluated at 20 (■) and 50(●)° C. Driest specimens displayed weight losses of 0.6% from as-prepared values. Moisture conditioning was done at 85% RH and 30° C for different time periods.

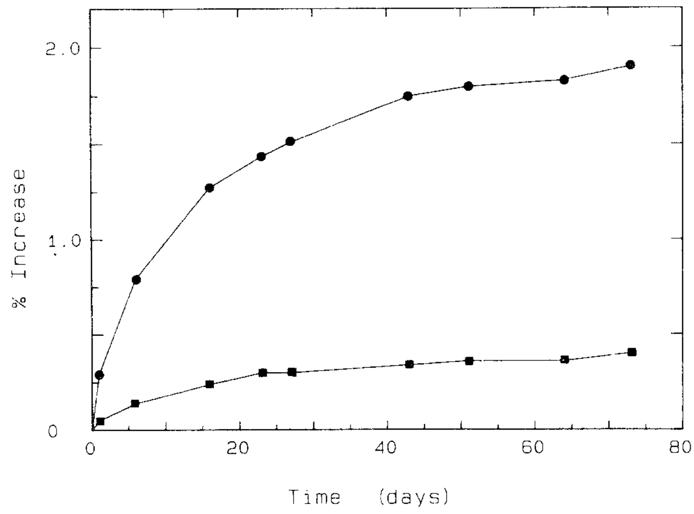

Figure 3 Per cent increase in weight (●) and length (■) of Plexiglas V811, sample B3, plotted against time of immersion in water at 20° C. Measurements were made in air after surface drying. Subsequent vacuum drying lowered the weight and length from the initial values on plot (see text).

contents. Some scatter in the data undoubtedly occurs due to the lack of control on the conditioning of the original samples, but the trends in CTE with temperature and moisture content remain. As shown by this plot, no specimen lost more than 0.6% of the starting weight, even after several days of oven drying (until no change in weight was seen). Typically then, the original weights were about 0.6% heavier than dry weights. Maximum abscissa values displayed in the plot (weight gains of 1.2%) were obtained after 22 to 30 days at 30° C at 85% relative humidity. Not only does the CTE increase with temperature (due to the positive curvature of the LTE curves) and with moisture content at a given temperature, but the CTE dependence on moisture increases more rapidly at higher temperatures, as can be seen by the increase in slope from 20 to 50° C in Fig. 2.

To eliminate uncertainty due to different original moisture contents among different specimens, a single specimen (B3) was investigated. First, the sample was oven dried for 9 days at 50° C until no further weight loss was observed. Then the sample was immersed in water at 20° C for several days. Periodically, the sample's thermal expansion, weight, and length were measured in air after surface drying. Finally, the sample was vacuum dried at 50° C for ten days until no weight loss was observed, and the expansion was again measured. Fig. 3 shows the per cent increase in weight and length during immersion for this specimen. Following the final vacuum drying, the sample weight and length were 0.11% and 0.10%, respectively, below the pre-immersion values. From the driest state to that following 75 days of immersion, an overall length change of 0.5% and weight change of 2.02% were observed.

Thermal expansion measurements were obtained on this sample (B3) at a number of moisture contents during the overall conditioning cycle. The measured CTE at 50° C is shown in Fig. 4, where the abscissa represents the weight gain of the specimen above the driest observed state. The initial and final measurements in the dry condition are shown. The CTE dependence on moisture content was found to be largely reversible, within the error of the CTE measurements. When adjusted for the moisture content of the original specimens, the data in Fig. 2 agree well with the CTE against weight gain results displayed in Fig. 4, both in CTE value and change with moisture content.

Data in Fig. 4 are plotted from Table I, which also gives the per cent weight increase (over the vacuum dried state), the temperature-dependent CTE, and CTEs at 20 and 50° C for specimen B3 as a function of time and conditioning. We have least-squares fit the constant and linear CTE terms as a function of per cent weight gain to provide an expression for the CTE of PMMA against weight gain and temperature, as follows

$$\mathrm{CTE}\,(1 \times 10^{-6}\,\mathrm{K}^{-1}) = 59.3 + 4.26\,W + 0.222\,T + 0.139\,WT \qquad (1)$$

for T in °C and W in % weight gain.

For Plexiglas sheet compound (not V811), the equilibrium water uptake is reported to be approximately

TABLE I CTE functions and CTEs at 20 and 50° C for PMMA, specimen B3, as a function of time, moisture conditioning, and % weight gain. CTEs in units $1 \times 10^{-6}\,\mathrm{K}^{-1}$. Data are arranged in chronological order of measurement. Weight gains are reported relative to the driest observed condition. All temperatures, T, are in °C.

Weight gain (%)	Fitted CTE against T	CTE at 20° C	CTE at 50° C	Condition
0.02	$59.3 + 0.147\,T$	62.2	66.7	oven dried
0.41	$61.4 + 0.268\,T$	66.8	74.8	immersed 1 day
0.91	$63.8 + 0.352\,T$	70.8	81.4	immersed 6 days
1.63	$68.6 + 0.424\,T$	77.1	89.8	immersed 28 days
1.91	$62.5 + 0.532\,T$	73.1	89.1	immersed 51 days
2.02	$70.3 + 0.477\,T$	79.8	94.2	immersed 73 days
0.04	$59.5 + 0.286\,T$	65.2	73.8	vacuum dried
0.06	$58.6 + 0.258\,T$	63.8	71.5	vacuum dried, repeat

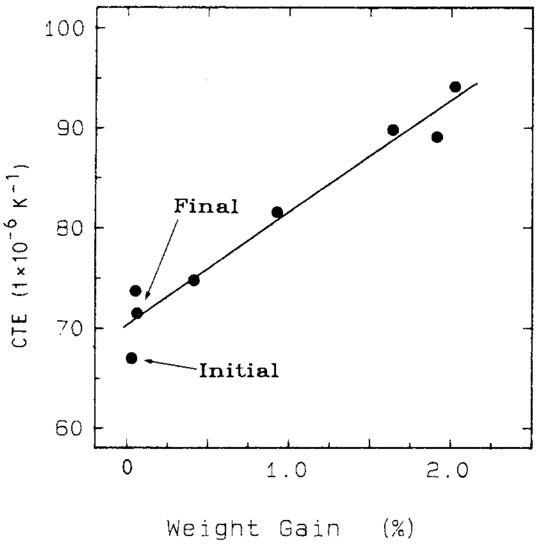

Figure 4 CTE (evaluated at 50° C) plotted against per cent weight gain for a single V811 specimen, moisture conditioned by immersion as in Fig. 3. Initial and final dried states demonstrate reversibility.

1.7 wt % at 23.5° C and 100% relative humidity [1]. At 80% RH, the expected value is 1.45%, since the sorption isotherm is roughly linear with RH. These values are somewhat lower than the values obtained in this work for Plexiglas V811, which were found to be about 1.8% at 85% RH (from the extremes of the data in Fig. 2) and approximately 2.0% at 100% RH (immersion). Product information available for type V811 Plexiglas [1] gives an equilibrium value of 0.36% dimensional change at 100% RH and a weight increase of 0.3% for 24 h immersion, both of which agree with the data reported here.

Our data on long-term weight gain in this material (Fig. 3) is similar to previous results [5], which showed a rapid initial increase followed by a much slower gain. In this study, a stable weight was not achieved after 75 days of immersion. A dual mode sorption mechanism has been suggested for this behaviour [5, 6], wherein part of the water uptake is due to dissolution in the polymer network (swelling of the structure) and the remainder is accommodated in pre-existing microvoids. Turner [15] estimated that 40 to 60% of the water was partitioned into the swelling sorption mode. Further analysis by Masi, *et al.* [6] suggested that the partitioning fraction varied from 0.2 to 0.6 (fraction = dissolved water/total water uptake) as the weight change increased from 0 to 2.5%. The data shown in Fig. 3 (corrected for the slight difference between the initial and driest states) suggest an approximate partitioning fraction near 0.7 in our case, since the asymptotic dimensional change of 0.5% translates to a volume increase of 1.5%, compared to an observed weight increase of about 2.0%.

Glass transition temperatures were determined by DSC (Perkin-Elmer Series 7 Differential Scanning Calorimeter) for representative wet and dry type V811 PMMA. A vacuum dried sample demonstrated a T_g of 109.6° C by this method. For the wet material, a separate specimen was immersed in water for 13 days, and displayed a weight gain of 1.17%. In this case, the T_g was observed at 99.4° C, about 10° C below T_g for the dried material. This depression is consistent with the expansion data shown in Fig. 1, where an equivalent expanded volume for a wet sample, evaluated at the highest temperature, was observed to occur at roughly 10° C lower in temperature than for a dry sample.

Brand [2] showed a similar correlation among CTE, T_g, and moisture content in epoxy–glass laminates; in that study, the CTE increased about $7 \times 10^{-6}\,K^{-1}$ and T_g decreased approximately 3° C for each 0.1% water absorbed. From Equation 1 corresponding values for PMMA from this work are $1.1 \times 10^{-6}\,K^{-1}$ and 0.9° C, respectively, where the moisture effect on CTE was evaluated at 50° C.

5. Summary

While the effects of moisture uptake on the dimensional changes of PMMA are well known, the effect on thermal expansion has not been extensively measured. In this work, the effects of moisture on the thermal expansion of compression-moulded PMMA (Plexiglas V811) were investigated by pushrod dilatometry. 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. Overall dimensional swelling of the PMMA with water uptake agreed with earlier work. A significant result of this study was the demonstration of the reversible effect of moisture content on the coefficient of thermal expansion of the acrylic material. For a 2% weight gain, the linear dimensional swelling of PMMA is only about 0.5%. However, for the same water uptake, the expansion coefficient at 50° C was observed to increase 32% (from 70.4 to $92.8 \times 10^{-6}\,K^{-1}$). This strong influence of moisture on the expansion properties of the material could have a significant impact on applications which require a clear understanding of the dimensional behaviour of PMMA under varying conditions of temperature and humidity. In addition to the effect on CTE, a significant correlation was observed between T_g and moisture content, of approximately -1° C per 0.1% weight increase.

Acknowledgements

This work was performed at Sandia National Laboratories supported by the US Department of Energy under Contract Number DE-AC04-76-DP00789.

References

1. Plexiglas V product information, supplied by Rohm and Haas Co., Philadelphia, Pennsylvania.
2. J. BRAND, "Thermal Analysis of Multilayer Printed Wiring Boards," IPC Technical Paper IPC-TP-152, Institute of Printed Circuits, Evanston, Illinois (1977).
3. M. J. ADAMSON, *J. Mater. Sci.* **15** (1980) 1736.
4. T. A. HAHN and R. K. KIRBY, in "Thermal Expansion–1971", edited by M. G. Graham and H. E. Hagy, Proceedings of the 1971 Thermal Expansion Symposium, AIP Conference Proceedings No. 3 (American Institute of Physics, New York, 1972).
5. D. T. TURNER, *Polymer* **23** (1982) 197.
6. P. MASI, L. NICODEMO, C. MIGLIARESI and L. NICOLAIS, *Polym. Commun.* **25** (1984) 331.

Received 21 June
and accepted 8 December 1988