

A Dilatometer for Measuring Compressibilities of Polymers in Their Melting Range

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Synopsis

A dilatometer was developed for studying the compressibility of polymers in their melting range at pressures to 8500 atm and temperatures to 370°C. Temperature was controlled to $\pm 0.01^\circ\text{C}$ and pressures were maintained and controlled by means of a hydraulic deadweight gauge system. The device was sensitive to volume changes of 1 part in 30,000.

INTRODUCTION

The study of polymer compressibility gives information regarding the structural configuration of polymers and also provides data for the design of extruders, injection molders, and similar polymer processing equipment where phase changes occur.

Foster and Griskey¹ have described a device for measuring polymer compressibilities at high temperatures and pressures. The device was subsequently used by Foster,² Haug,³ and Grindstaff⁴ for the compressibility studies of several polymers. Data from these studies were found to be inconsistent in the melting range of the polymers studied. A study of the apparatus and experimental techniques employed by the above mentioned investigators was conducted to determine the source of the inconsistency. The study revealed that temperature control and sample preparation techniques were the major sources of error.

The rate of change of the coefficient of thermal expansion of polymeric materials is greatest in the melting range. Temperature control in the melting range must therefore be most precise to achieve consistent compressibility data.

The specific volume of crystalline polymers is dependent on polymer structure. Investigations of polymer structure by Geil,⁵ Wunderlich,⁶ and others have shown that polymer structure varies with the thermal and pressure history of the sample. Improved sample preparation techniques were therefore required.

An improved dilatometer was designed and constructed to enable compressibility measurements on polymeric materials to pressures of 8500 atmospheres and temperatures of 370°C. Temperature was controlled to $\pm 0.01^\circ\text{C}$ and volume changes of one part in 30,000 were detected.

APPARATUS

The schematic of the apparatus is shown in Figure 1. A hydraulic hand-pump was used for pressurizing the dilatometer, the details of which are presented in Figure 2. The apparatus consists of four major subassemblies: (1) the deadweight gauge and the hydraulic handpump used to inject oil into the system and exert pressure on the sample; (2) a sample chamber assembly in which the sample length varied due to changes in temperature or changes in pressure; (3) a constant temperature bath in which the entire sample chamber assembly was immersed; the bath also contained a thermopile to record temperature, a thermoregulator for temperature control, and a high-speed stirrer; (4) a linear variable differential transformer (LVDT) to follow movement of the piston in the sample chamber and thereby determine changes in sample specific volume.

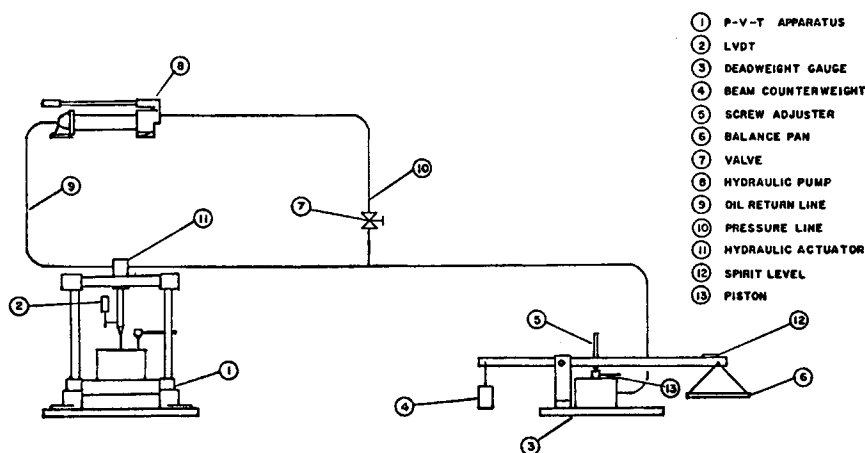


Fig. 1. Schematic diagram of dilatometer apparatus: 1) P-V-T apparatus; 2) LVDT; 3) deadweight gauge; 4) beam counterweight; 5) screw adjuster; 6) balance pan; 7) valve; 8) hydraulic pump; 9) oil return line; 10) pressure line; 11) hydraulic actuator; 12) spirit level; 13) piston.

The deadweight gauge was used to measure and control the pressure on the sample. The desired pressure was obtained by placing the proper amount of weight on the balance pan of the deadweight gauge and using the handpump to inject hydraulic oil into the system until the beam of the gauge became level. By alternating the inlet and outlet to the hydraulic handpump, the piston contacting the sample could be extended or retracted. The parts were machined from a 440C stainless steel alloy. This alloy, containing 16%–18% chromium and 0% nickel, develops a tensile strength of 285,000 psi when tempered at 600°F. The finished parts had a Rockwell C hardness of 57. The alloy was selected to give minimum distortion under the design conditions. The piston and the sample chamber were machined to a tolerance of $+0.0000$, -0.0001 in. and given a 3 micron finish.

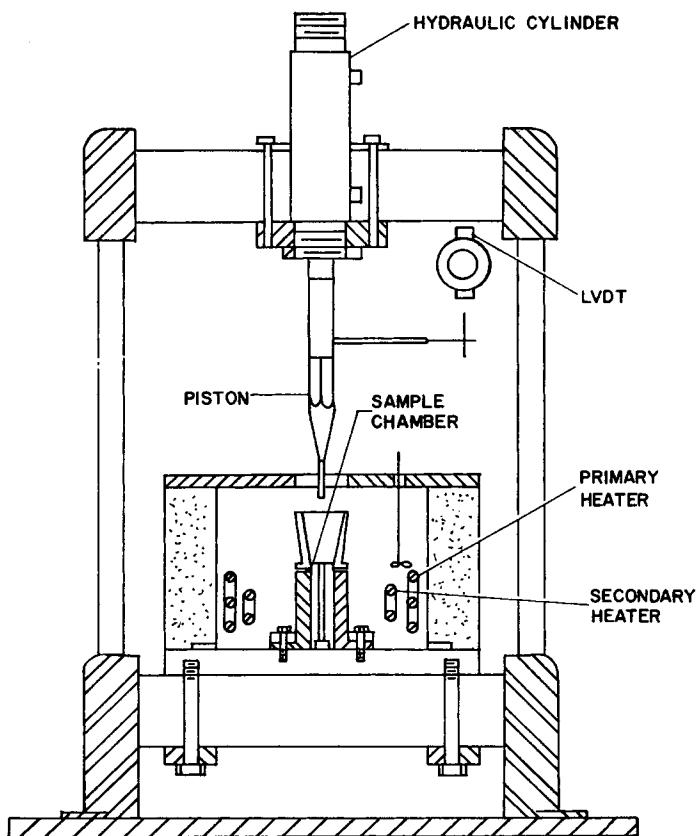


Fig. 2. Dilatometer.

The constant temperature bath is shown in Figure 2 with the sample chamber assembly in place. An oil dam attached to the sample chamber prevented the heat transfer fluid from directly contacting the sample. An indexing device held the sample chamber in a fixed position within the bath. A 1000-watt immersion heater connected to a variable transformer was used to bring the bath to a temperature less than 0.5°C below the desired temperature. Temperature was measured by a five-junction iron-Constantan thermopile. A 250-watt immersion heater, also connected to a variable transformer, was used to control the bath temperature to $\pm 0.01^{\circ}\text{C}$. Control of this secondary heater was by thermoregulator (Fisher Scientific Co., 1965, catalog no. 15-180-15) operating through a transistorized relay (Model 32, Fisher Scientific Co., 115 V, ac, 60 cps, 15 amperes maximum load and 1 megaohm sensitivity). The heat transfer fluid was a fluoro-silicone oil (Dow Corning Co., type F-6-7039) with a maximum continuous use temperature of 700°F .

Since sample diameter was constrained to the diameter of the sample chamber, changes in specific volume were evidenced as changes in sample

length accompanied by corresponding changes in piston position. Connected to the piston was the core of the linear variable differential transformer (Schaevitz Engineering Co., Model E300D). The LVDT, capable of sensing changes in length from 0.0001 to 0.3000 in., produced a voltage output proportional to the change of position of its transformer core. Voltage to the LVDT was first stabilized and then reduced through a transformer to 6.3 V. The LVDT output was rectified and recorded on a Leeds and Northrup Speedomax H recorder. The output was adjusted by means of a potentiometer to take full advantage of the 150 mV span of the recorder.

EXPERIMENTAL PROCEDURE

Sample Preparation

Samples were prepared by extruding molten polymer into a mold utilizing the sample chamber shown in Figure 3. Polymer was allowed to solidify in the mold after which it was removed from the mold and cut to a length of approximately $1\frac{1}{4}$ in. A plug was placed in the base of the sample chamber and the oil dam (Fig. 2) was threaded to the top of the chamber. The sample was inserted in the sample chamber and the assembly was placed in

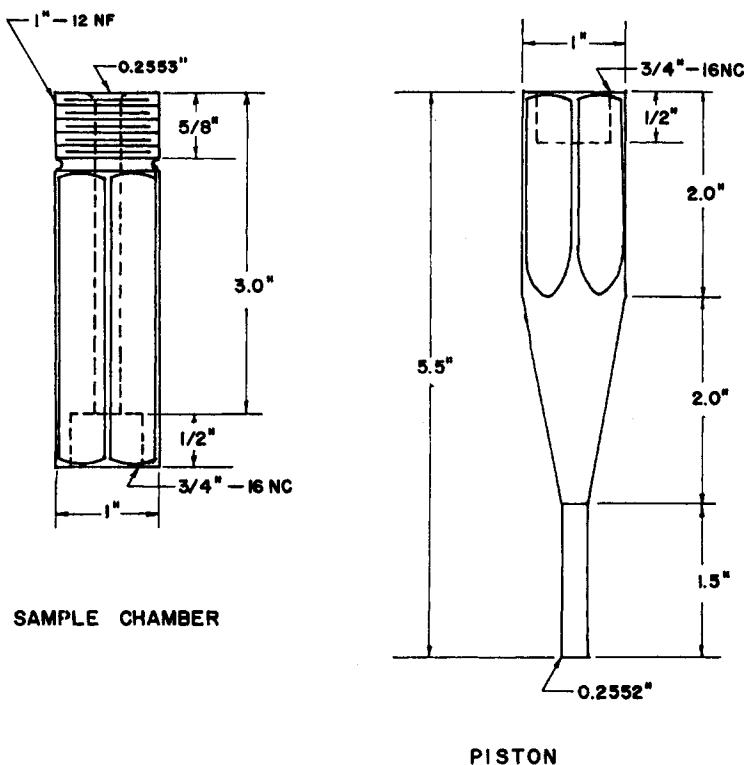


Fig. 3. Details of sample chamber and piston.

the indexer of the constant temperature bath and locked in place. After bringing the piston in contact with the sample, the annealing procedure was begun.

Annealing Procedure

The bath temperature was increased to a point approximately 200°C above the melting point of the polymer while the sample was held at 100 psig. A lower temperature would be required for heat sensitive materials. The sample was held at the temperature and pressure for 2 hr at which time the pressure was increased to 8000 psig and held for 1 hr. Following the 1-hr period, the heat input to the bath was adjusted to allow a cooling rate of approximately 0.5°C per min. During the cooling period, the pressure was maintained constant at 8000 psig. After the sample reached room temperature, the pressure was reduced to atmospheric and the sample was ready for compressibility measurements. This procedure was repeated for each measurement with the LVDT output adjusted to keep the readings within the range of the recorder.

Accuracy of Measurement and Possible Sources of Error

Sample volume determinations were accurate to 1 part in 30,000. The sample weight was accurate to 1 part in 10,000. A possible source of error was leakage of polymer past the piston. Sample weights were determined before and after the compressibility measurements and the maximum weight loss encountered was 0.0005 g for a 1.75-g sample. The maximum error in determining specific volume was therefore 0.03%.

Pressure measurement accuracy increased as pressure increased. At pressures exceeding 1000 atm, error was less than 1%. Due to friction within the deadweight gauge, the maximum possible error in pressure measurement increased to 2% at pressures less than 1000 atm.

The dilatometer was unique in that the sample chamber was in direct contact with the heat transfer medium. This design feature plus the constancy of bath temperature and time required for equilibrium eliminated the possibility of thermal gradients within the sample.

Thermal expansion of the dilatometer frame, sample chamber assembly, and other related parts was considered as a source of error. Displacement of the LVDT with respect to the sample due to thermal expansion of the apparatus was found to be less than 0.0001 in. The effect of this displacement on specific volume was negligible.

Using the dilatometer and sample preparation techniques described above, compressibility measurements on a high density polyethylene in its melting range were reproducible to a maximum deviation of 0.86%.

Tables I and II are data collected for a high-density polyethylene. A plot of the thermal expansion data in Table I indicates the melting point to be 141°C, as evidenced by a discontinuity in the curve.

TABLE I
Thermal Expansion of Marlex 6001^a

Temperature			LVDT output			Sample length, in.	Specific volume, cc/g
m.v.	°F	°C	Initial, m.v.	Final, m.v.	Expansion, Δ in.		
6.40	77.0	25.0	98.3	98.30	0.0000	2.0714	1.0359
12.89	122.0	50.0	98.3	84.50	+0.0118	2.0832	1.0418
19.74	167.0	75.0	84.5	59.80	+0.0209	2.1041	1.0523
26.59	212.0	100.0	59.8	23.20	+0.0310	2.1351	1.0678
32.07	248.0	120.0	128.4	92.30	+0.0308	2.1659	1.0832
34.81	266.0	130.0	92.3	59.90	+0.0317	2.1976	1.0992
36.18	275.0	135.0	127.9	88.30	+0.0340	2.2316	1.1160
36.86	279.5	137.5	88.3	63.45	+0.0559	2.2875	1.1440
37.27	282.2	139.0	129.2	99.97	+0.0679	2.3554	1.1780
37.82	285.8	141.0	130.4	27.30	+0.0877	2.4431	1.2218
38.37	289.4	143.0	129.7	126.00	+0.0031	2.4462	1.2234
40.29	302.0	150.0	126.0	109.20	+0.0144	2.4606	1.2306
43.03	320.0	160.0	109.2	92.00	+0.0147	2.4753	1.2379

^a Test pressure = 0 psig; sample weight = 1.6776 g; sample length = 2.0714 in.; sample density at 25°C = 0.965 g/cc.

TABLE II
Compressibility of Marlex 6001^a

Balance pan weight, lb	Pressure psig	LVDT output			Sample length, in.	Specific volume, cc/g
		Initial, m.v.	Final, m.v.	Compression, Δ in.		
0.00	0	25.1	25.1	0.0000	2.4199	1.2218
8.50	3,510	25.1	415.1	-0.2707	2.1492	1.0850
17.06	7,046	38.3	106.4	-0.0575	2.0917	1.0560
21.31	8,801	32.2	63.4	-0.0260	2.0757	1.0479
29.84	12,324	39.3	77.1	-0.0321	2.0436	1.0317
34.12	14,091	77.1	94.6	-0.0148	2.0288	1.0242
38.37	15,847	94.6	107.7	-0.0070	2.0218	1.0207
42.62	17,602	107.7	104.8	-0.0017	2.0201	1.0198
63.94	26,407	104.8	106.7	-0.0017	2.0184	1.0190

^a Test temperature = 141.0°C; sample weight = 1.6619 g; sample length = 2.0519 in.; sample density = 0.965 g/cc.

The compressibility of the polyethylene at its melting point is indicated by the data in Table II. Table III compares specific volumes of the polyethylene determined at constant pressure to specific volumes determined at constant temperature. The deviations indicated in Table III are within the reproducibility of the data.

TABLE III
Comparison of Thermal Expansion and Compressibility
Data for Marlex Polyethylene (Marlex 6001)^a

Temperature, °C	3510 psig		8802 psig	
	α	β	α	β
120.0	1.0622 ^b	1.0622	1.3065	1.0341
130.0	1.0736 ^c	1.0709	1.0405 ^c	1.0413 ^c
135.0	1.0790	1.0765	1.0446	1.0443 ^c
137.5	1.0821 ^c	1.0798	1.0448 ^c	1.0450 ^c
139.0	1.0839 ^c	1.0819	1.0454 ^c	1.0465
141.0	1.0865 ^c	1.0850	1.0468 ^c	1.0479

^a Alpha denotes thermal expansion data; β denotes compressibility data.

^b Specific volume, cc/g.

^c Denotes interpolated values.

CONCLUSIONS

A high-pressure, high-temperature dilatometer has been developed which is sufficiently sensitive for the measurement of polymer compressibilities in the melting region. The dilatometer can operate to pressures of 8500 atm and temperatures of 370°C.

The design of the apparatus, the sample preparation techniques, and pressure and temperature control made possible polymer compressibility measurements with errors of less than 1%.

Appreciation is expressed to the Dow Chemical Company for the construction of the sample chamber and piston, the critical part of the apparatus.

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