

Pressure-Volume-Temperature Behavior of Polyisobutylene

The effect of pressure on the physical and chemical behavior of polymers is an important consideration to polymer scientists and engineers. One area of particular interest is the compressibility behavior of polymers.

A number of investigators, Bridgman,¹ Parks and Richards,² Spencer and Gilmore,^{3,4} Weir,⁵⁻⁷ Heydemann and Guicking,⁸ Hellwege et al.,⁹ Foster et al.,^{10,11} and Griskey and Haug¹² have measured pressure-volume-temperature data. Many of these studies have, however, been limited with respect to temperature, pressure, or types of polymers studied. (There were, for example, no data for polyisobutylene.)

The present work was undertaken to study as completely as possible the compressibility behavior of polyisobutylene.

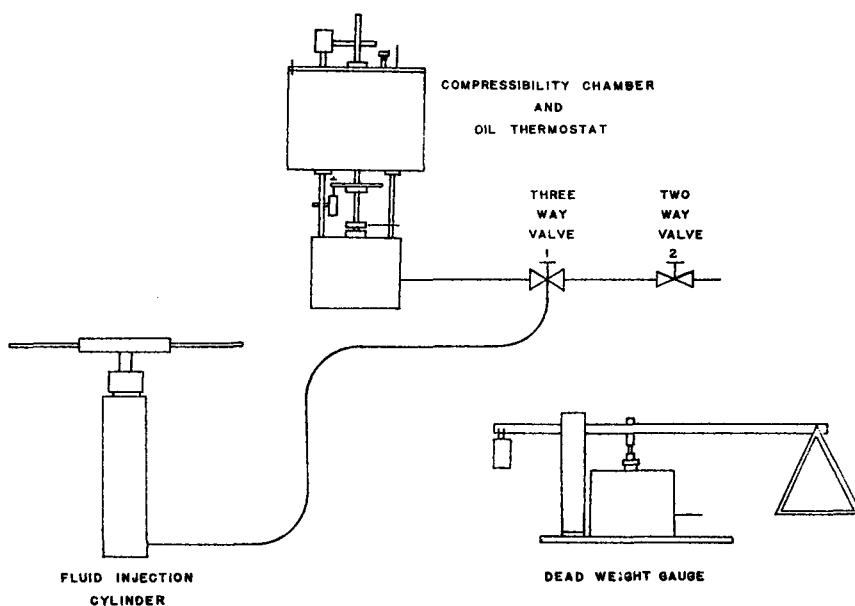


Fig. 1. Schematic of compressibility apparatus.

Figure 1 is a schematic of the experimental apparatus. Figure 2 depicts the compressibility chamber and piston. Polymer samples were placed in the chamber which was evacuated after it had been immersed in the oil bath thermostat. The device was then thoroughly seasoned. A careful annealing procedure was followed for solid-phase measurements. Readings were taken by holding temperature constant, changing volume, and then balancing the pressure for a long enough period of time to assure the proper equilibrium pressure-volume-temperature combination. A detailed description of apparatus and procedure is given elsewhere.¹³

Temperatures were controlled to $\pm 0.10^\circ\text{C}$. Volume accuracy was 0.25% or better, while the accuracy of pressure measurements was within 1% or less.

Data were measured for pressures up to 618 atmospheres and temperatures up to 200°C . These raw data were smoothed by using volume and pressure residual curves

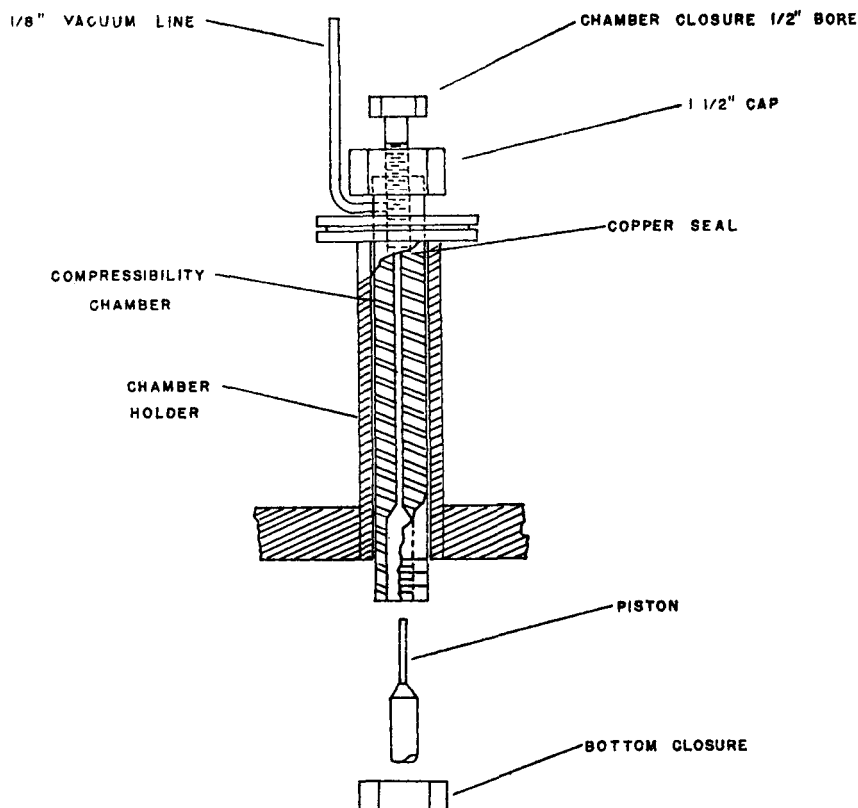


Fig. 2. Compressibility chamber.

The technique of smoothing with residuals involves first calculating either a volume or pressure from an equation of state (at a selected temperature and pressure or a selected volume and pressure). In this work the Spencer and Gilmore^{3,4} equation of state was used:

$$(P + \pi)(V - W) = (R/M)T \quad (1)$$

where P is pressure, V is specific volume, R is the gas constant, T is absolute temperature, M the molecular weight of an interaction unit, and π and W are constants. Next the pressure or volume residual is calculated.

$$r_p = P_{\text{calc}} - P_{\text{exp}} \quad (2)$$

$$r_v = V_{\text{calc}} - V_{\text{exp}} \quad (3)$$

These residual values can then be plotted as isothermal curves versus either volume or pressure. Smoothed data points can then be obtained by using the residual together with calculated values:

$$P_{\text{exp}} = P_{\text{calc}} - r_p \quad (4)$$

$$V_{\text{exp}} = V_{\text{calc}} - r_v \quad (5)$$

The smoothed data are presented in Figures 3 and 4 and Table I.

As pointed out previously, there were no other compressibility data for polyisobutylene. As a result, the present data cannot be compared directly to any other experimental work. Indirect comparisons can, however, be made. Figure 5 represents one such

TABLE I
Experimental Values of the Specific Volume^a
of Polyisobutylene as a Function of Temperature and Pressure

Temperature, °C	Pressure, atm						
	1	79	158	238	316	474	618
26	1.0900	1.0794	1.0755	1.0730	1.0701	1.0645	1.0599
57	1.1002	1.0894	1.0848	1.0798	1.0753	1.0673	1.0605
75	1.1070	1.0957	1.0908	1.0862	1.0819	1.0710	—
106	1.1203	1.1090	1.1022	1.0967	1.0909	1.0793	—
137	1.1348	—	1.1183	1.1089	1.1011	—	—
165	1.1481	1.1316	1.1250	1.1169	1.1083	1.0926	—
200	1.1634	1.1420	1.1325	1.1223	—	—	—

^a Expressed in cm³/g.

comparison. Compressibilities for both polymethylmethacrylate⁸ (solid curves) and polyisobutylene (dotted curves) are shown. As can be seen the data are of the same order of magnitude. Furthermore, as might be expected the elastomeric polyisobutylene is more compressible than the poly(methyl methacrylate).

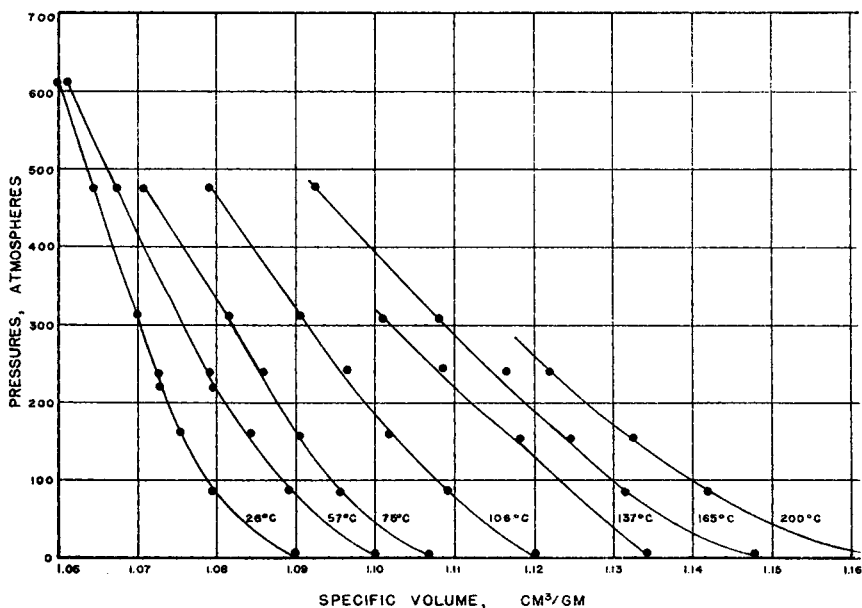


Fig. 3. Pressure versus volume at constant temperature for polyisobutylene.

An even more convincing check was made with the generalized equation of state for polymers developed by Griskey and Whitaker.¹⁴ This equation based on a modification of the theory of corresponding states was

$$V = [(0.01205)/(\rho_0)^{0.94211}(P)^n - 1(T/T_g)^{m+1}R] \quad (6)$$

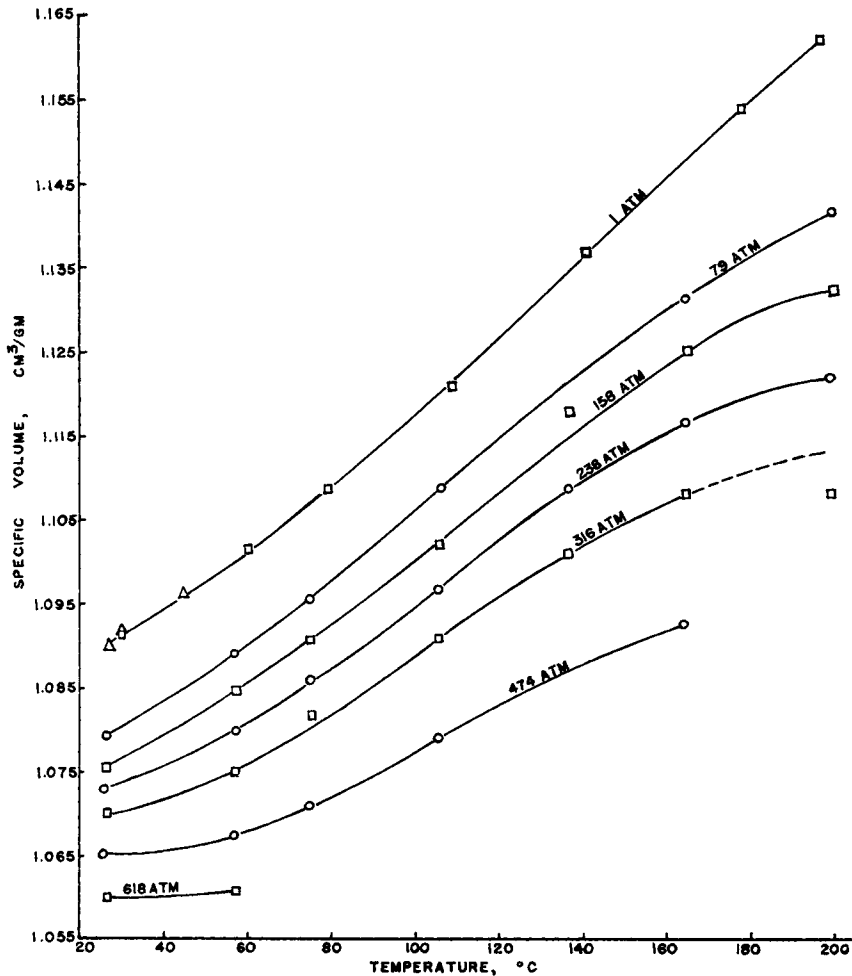


Fig. 4. Volume versus temperature at constant pressure for polyisobutylene.

where V is volume in cc/g, ρ_0 the polymer density at 1 atmosphere and 25°C, P the pressure in atmospheres, T the absolute temperature in °K, T_g the polymer's glass temperature in °K, and R the gas constant in atm-cc/gm-mole-°K. The average per cent deviation of calculated from experimental data was 2.2% for the following polymers: polyethylene, polypropylene, poly(vinyl fluoride), polytetrafluoroethylene, poly(vinyl alcohol), polystyrene, poly(methyl methacrylate), poly(vinylidene fluoride), poly(vinyl chloride), polymonochlorotrifluoroethylene, and nylon 610.

Pressure-volume-temperature data was calculated using eq. (6) and then compared to the experimental data of this paper. The average per cent deviation was 2.08% which

showed that the data fit the generalized equation as well as the foregoing listed polymers.

Summary

Equilibrium pressure-volume-temperature data were determined for polyisobutylene for pressures up to 618 atm and temperatures up to 200°C. These data were

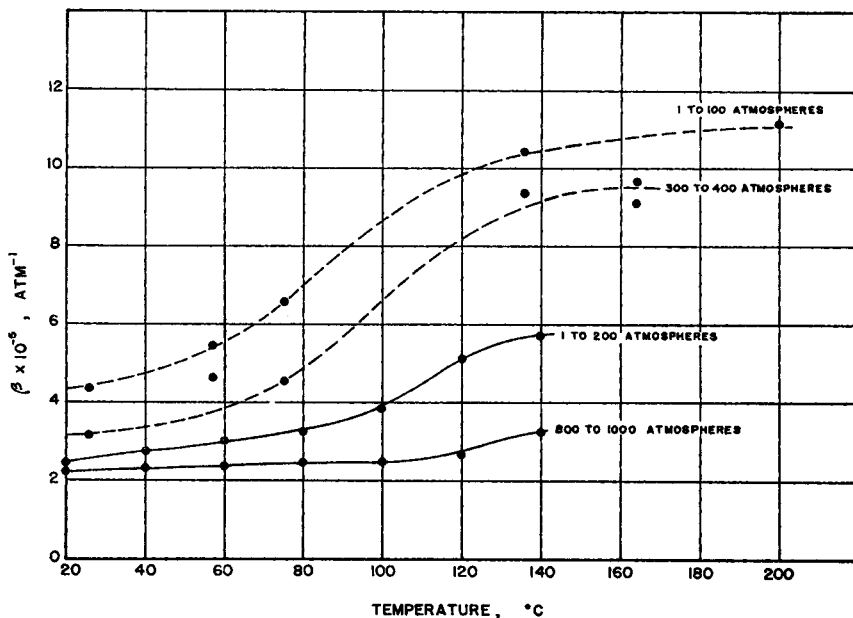


Fig. 5. Compressibilities versus temperature (---), polyisobutylene; (—) poly(methyl methacrylate).

measured with a compressibility device capable of obtaining precise and accurate data. Compressibilities computed from the data compared in an expected manner to values for poly(methyl methacrylate). In addition, the polyisobutylene data were found to fit the generalized equation of state for polymers developed by Griskey and Whitaker.¹⁴

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