Pressure–Volume–Temperature Behavior of Nylon 610

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Synopsis

Equilibrium pressure–volume–temperature behavior in both the solid and molten regions was determined for nylon 610. Data were measured with a compressibility device capable of obtaining precise and accurate data. Residual curve treatment showed that the data were true equilibrium data. A volume extrapolated to 2419 atm. at room temperature from the present data compared favorably to the sole literature value reported by Bridgman. The data of this work showed the existence of what appears to be a second-order transition point for nylon 610. This point ranged from 140°C. at 232 atm. to about 170°C. at 1855 atm. The Spencer-Gilmore equation was fitted to the data of this study.

Investigations on the effect of pressure on the physical and chemical behavior of polymers are subjects of interest to both polymer engineers and scientists. An area of particular interest is that involving the pressure–volume–temperature relations of polymers.

A number of investigators, Bridgman,[1] Parks and Richards,[2] Spencer and Gilmore,[3,4] Weir,[5–7] Matsuoka,[8–10] Heydemann and Guicking,[11] Hellwege et al.[12] and Foster et al.[13,14] have measured pressure–volume–temperature data. Many of these studies have, however, been limited with respect to temperature, pressure, or types of polymers studied. In particular nylon 610 is one polymer that has been neglected. The only available literature data is one value of compressibility.[1]

The present work was undertaken to study as completely as possible both the solid and melt compressibility behavior of nylon 610.

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 then 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.[15]

Temperatures were controlled to ±0.10°C. Volume accuracy was 0.25% or better, while the accuracy of pressure measurements was within 1% or less.

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Data were measured for both the solid and molten regions from pressures of 1–1855 atm. and temperatures of 23–260°C. These raw data were smoothed by using volume and pressure residual curves. The technique of smoothing with residuals involves first calculating either a volume or

LEGEND

A — SAMPLE PISTON
B — SAMPLE CELL
C-I — FIXED COLLAR
C-2 — FIXED COLLAR
C-3 — MOVABLE COLLAR, LVDT CORE SUPPORT
C-4 — FIXED COLLAR, LVDT CORE SUPPORT
D — O-RING SEAL NUT
E — TEFLON O-RING
F — SAMPLE-CELL RETAINING NUT
G — LEVEL GLASS
H-I — 300-WATT HEATER
H-2 — 250-WATT HEATER
I — BREECH SCREW
J — LEAD SEAL
K — FLUID INJECTOR
L-I — ROTATION LEVER, SAMPLE PISTON
L-2 — ROTATION LEVER, DEAD-WEIGHT
        GAGE PISTON
M — THERMOSTAT
N — DEAD-WEIGHT GAGE PISTON
O — OIL-BATH CASE
P — ICE-WATER BATH
R — LVDT
S — VACUUM LINE
T — THERMOPILES
U — TWO-WAY SWITCH
V-I FLUID INJECTOR VALVE
V-2 DEAD-WEIGHT GAGE VALVE
V-3 COOLING WATER VALVE
W-I WEIGHT PAN
W-2 COUNTERWEIGHT PAN
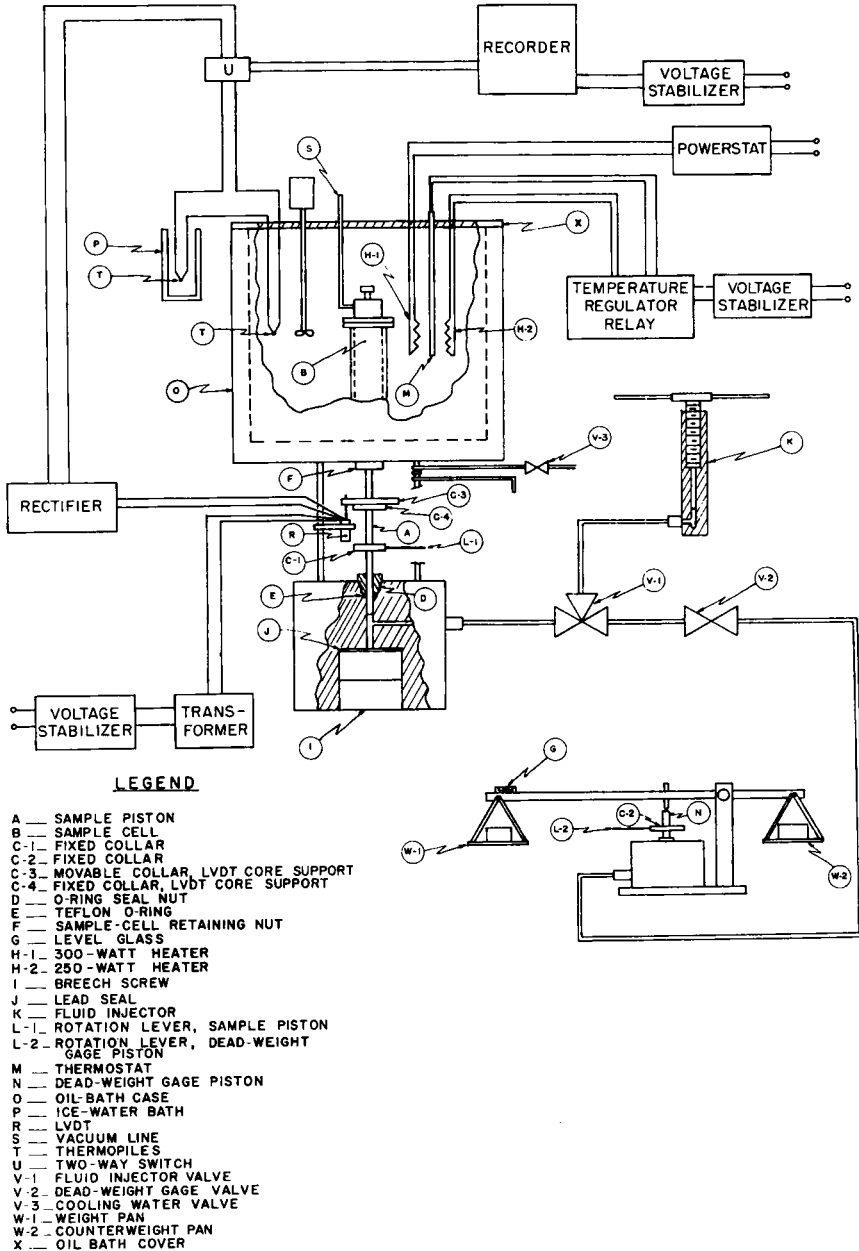X — OIL BATH COVER

Fig. 1. Schematic of apparatus.

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:

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

where P is pressure, V is specific volume, R is the gas constant, T is absolute temperature, M is the molecular weight of an interaction unit, and
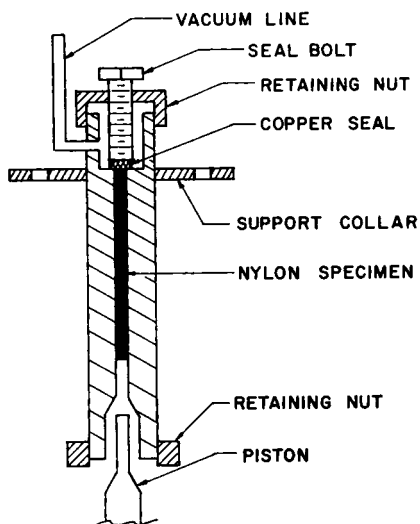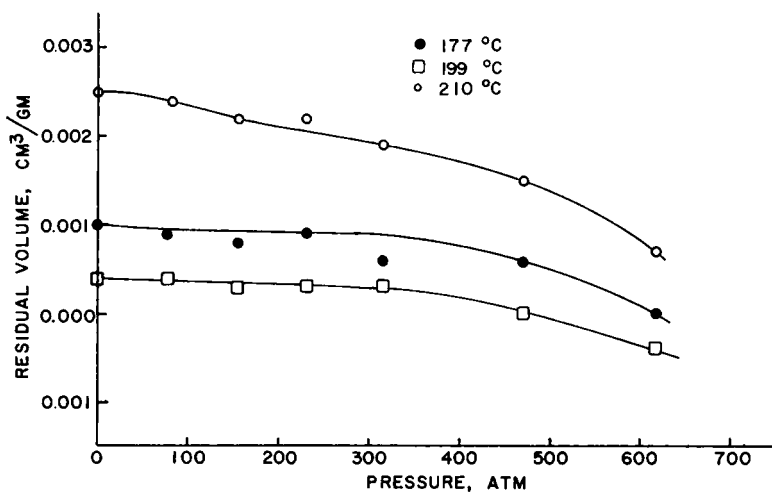

Fig. 2. Compressibility chamber.

Fig. 3. Volume residual vs. pressure.

Fig. 4. Pressure vs. volume at constant temperature.

π and W are constants. Next the pressure or volume residual is calculated.

$$r_p = P_{\text{calculated}} - P_{\text{experimental}} \tag{2}$$

$$r_v = V_{\text{calculated}} - V_{\text{experimental}} \tag{3}$$

These residual values can then be plotted as isothermal curves versus either volume or pressure. Figure 3 is such a plot. Smoothed data points can then be obtained by using the residual together with calculated values:

$$P_{\text{experimental}} = P_{\text{calculated}} - r_p \tag{4}$$

$$V_{\text{experimental}} = V_{\text{calculated}} - r_v \tag{5}$$

The smoothed data are presented in Figures 4 and 5 and Table I.

TABLE I

Smoothed Values of the Specific Volume of Nylon 610 for Temperatures
of 25–260°C. and Pressures of 1–1855 atm.

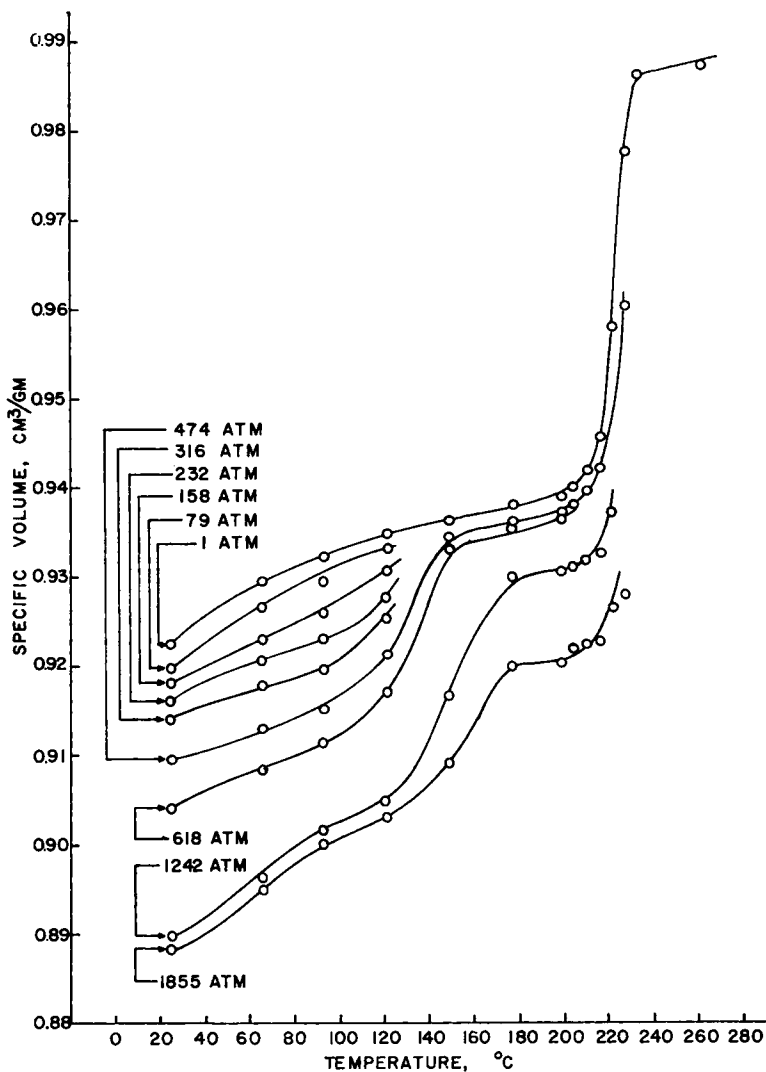| Tempera-ture, °C.	Specific volume, cm.³/g. $\times 10^4$								
	1 atm.	79	158	232	316	474	618	1242	1855
25	9226	9198	9182	9161	9140	9097	9040	8898	8881
66	9296	9266	9231	9206	9178	9131	9084	8963	8948
93	9324	9292	9260	9233	9197	9151	9113	9015	9000
121	9350	9333	9307	9276	9255	9212	9170	9048	9032
149	9364	9362	9361	9359	9355	9347	9331	9167	9094
177	9382	9379	9377	9375	9373	9365	9356	9300	9200
199	9391	9389	9386	9384	9381	9374	9366	9306	9205
204	9401	9396	9394	9392	9389	9381	9371	9312	9220
210	9420	9417	9412	9409	9405	9396	9384	9320	9225
216	9459	9456	9451	9447	9441	9424	9408	9327	9227
221	9582	9579	9574	9567	9557	9532	9506	9373	9268
227	9778	9753	9723	9695	9663	9578	9528	9391	9282
232	9865	9832	9774	9727	9679	9587	9530	—	—
260	9874	—	—	—	—	—	—	—	—

Fig. 5. Volume vs. temperature at constant pressure.

Residual curves can also be used to check the consistency of experimental data as well as the attainment of equilibrium during the experiments.[16,17] Smooth curves, as in Figure 3, indicate that data are consistent and that equilibrium was attained.

The only other compressibility datum for nylon 610 was a single point reported by Bridgman[1] at room temperature and a pressure of 2419 atm. A direct comparison of the data of this work and the point of Bridgman[1] was not possible, since the highest pressure studied in the present investigation was 1855 atm. It was found, however, that a volume extrapolated

to 2419 atm. at 25°C. from the data of the present work compared quite favorably to the value reported at that pressure by Bridgman.[1]

The curves of Figure 5 show two distinct discontinuities. One of these, which appears in the range of 200–220°C., represents the melting of the sample. There is, however, another which appears from about 140°C. at 232 atm. to about 170°C. at 1855 atm. This latter discontinuity is not as readily explained.

The most obvious explanation for the discontinuity is that it might be due to experimental error. This, however, did not seem to be the case since a number of independent rechecks yielded essentially the same behavior.

Another possibility is that the discontinuity might be the glass transition point. Nielsen,[18] however, reports the T_g for nylon 610 as 40°C., which discounts this explanation. It appears more likely that the discontinuity represents a second-order transition in the polymer.

Shifts of both glass transition points and second-order transitions with increasing pressure have been observed previously by other investigators.[11] These shifts ranged from 0.013 to 0.018°C./atm. pressure. In the present work the shift was about 0.016°C./atm. which was approximately the same as those observed earlier.[11]

The Spencer-Gilmore equation was fitted to the data of the present work in the solid region. Two sets of constants were determined—one below the second-order transition point and the other between that point and the melting region. These constants are given in Table II.

TABLE II

R', cm.^{3}-atm./g.-°K.[a]	π, atm.	W, cm.^{3}/g.	Temperature range, °C.
1.85	1,351	0.8603	25–121
0.738	10,768	0.9064	177–221

[a] $R' = R/M$.

References

1. P. W. Bridgman, *Proc. Am. Acad. Arts Sci.*, **76**, 71 (1948).
2. W. Parks and R. B. Richards, *Trans. Faraday Soc.*, **45**, 206 (1949).
3. R. S. Spencer and G. D. Gilmore, *J. Appl. Phys.*, **20**, 502 (1949).
4. R. S. Spencer and G. D. Gilmore, *J. Appl. Phys.*, **21**, 523 (1950).
5. C. E. Weir, *J. Res. Natl. Bur. Std.*, **45**, 468 (1949).
6. C. E. Weir, *J. Res. Natl. Bur. Std.*, **50**, 153 (1953).
7. C. E. Weir, *J. Res. Natl. Bur. Std.*, **53**, 245 (1954).
8. S. Matsuoka, *J. Polymer Sci.*, **42**, 511 (1960).
9. S. Matsuoka, *J. Polymer Sci.*, **57**, 567 (1962).
10. S. Matsuoka and B. Maxwell, *J. Polymer Sci.*, **32**, 131 (1958).
11. P. Heydemann and H. D. Guicking, *Kolloid-Z.*, **193**, 16 (1963).
12. K. H. Hellwege, W. Knappe, and P. Lehmann, *Kolloid-Z.*, **183**, 110 (1962).
13. G. N. Foster, N. Waldman, and R. G. Griskey, *Polymer Eng. Sci.*, **2**, 131 (1966).

14. G. N. Foster, N. Waldman, and R. G. Griskey, *J. Appl. Polymer Sci.*, **10**, 201 (1966).

15. G. N. Foster and R. G. Griskey, *J. Sci. Instr.*, **41**, 759 (1964).

16. K. Li and L. N. Canjar, *Chem. Eng. Progr. Symp. Ser.*, **49**, No. 7, 147 (1953).

17. L. N. Canjar, paper presented to the Division of Petroleum Chemistry, 132nd Meeting, American Chemical Society, New York, September 9, 1957.

18. L. E. Nielsen, *Mechanical Properties of Polymers*, Reinhold, New York, 1962, p. 21.

Résumé

Le comportement pression–volume–température à l'équilibre à la fois dans les régions du solide et liquide a été déterminé pour du nylon 610. Les résultats ont été obtenus grâce à un appareillage de mesures de compressibilité permettant l'obtention de données précises. Le traitement de la courbe montrait que ces résultats correspondaient à un véritable équilibre. Le volume-extrapolé à 2.409 atmosphères à température de chambre au départ des résultats actuels peuvent être comparés favorablement à la seule valeur indiquée dans la littérature et qui est rapportée par Bridgman. Les résultats de ce travail montraient l'existence de ce qui semblait être un point de transition de second ordre pour le nylon 610. Ce point se situe entre 140° sous 232 atmosphères jusqu'à environ 170°C sous 1.855 atmosphères. L'équation de Spencer-Gilmore était en accord avec les résultats de cette étude.

Zusammenfassung

Das Gleichgewichtsvolumen von Nylon 610 in Abhängigkeit von Druck und Temperatur wurde in geschmolzener und fester Phase bestimmt. Die Messung erfolgte mit einem Kompressibilitätsapparat, der Präzisionsdaten lieferte. Das aus den erhaltenen Daten bei Raumtemperatur auf 2419 Atmosphären extrapolierte Volumen stimmte gut mit dem einzigen, in der Literatur vorhandenen, von Bridgman bestimmten Wert überein. Die Ergebnisse der vorliegenden Arbeit lassen anscheinend das Vorhandensein eins Umwandlungspunkts zweiter Ordnung bei Nylon 610 erkennen. Dieser Punkt verschob sich von 140°C bei 232 Atmosphären zu etwa 170°C bei 1855 Atmosphären. Die Ergebnisse konnten mit der Spencer-Gilmore-Gleichung wiedergegeben werden.