

Densities of Amorphous Polymers at High Pressures

Experimentally determined densities and compressibilities of amorphous polymers are frequently available; but, because of experimental difficulties, few experimental results have been reported at high pressures. Such densities, however, are sometimes required for rational design of extrusion and similar processes. We report here a simple method for estimating densities and compressibilities at high pressures from experimental compressibilities at low pressure. Our method is based on a relation for liquids suggested by Wada¹ and developed by Chueh and Prausnitz.² The purpose of this note is to suggest a method for estimating polymer densities at high pressure wherever experimental data are insufficient for obtaining parameters needed in an equation of state, as, for example, the Tait equation.

The isothermal compressibility β is defined by

$$\beta = \frac{1}{\rho} \left(\frac{\partial \rho}{\partial P} \right)_T \quad (1)$$

where P = pressure, T = temperature, and ρ = density.

Compressibility β is a function of both temperature and density. As suggested by Wada,¹ the effect of density is given to a good approximation by

$$\rho(\beta^{1/n}) = \rho^0(\beta^0)^{1/n} = \text{constant } (T) \quad (2)$$

where superscript 0 denotes low pressure and n is a positive empirical constant. For ordinary liquids, n is in the range of 7–10.

Chueh and Prausnitz² substituted eq. (1) into eq. (2) and integrated, obtaining

$$(\rho/\rho^0)^n = 1 + n\beta^0(P - P^0) \quad (3)$$

We find that eq. (3) is applicable to amorphous polymers when $n = 10$. In comparison calculated and experimental results, we have set $P^0 = 0$.

While $n = 10$ gives good results, the calculations are not strongly sensitive to n . This lack of sensitivity becomes clear if we write eq. (3) in logarithmic form:

$$\ln(\rho/\rho^0) = \frac{1}{n} \ln [1 + n\beta^0 P] \\ \approx \frac{1}{n} \left[n\beta^0 P - \frac{(n\beta^0 P)^2}{2} + \dots \right] \approx \beta^0 P - \frac{n}{2} (\beta^0 P)^2 + \dots \quad (4)$$

For pressures up to 1000 bars, $n\beta^0 P$ is in the vicinity of 0.5 or less; therefore, the expansion converges rapidly and the precise value of n is not important. We find that for polymers, $n = 9.8, 9.9$, or 10 gives equally good results within the experimental uncertainty of the data.

TABLE I
Compressibilities of Polystyrene at 155.8°C^a

P , bars	ρ , g/cc	$\beta \times 10^6$, bars ⁻¹	$\rho(\beta^{1/10}) \times 10^1$
1	0.9940	6.91	3.814
200	1.0069	6.07	3.813
400	1.0184	5.41	3.814
600	1.0290	4.89	3.814
800	1.0390	4.46	3.815
1000	1.0479	4.11	3.816

^a Data from Quach and Simha.³

TABLE II
Densities of Polystyrene at 155.8°C^a

<i>P</i> , bars	ρ , g/cc		$(\rho_{\text{exp}} - \rho_{\text{calc}}) \times 10^4$
	Experimental	Calculated	
1	0.9940	0.9941	1
100	1.0005	1.0007	2
200	1.0069	1.0070	1
400	1.0184	1.0186	2
600	1.0290	1.0291	1
800	1.0390	1.0388	2
1000	1.0479	1.0477	2

^a Data from Quach and Simha.³

TABLE III
Experimental and Calculated Densities of Amorphous Polymers at High Pressures

Polymer	<i>T</i> , °C	<i>P</i> , bars	ρ , g/cc		$(\rho_{\text{exp}} - \rho_{\text{calc}}) \times 10^4$	Reference
			Experimental	Calculated		
PS	140.2	100	1.0083	1.0084	1	3
		400	1.0255	1.0255	0	
		800	1.0448	1.0450	2	
PS	173.5	100	0.9919	0.9921	2	3
		400	1.0104	1.0109	5	
		800	1.0318	1.0319	1	
POMS	168.1	100	0.9799	0.9799	0	3
		800	1.0163	1.0165	2	
POMS	179.2	100	0.9744	0.9744	0	3
		800	1.0124	1.0122	2	
POMS	187.6	100	0.9705	0.9704	1	3
		800	1.0096	1.0091	5	
PMMA	139.3	100	1.1447	1.1442	5	4
		400	1.1625	1.1622	3	
		800	1.1823	1.1827	4	
PVC	97	100	1.3633	1.3628	5	4
		800	1.3986	1.3986	0	

Table I shows that for polystyrene, the quantity $\epsilon(\beta^{1/n})$ is independent of pressure, in agreement with Wada's relation. The isothermal compressibilities at high pressures were calculated by fitting the densities to the Tait equation and then differentiating the Tait equation accordingly. Table II compares observed liquid densities at high pressures with those calculated from eq. (3). In both tables, n is taken as 10. Experimental data are from Quach and Simha.³ Table III shows a few results for poly(orthomethylstyrene),³ PMMA, and PVC.⁴

In all cases, agreement between calculated and observed results is good. The deviations are always less than, or equal to the estimated experimental error. It appears, therefore, that eq. (3) provides a useful method for estimating densities of amorphous polymers at high pressure from volumetric data at low pressure up to 1000 bars.

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