A Generalized Equation of State for Polymers

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Synopsis

A simple, generalized equation of state has been developed that describes the pressure–volume–temperature behavior of both addition and condensation polymers. Use of the equation requires only that the polymer's glass temperature and density at 25°C. and one atmosphere be known. The equation applies to both amorphous and crystalline polymers for pressures up to 10,000 atm. It also appears to hold for copolymers. Polymer glass temperatures can also be estimated with the equation.

The pressure–volume–temperature behavior of polymers is a subject of considerable importance to polymer engineers and scientists. Equally important is the need for an equation of state which will suitably describe this behavior. Such an equation should meet several standards. First of all, it must be applicable over wide ranges of temperature and pressure. Next, it should be as general as possible. In addition it should be simple and easily used. Finally, it should be able to predict the behavior of polymers for which no data are available.

Several polymer equations of state exist. Unfortunately, these fail to meet one or more of the above standards.

The oldest of these equations was that developed by Spencer and Gilmore.[1] This equation was a form of the van der Waals equation containing three constants. It had to be fitted to the pressure–volume–temperature data for each individual polymer. This meant that different constants were obtained for each polymer. The equation then was not general and furthermore it could not be used to predict the behavior of polymers for which data were not available. The same deficiencies applied to a virial type of equation developed by Weir.[2,3]

More recently two investigators, Flory[4] and Di Benedetto,[4] have attempted to use quantum mechanics to describe the pressure–volume–temperature behavior of polymers. Flory developed an equation which he applied to long chain hydrocarbons (with repeating units up to 40). His equation was never applied to polymers. Furthermore, he indicated that the equation did not too satisfactorily describe the hydrocarbon behavior over wide temperature and pressure ranges.

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Di Benedetto's equation was a complex form based on cell theory that was derived specifically for amorphous polymers. Some data were needed before some of the parameters could be determined for a given polymer. There also was some question as to the equation's applicability at high pressures.

The present work was undertaken to develop a generalized equation of state that met all of the criteria set earlier since these were not met by the existing equations.

It was decided to try first to use the very successful approach for gases and liquids based on the theory of corresponding states. This approach involves the use of a compressibility factor, Z, as

$$Pv = ZRT \tag{1}$$

The Z is then correlated with the reduced temperature (temperature divided by substance's critical temperature) and reduced pressure (pressure divided by substance's critical pressure).

Taking this approach we first wrote

$$PV = \gamma R'T \tag{2}$$

Next, we calculated γ values from equilibrium pressure–volume–temperature for various polymers. These materials ranged from amorphous to highly crystalline polymers. A summary of the data used is given in Table I. The γ data were then correlated. A reduced temperature was

TABLE I
Characteristics of Selected Polymers

Polymer	PVT data pressure range, atm.	PVT data temperature range, °C.	PVT data references
Polytetrafluoro- ethylene	1.0 to 10,000	10 to 80	3
Poly(methyl methacrylate)	1.0 to 2,000	−60 to 150	6
Polypropylene	1.0 to 600	23 to 250	7
Poly(vinylidene fluoride)	1.0 to 10,000	20 to 70	3
Poly(vinyl fluoride)	1.0 to 10,000	20 to 80	3
Poly(vinyl chloride)	1.0 to 2,000	−60 to 100	6,8
Poly(vinyl alcohol)	1.0 to 10,000	20 to 80	3
Polystyrene	1.0 to 2,000	20 to 248.9	6
Polymonochloro- trifluoro- ethylene	1.0 to 10,000	20 to 80	3
Low density polyethylene	1.0 to 10,000	0 to 186	3,6,9

derived by dividing the temperature by the polymer's glass temperature (both temperatures were in absolute units). No reduced pressure was used since there was no characteristic pressure for a polymer corresponding to a substance's critical pressure. The result of the correlation was a family of curves at any given pressure. This is illustrated in Figure 1. The discontinuities for polyethylene and polypropylene are due to transitions into the melt region. Similar families of curves were obtained at higher pressures.
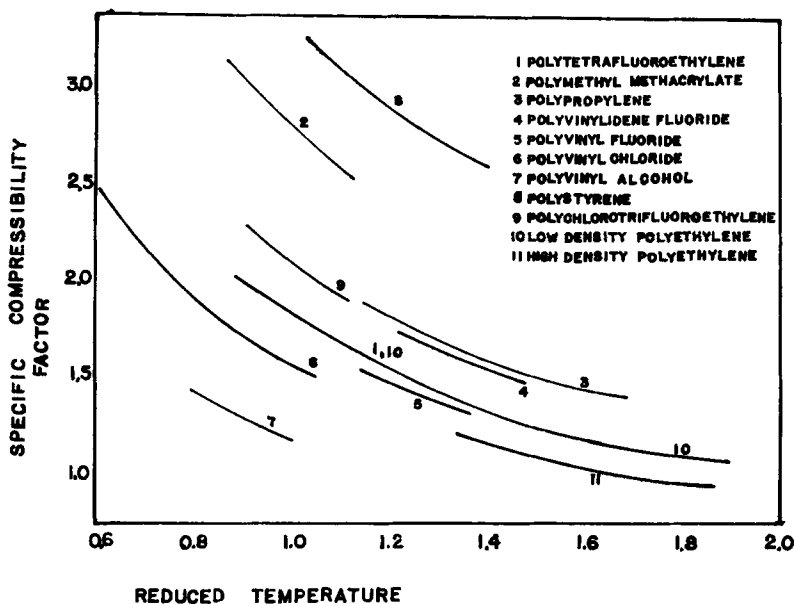

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Ftg. 1. Specific polymer compressibility factors vs. reduced temperature at 1.0 atm.: (1) polytetrafluoroethylene; (2) poly(methyl methacrylate); (3) polypropylene; (4) poly(vinylidene fluoride); (5) poly(vinyl fluoride); (6) poly(vinyl chloride); (7) poly-(vinyl alcohol); (8) polystyrene; (9) polychlorotrifluoroethylene; (10) low density polyethylene; (11) high density polyethylene; (——) base curve.

The behavior in Figure 1 indicated that it might be possible, at a given pressure, to correlate all of the data on a single base or master curve. The resultant master curve is shown in Figure 2. This now meant that the original equation was now

$$PV = \alpha\gamma'R'T \tag{3}$$

where

$$\alpha = \gamma/\gamma' \tag{4}$$

The next step was to determine whether α could be correlated with simple structural features of the polymers used in the correlation.
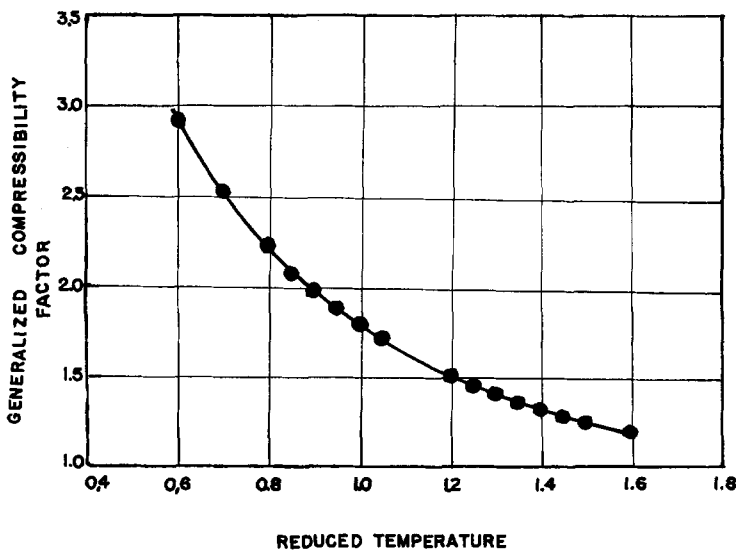
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Fig. 2. Generalized polymer compressibility chart for 1.0 atm.

It was, indeed, found that α would correlate in this manner (Figure 2). The result for the 1-atm. data was

$$\alpha = (0.9178/\rho_0)^{0.9421}(M/28)(204/T_g) \tag{5}$$

In eq. (5) ρ_0 represents the density of a given polymer at 25°C. and 1 atm., M the mer weight or interaction unit, and T_g the glass temperature. The numbers 0.9178, 28, and 204 represent, respectively, the values of ρ_0, M, and T_g for low density polyethylene which was used for the base polymer.

Equation (5) meant that the pressure–volume–temperature behavior for all the polymers used in the correlation could be described in a generalized manner at least at a constant pressure.

The next step was to generalize the relationship even further so as to include the effect of pressure. It was finally found that the form

$$V = [(0.01205)/(\rho_0)^{0.9421}](P)^{n-1}(T/T_g)^{m+1}R \tag{6}$$

would successfully describe the pressure–volume–temperature behavior for the polymers of Table I in a generalized manner. The n and m of eq. (6) are functions of pressure (see Figs. 3 and 4). It was now possible by using eq. (6), Figures 3 and 4 together with a polymer's ρ_0 and T_g to calculate that polymer's pressure–volume–temperature behavior.

The generalized equation was first tested by calculating the pressure–volume–temperature for all of the polymers of Table I and then comparing these data to all experimental values; the average per cent deviation for all of these data was 2.2%. Individual average deviations for the correlation polymers were: polypropylene (1.51%), poly(vinyl fluoride) (0.35%),

polytetrafluoroethylene (4.76%), poly(vinyl alcohol) (2.49%) polystyrene (2.46%), low density polyethylene (0.90%), poly(methyl methacrylate) (4.60%), poly(vinylidene fluoride) (2.40%), polymonochlorotrifluoro-ethylene (2.66%), and poly(vinyl chloride) (0.49%).

The equation of state was tested further by comparing calculated and experimental data for two polymers not used in the correlation–high density polyethylene[6,10] and polyisobutylene.[11] The average deviations were 1.31% and 2.08%, respectively. It is important to note again that the
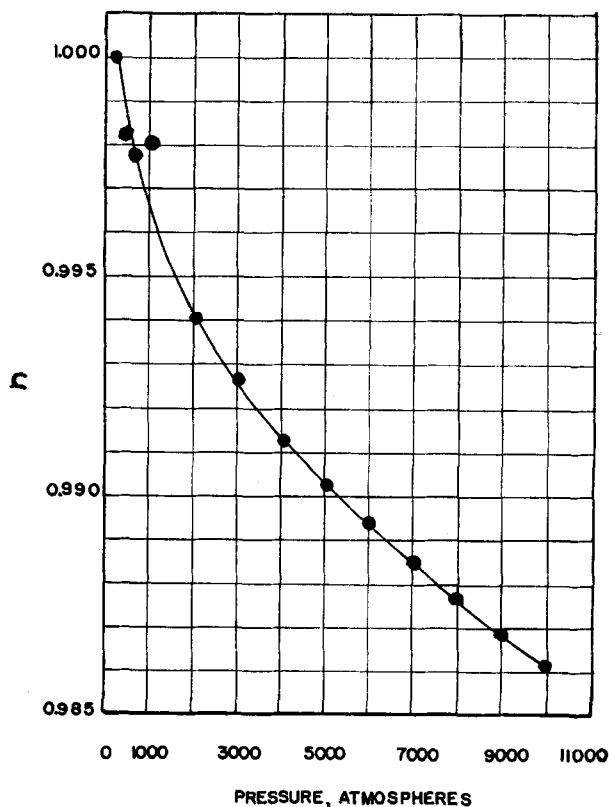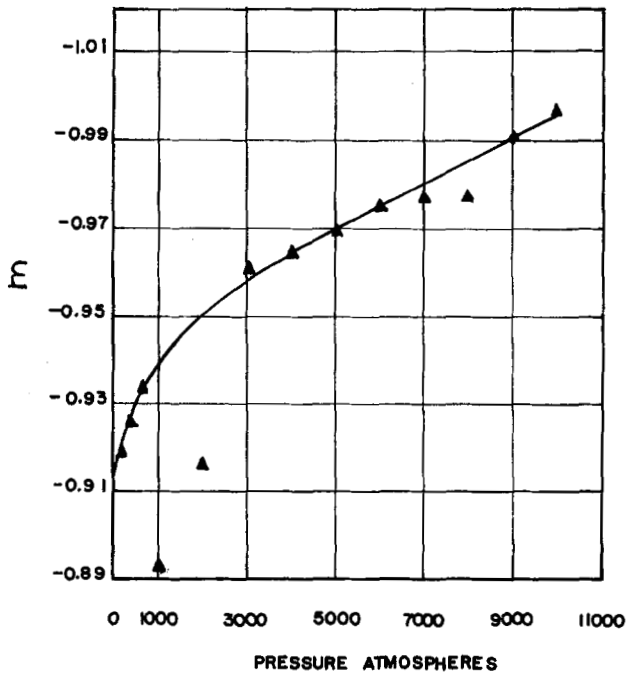

Fig. 3. The parameter n vs. pressure.

only information needed to calculate these data was the T_g's and ρ_0's for the two polymers.

A similar check was also made for a condensation polymer, 6-10 nylon,[12] since all of the polymers used in the correlation as well as high density polyethylene and polyisobutylene were of the addition type. An average deviation of 1.33% was obtained for the calculated nylon 6-10 pressure-volume–temperature data. A check was also made for an ethylene-tetrafluoroethylene copolymer.[3] The average deviation in this case was 1.3%.

Fig. 4. The parameter m vs. pressure.

The equation of the present work was then compared to the more complex equation of Di Benedetto.[5] Results are shown in Table II. As can be seen the generalized equation gives results as good or better than the Di Benedetto equation at low pressure. In addition at high pressures the equation of the present work is much better.

Summarizing the preceding, we can say that a simple generalized equation of state for both addition and condensation polymers has been developed. Application of this equation requires only that the glass temperature and one density (at 25°C. and 1 atm. pressure) be known. The

TABLE II
Comparison of Di Benedetto Equation
to Proposed State Equation

		Pressure, atm.			
		Di Benedetto equation		Proposed state equation	
Polymer	Temperature, °K.	1.0	1000	1.0	1000
Polystyrene	293	1.539	1.935	2.670	1.838
	393	2.762	5.576	3.160	1.843
Poly(vinyl chloride)	293	1.282	2.933	0.752	0.569
	393	2.950	1.690	1.272	0.183

equation holds for both amorphous and crystalline polymers and also appears to hold for copolymers. The equation can be applied for pressures up to 10,000 atm.

Another possible use of the equation is for estimating glass temperatures of polymers. This can be done if one additional density value is known at some condition other than that for ρ_0.

Notation

M = interaction unit or mer weight
P = pressure, atm.
R = gas constant, atm.-c.c./°K. g.-moles
R' = R/M, modified gas constant, atm.-c.c./°K.-g.
T = temperature, °K.
v = volume, c.c./mole
V = volume, c.c./g.
Z = compressibility factor
α = γ/γ'
ρ_0 = density at 25°C. and 1 atm.
γ = specific compressibility factor
γ' = generalized compressibility factor

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Résumé

Une équation simple d'état généralisée a été développée en vue de décrire le comportement pression–volume–température de polymères d'addition et de condensation. L'utilisation de l'équation requiert uniquement que la température de transition vitreuse du polymère et sa densité à 25°C et une atmosphère soient connues. L'équation s'applique aussi bien à des polymères amorphes que cristallins, à des pressions allant jusque 1000 atm. Il apparaît également que cette équation est valable pour les copolymères. Les températures vitreuses des polymères peuvent également être estimées avec cette équation.

Zusammenfassung

Eine einfache, verallgemeinerte Zustandsgleichung zur Beschreibung des Druck–Volum–Temperaturverhaltens von Additions- und Kondensationspolymeren wurde

aufgestellt. Zur Anwendung der Gleichung ist nur die Kenntnis der Glastemperatur des Polymeren und seiner Dichte bei 25°C und einer Atmosphäre erforderlich. Die Gleichung gilt für amorphe und kristalline Polymere bei Drucken bis zu 10.000 atm. Sie scheint auch auf Copolymere anwendbar zu sein. Schliesslich ist die Gleichung auch zur Bestimmung der Glastemperatur von Polymeren geeignet.