

An Equation of State for Molten Polymers

KRISHNA RAO* and RICHARD G. GRISKEY,† *Newark College of Engineering, Newark, New Jersey 07102*

Synopsis

A simple, generalized equation of state has been developed for molten polymers. The equation yielded calculated pressure-volume-temperature data that deviated by 1% or less from experimentally determined data. The use of the equation requires only that the polymer's glass temperature and density at 25°C and 1 atm be known. Polymer glass temperatures can also be estimated with the equation.

Physical property data are a major and important requirement for progress in polymer engineering and science. One particularly critical need is to correctly delineate the pressure-volume-temperature behavior of both solid and molten polymers. A knowledge of this behavior gives the basic information needed not only to treat fundamentally polymer processing, but also to develop a clearer understanding of the polymers themselves. The best method of elucidating pressure-volume-temperature data is by experimental measurement. Unfortunately, however, the magnitude of such an endeavor for the vast array of existing polymers eliminates experimental data as a way of satisfying the need. An alternate method would be the development of a generalized equation of state that would allow the polymer scientist or engineer to compute pressure-volume-temperature data. The present work deals with such an equation for molten polymers.

Any suitable equation of state should meet certain criteria. In the case of polymers these are:

1. The equation must be applicable over wide ranges of temperature and pressure.
2. If possible, the equation should be generalized. In other words, the equation should apply to a large number of different polymers rather than one particular polymer such as polyethylene.
3. The equation should be simple and easily used. Complex forms requiring excessive mathematical manipulation should be avoided.
4. The equation should be such that it can be used to predict the behavior of polymers for which no pressure-volume-temperature data are available. Ideally, we should be able to calculate pressure-volume-

* Present Address: Givaudan Corporation, Nutley, New Jersey 07014.

† Present Address: College of Engineering and Applied Science, University of Wisconsin-Milwaukee, Milwaukee, Wisconsin 53201.

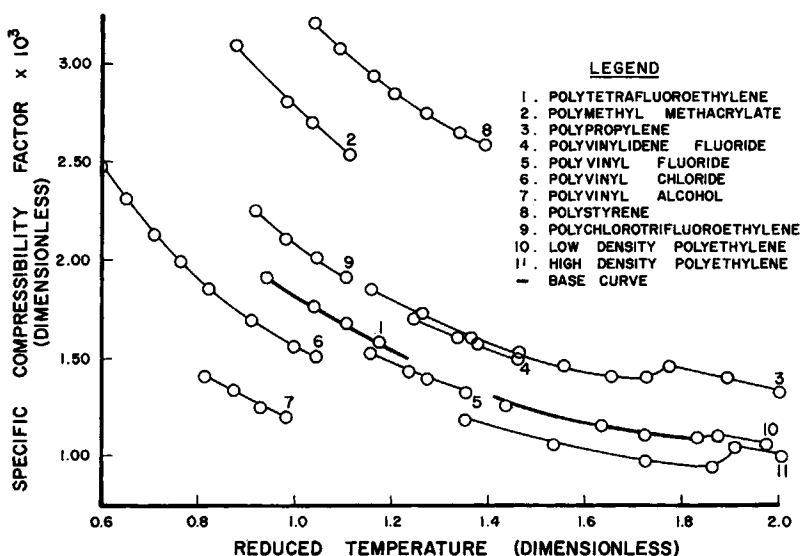


Fig. 1. Polymer compressibility factors vs. reduced temperature (T/T_g).

temperature data for a polymer where only easily measured physical properties are known (such as glass temperature at atmospheric pressure, melting temperature at atmospheric pressure, or density at room temperature and atmospheric pressure).

A number of equations of state¹⁻¹⁵ have been developed for polymers. These are summarized in Table I with respect to the criteria discussed above, the basis of the given equation and applicability.

The majority of polymer equations of state have been applied mainly for solid polymers. The exceptions were the work of Smith,¹¹ McGowan,^{12,13} Simha,¹⁴ and Kamal.¹⁵ None of these equations for the molten polymers, however, met all of the criteria. In fact, the only equation for either solid or molten polymers that did meet the criteria was that of Whitaker and Griskey.¹⁰

On this basis, it was felt that the original Whitaker-Griskey equation if modified could provide an equation of state for molten polymers that would satisfy all of the criteria of Table I.

At this point it is worthwhile to review the development of the Whitaker-Griskey equation of state. To begin with, the equation was based on the theory of corresponding states. More specifically, the concept of a compressibility factor,

$$\gamma = \frac{PV}{RT} \quad (1)$$

was introduced. It was then found that plots of γ versus a reduced temperature (temperature divided by the polymer's glass temperature) yielded a set of matching curves. An example is shown in Figure 1, where data for a variety of polymers at 1 atm pressure are plotted.

TABLE I
Comparison of Polymer Equations of State

Equation	Basis of equation	General?	Simple, easy to use?	Reference	Applicable at high pressure	Applicable at high temperature	Requires experimental pressure-volume-temperature data
Flory	quantum mechanics	no	no	1	no	?	yes
DiBenedetto	quantum mechanics	no	no	2	no	yes	yes
Spencer-Gilmore	modified Van der Waal's equation	no	yes	3	yes	yes	yes
Tait	semiempirical	no	yes	4, 5	yes	yes	yes
Murnaghan	semiempirical	no	yes	6	yes	yes	yes
Birch	semiempirical	no	yes	7	yes	yes	yes
Weir	virial equation of state	no	yes	8, 9	yes	?	yes
Whitaker-Griskey	corresponding state theory	yes	yes	10	yes	yes	no
Smith	Hirai-Eyring equation	no	yes	11	yes	yes	yes
McGowan	semiempirical	no	yes	12, 13	yes	yes	yes
Simha	quantum mechanics	no	no	14	?	?	yes
Kamal	virial equation of state	no	yes	15	yes	yes	yes

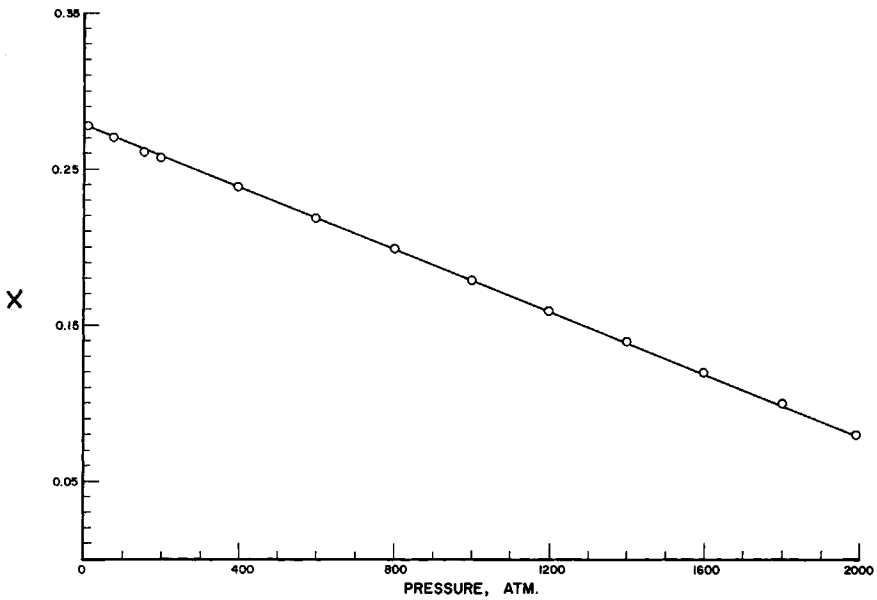
Fig. 2. Parameter x vs. pressure.

TABLE II
High-Density Polyethylene

Temp., °C	Specific volume experimental	Specific volume calculated	Per cent error
$P = 1$ atm			
140.	1.2720	1.2715	0.038
150.	1.2800	1.2802	0.018
161.	1.2890	1.2893	0.022
172.	1.2990	1.2982	0.063
182.	1.3060	1.3060	0.003
203.	1.3220	1.3229	0.067
$P = 200$ atm			
140.	1.2490	1.2572	0.658
150.	1.2560	1.2652	0.734
161.	1.2640	1.2735	0.754
172.	1.2730	1.2817	0.683
182.	1.2790	1.2889	0.774
203.	1.2910	1.3043	1.033
$P = 400$ atm			
150.	1.2370	1.2508	1.117
161.	1.2430	1.2584	1.239
172.	1.2520	1.2658	1.106
182.	1.2570	1.2724	1.226
203.	1.2670	1.2865	1.537

(continued)

TABLE II (continued)

Temp., °C	Specific volume experimental	Specific volume calculated	Per cent error
<i>P</i> = 600 atm			
161.	1.2270	1.2437	1.357
172.	1.2340	1.2504	1.329
182.	1.2390	1.2563	1.400
203.	1.2470	1.2691	1.769
<i>P</i> = 800 atm			
161.	1.2130	1.2292	1.336
172.	1.2190	1.2353	1.334
182.	1.2230	1.2406	1.439
203.	1.2310	1.2520	1.707
<i>P</i> = 1000 atm			
161.	1.1930	1.2150	1.845
172.	1.2060	1.2204	1.194
182.	1.2090	1.2251	1.335
203.	1.2160	1.2353	1.586
<i>P</i> = 1200 atm			
172.	1.1940	1.2058	0.987
182.	1.1970	1.2100	1.082
203.	1.2030	1.2189	1.318
<i>P</i> = 1400 atm			
172.	1.1830	1.1914	0.711
182.	1.1860	1.1950	0.760
203.	1.1920	1.2027	0.898
<i>P</i> = 1600 atm			
182.	1.1760	1.1803	0.366
203.	1.1810	1.1868	0.492
<i>P</i> = 1800 atm			
182.	1.1660	1.1658	0.015
203.	1.1710	1.1712	0.015
<i>P</i> = 2000 atm			
182.	1.1580	1.1516	0.556
203.	1.1620	1.1558	0.534

The behavior of Figure 1 led to the concept of a generalized relationship for the pressure-volume-temperature relationship for polymers. The ultimate equation attained in this manner was

$$V = [(0.01205)/(\rho_0)^{0.9421}](p)^{n-1} \left(\frac{T}{T_g}\right)^{m+1} R. \quad (2)$$

Pressure-volume-temperature data computed from the equation deviated on the average by only about 2% from experimental data for the polymers of Figure 1. In addition, it was found that the equation applied

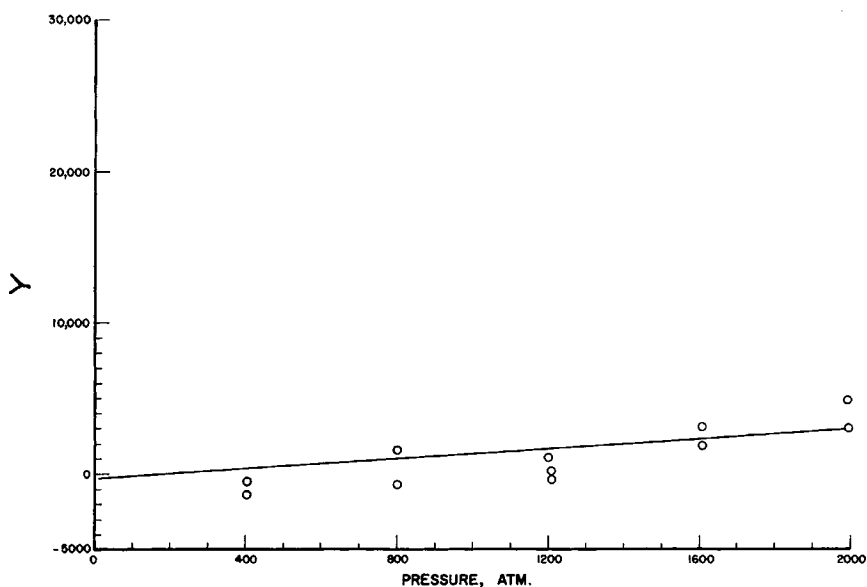
Fig. 3. Parameter y vs. pressure.

TABLE III
Low-Density Polyethylene

Temp., °C	Specific volume experimental	Specific volume calculated	Per cent error
$P = 1 \text{ atm}$			
121.	1.2560	1.2548	0.095
130.	1.2630	1.2629	0.012
141.	1.2710	1.2722	0.091
151.	1.2800	1.2809	0.067
175.	1.3010	1.3006	0.031
$P = 200 \text{ atm}$			
121.	1.2370	1.2405	0.279
130.	1.2430	1.2478	0.390
141.	1.2490	1.2564	0.591
151.	1.2570	1.2644	0.586
175.	1.2760	1.2825	0.506
$P = 400 \text{ atm}$			
121.	1.2150	1.2267	0.962
130.	1.2250	1.2334	0.689
141.	1.2310	1.2412	0.831
151.	1.2380	1.2485	0.849
175.	1.2540	1.2650	0.876
$P = 600 \text{ atm}$			
130.	1.2110	1.2194	0.693
141.	1.2150	1.2264	0.942
151.	1.2210	1.2330	0.986
175.	1.2360	1.2480	0.968

(continued)

TABLE III (continued)

Temp., °C	Specific volume experimental	Specific volume calculated	Per cent error
<i>P</i> = 800 atm			
130.	1.1910	1.2056	1.229
141.	1.2020	1.2120	0.830
151.	1.2070	1.2179	0.903
175.	1.2210	1.2313	0.842
<i>P</i> = 1000 atm			
130.	1.1850	1.1921	0.601
141.	1.1890	1.9978	0.737
151.	1.1960	1.2030	0.587
175.	1.2090	1.2149	0.490
<i>P</i> = 1200 atm			
141.	1.1750	1.1838	0.747
151.	1.1840	1.1884	0.372
175.	1.1970	1.1988	0.154
<i>P</i> = 1400 atm			
151.	1.1740	1.1740	0.002
175.	1.1860	1.1830	0.249
<i>P</i> = 1600 atm			
151.	1.1640	1.1599	0.355
175.	1.1770	1.1675	0.807
<i>P</i> = 1800 atm			
151.	1.1550	1.1459	0.786
175.	1.1670	1.1522	1.268
<i>P</i> = 2000 atm			
151.	1.1460	1.1322	1.205
175.	1.1580	1.1372	1.800

equally well to such polymers as polyisobutylene, an ethylene-propylene copolymer, and nylon 66 that were not included in the generalized equation development.

The only area where the equation did not fit was for molten region data. It should be noted that this was true only for polymers with definite melting regions such as polypropylene and polyethylene. Those polymers that had no definite melting region such as polystyrene presented no problem. The reason for the failure of the Griskey-Whitaker equation as given above to fit the molten region can be seen by considering Figure 1. Note that there is a discontinuity for all the polymers with melting regions (curves 3, 10, and 11). In addition, the molten region is effectively displaced from the portion of the curve representing the solid polymers.

The development of the modification of the Whitaker-Griskey equation was undertaken in the same manner as in the original case except that only molten polymer data were used. The polymers included were low-density polyethylene^{17,18} high-density polyethylene,^{17,19} polypropylene,²⁰ nylon 6-10,²¹ and an ethylene-propylene copolymer.²²

TABLE IV
 Isotactic Polypropylene

Temp., °C	Specific volume experimental	Specific volume calculated	Per cent error
<i>P</i> = 1 atm			
180.	1.3250	1.3259	0.065
200.	1.3380	1.3420	0.298
210.	1.3500	1.3499	0.009
250.	1.3850	1.3803	0.341
<i>P</i> = 100 atm			
180.	1.3120	1.3192	0.552
200.	1.3260	1.3347	0.658
210.	1.3380	1.3423	0.320
250.	1.3670	1.3714	0.324
<i>P</i> = 200 atm			
180.	1.2980	1.3129	1.145
200.	1.3140	1.3277	1.042
210.	1.3240	1.3349	0.826
250.	1.3480	1.3628	1.101
<i>P</i> = 300 atm			
180.	1.2840	1.3066	1.761
200.	1.3020	1.3208	1.444
210.	1.3110	1.3277	1.276
250.	1.3310	1.3544	1.758
<i>P</i> = 400 atm			
200.	1.2940	1.3140	1.546
210.	1.3020	1.3206	1.431
250.	1.3170	1.3461	2.209
<i>P</i> = 500 atm			
200.	1.2840	1.3073	1.815
210.	1.2940	1.3136	1.516
250.	1.3060	1.3379	2.441
<i>P</i> = 600 atm			
200.	1.2760	1.3007	1.934
210.	1.2820	1.3067	1.925
250.	1.3010	1.3298	2.210

The final form of the derived equation was

$$V = K \left(\frac{T}{T_0} \right)^x P^y. \quad (3)$$

Note that this equation, while similar to eq. (2), has different constants and exponents. The exponents x and y were solely functions of pressure. Their correlation is shown in Figures 2 and 3. Note that the apparent scatter of Figure 3 is not serious since the ordinate actually ranges from 0 to 0.03.

TABLE V
Ethylene-Propylene Copolymer

Temp., °C	Specific volume experimental	Specific volume calculated	Per cent error
<i>P</i> = 1 atm			
140.	1.2758	1.2739	0.148
175.	1.2992	1.3033	0.312
210.	1.3281	1.3310	0.217
250.	1.3663	1.3610	0.391
<i>P</i> = 79 atm			
140.	1.2722	1.2682	0.315
175.	1.2936	1.2966	0.230
210.	1.3197	1.3234	0.279
250.	1.3512	1.3523	0.085
<i>P</i> = 159 atm			
140.	1.2655	1.2626	0.226
175.	1.2855	1.2901	0.355
210.	1.3099	1.3160	0.463
250.	1.3389	1.3439	0.374
<i>P</i> = 232 atm			
140.	1.2594	1.2576	0.144
175.	1.2775	1.2841	0.519
210.	1.3008	1.3092	0.645
250.	1.3279	1.3362	0.626
<i>P</i> = 316 atm			
140.	1.2506	1.2519	0.102
175.	1.2677	1.2774	0.768
210.	1.2902	1.3015	0.878
250.	1.3153	1.3275	0.928
<i>P</i> = 474 atm			
140.	1.2353	1.2413	0.487
175.	1.2531	1.2650	0.952
210.	1.2737	1.2874	1.072
250.	1.2953	1.3114	1.243
<i>P</i> = 618 atm			
140.	1.2258	1.2319	0.494
175.	1.2433	1.2539	0.854
210.	1.2632	1.2747	0.908
250.	1.2847	1.2970	0.957

The *K* in eq. (3) was found to be a function of ρ_0 , the density at 25°C and 1 atm, as shown in Figure 4.

Data computed from eq. (3) are compared to experimental values in Tables II to V. As can be seen, the per cent deviations are generally 1% or less. The average deviations for each polymer are: high-density polyethylene, 0.89%; low-density polyethylene, 0.64%; polypropylene, 1.20%; ethylene-propylene copolymer, 0.79%; and nylon 6-10, 0.71%.

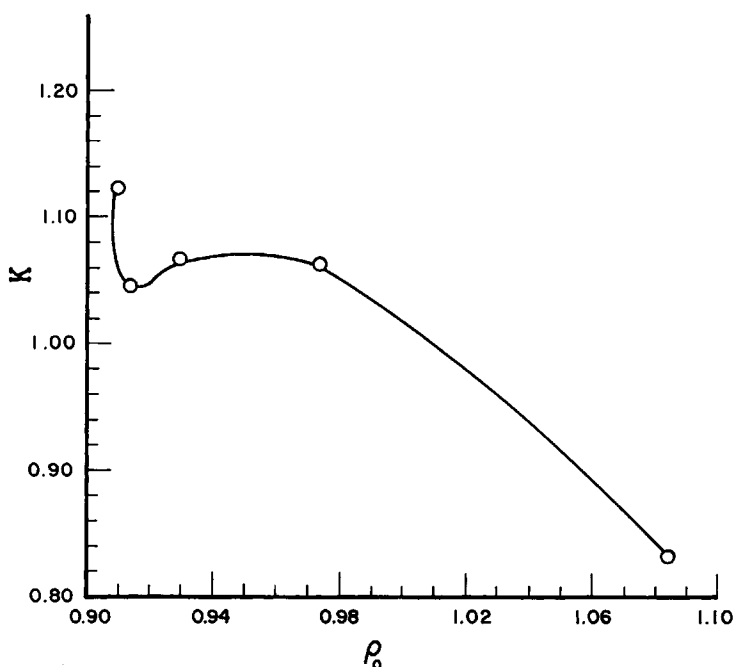


Fig. 4. Parameter K vs. ρ_0 .

On the basis of the deviations between the calculated and experimental values, it can be concluded that the modified Whitaker-Griskey equation represents an effective generalized equation of state for molten polymers. It should be noted that pressure-volume-temperature data can be calculated for a polymer simply by knowing its ρ_0 and T_g . The first item is readily available for most polymers. The second (T_g) also can be found either in the literature or estimated from the melting temperature by using Beaman's rule.¹⁶ When ρ_0 and T_g are known, the procedure is then (1) obtain the K value from Figure 4 using ρ_0 ; (2) determine x and y from Figures 2 and 3 (i.e., for the pressure needed); and (3) substitute desired temperature and pressure together with T_g in eq. (3) and calculate V corresponding to the given temperature and pressure.

Equation (3) can also be used to estimate a value for T_g if one piece of data is available, namely, a specific volume at a specific temperature and pressure.

CONCLUSIONS

The conclusions of this work are:

1. A generalized equation of state has been developed for molten polymers.
2. The equation requires only a value of ρ_0 (density at 25°C and 1 atm) and the glass temperature to calculate pressure-volume-temperature data.

3. Calculated values of pressure-volume-temperature data generally deviated by less than 1% from experimental data.

Notation

K	parameter of equation
P	pressure, atm
R	gas constant, atm cc/°K g moles
T	temperature °K
T_g	glass temperature °K
V	volume, cc/gm
m, n	equation parameter
x, y	equation parameter
ρ_0	density, g/cc at 25°C and 1 atm
γ	compressibility factor

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