

# NOTES

## Pressure–Volume–Temperature–Viscosity Relations in Fluorinated Polymers

L. A. UTRACKI

National Research Council Canada, Industrial Materials Institute, 75 de Mortagne, Boucherville, Quebec, Canada, J4B 6Y4

Received 24 April 2001; accepted 8 August 2001

### INTRODUCTION

Recently, Mekhilef<sup>1</sup> published new data on the pressure–volume–temperature (PVT) behavior of fluorinated polymers, polyvinylidene fluoride (PVDF), and copolymers of poly(vinylidene-co-hexafluoropropylene) (PVDF-HFP). The author also reported on the viscoelastic performance of these resins in the solid and molten states.

Since 1969, PVT dependencies have been analyzed by means of the Simha–Somcynsky (S–S) equation of state (EoS). The EoS has the form of coupled equations written in terms of the reduced variables:<sup>2</sup>  $\tilde{P} = P/P^*$ ,  $\tilde{V} = V/V^*$ , and  $\tilde{T} = T/T^*$ . According to Rodgers's evaluation of several EoSs, the S–S EoS has provided the best description of the PVT behavior in the whole range of independent variables.<sup>3</sup>

From the fundamental point of view, the S–S EoS has a significant advantage over other EoS relations; simultaneously with  $V = V(T, P)$ , it provides the hole fraction ( $h$ ) as a function of  $P$  and  $T$ :  $h = h(T, P)$ . The latter function has been shown<sup>4</sup> to be directly related to the free volume fraction ( $f$ ), for example, as determined by positron annihilation lifetime spectroscopy.<sup>5</sup> The knowledge of  $h$  has been found useful in many applications, namely, the correlation of surface tension with bulk properties.<sup>6</sup> Furthermore, it relates the equilibrium with transport properties, for example, the constant stress viscosity of melts and their mixtures<sup>7–9</sup> and other viscoelastic functions.<sup>10</sup>

Analysis of the new PVT data for fluoropolymers is of interest for several reasons. Because the tested samples were well characterized,<sup>1</sup> it would be interesting to

know how the changes of molecular weight and composition affect the reducing parameters,  $P^*$ ,  $V^*$ , and  $T^*$ . Once these parameters are known, the compressibility, thermal expansion coefficient, and cohesive energy density (or the solubility parameter) can easily be calculated.<sup>4</sup> Furthermore, the interrelation between the melt viscosity and  $h$  should be examined.

### PVT DEPENDENCE

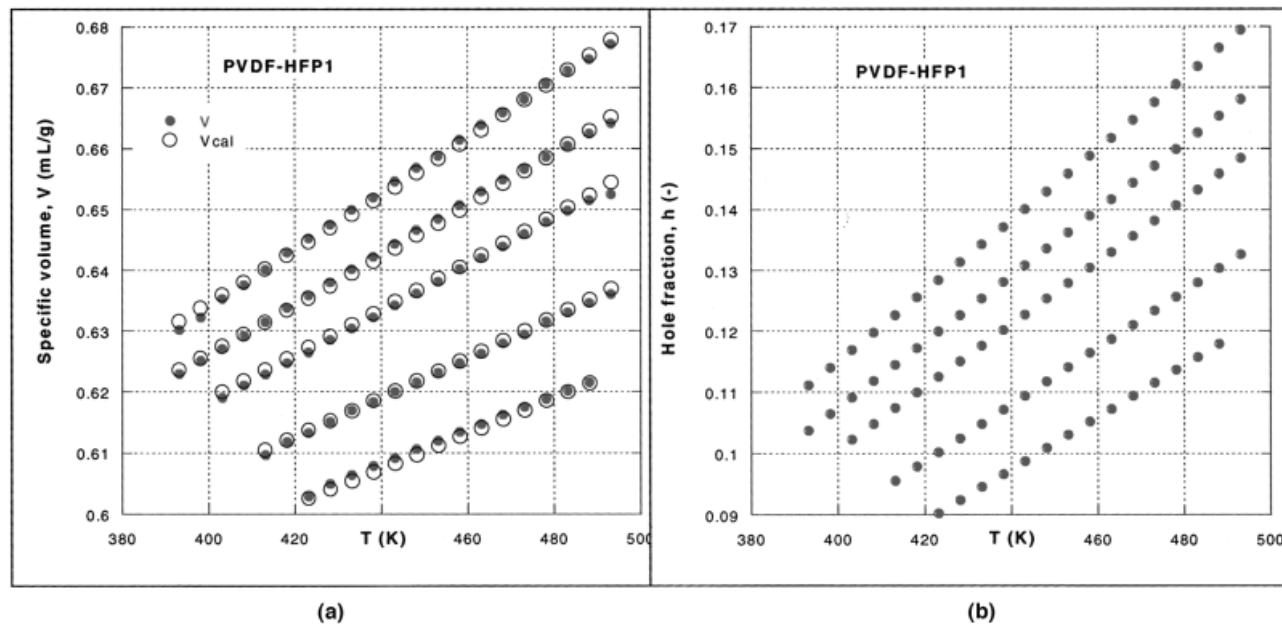
We fitted experimental PVT data in the molten state (kindly provided by Mekhilef) of two PVDF and three PVDF–HFP resins to the S–S EoS following the described procedure.<sup>4</sup> An example of the obtained fits is shown in Figure 1. The computed reducing parameters and the statistical measures of the fit are given in Table I.

Figure 1(a) shows the experimental data as solid points and the values computed from the S–S theory as open circles. Except for a few points at the limiting temperatures, the fit is excellent. This is also evident from the statistical evaluation of fit listed in the last three rows of Table I. The standard deviation of data ( $\sigma = 0.0007–0.0008$ ) the correlation coefficient squared ( $r^2 = 0.999998–0.999999$ ), and the coefficient of determination (CD = 0.997–0.999) are also shown in Table I. In short, the EoS provides precise description for the observed dependencies. Figure 1(b) shows the corresponding dependence for  $h$ ,  $h = h(P, T)$ . Within the range of the explored independent variables,  $h$  changed from about 9 to 17%.

The resin characteristics<sup>1</sup> {weight-average molecular weight [ $M_w$ ] polydispersity factor [ $M_w$ /number-average molecular weight ( $M_n$ )], and percentage of hexafluoropropylene [HFP] are also listed in Table I. The next three rows show values of the three reducing

Correspondence to: L. A. Utracki (leszek.utracki@nrc.ca).

Journal of Applied Polymer Science, Vol. 84, 1101–1105 (2002)  
© 2002 Wiley Periodicals, Inc.  
DOI 10.1002/app.10344



**Figure 1** (a) PVDF-HFP1 at (from top)  $P = 1, 200, 400, 800,$  and  $1200$  bar. The points are experimental; the circles around them were computed from the S-S EoS fit. (b)  $h$  at  $P = 1$ – $1200$  bar versus  $T$ , corresponding to  $V$  versus  $T$  dependence.

parameters:  $P^*$ ,  $V^*$ , and  $T^*$ , each with its own statistical deviation. Next, the molecular weight of the statistical segment ( $M_0 = RT^*/3P^*V^*$ ) is given. The molecular weight of the monomers are vinylidene fluoride (VDF) = 64.04 and HFP = 150.02. Hence, the statistical segment that occupies a single lattice cell corresponds to a single VDF mer.

Rodgers<sup>11</sup> computed for PVDF ( $M_w = 100$ ,  $M_w/M_n = 2.38$  at  $T = 178$ – $248^\circ\text{C}$  and  $P = 0$ – $2000$  bar)  $P^* = 9022$ ,  $V^* = 0.5964$ , and  $T^* = 10,440$ , with the average deviation of data  $\Delta V = 0.00091$ . The new computational procedure<sup>4,8,9</sup> gave similar values:  $P^* = 8946 \pm 169$  bar,  $V^* = 0.5959 \pm 0.0019$  (mL/g), and  $T^* = 10,360 \pm 92$  (K). When these parameters were compared with those listed in Table I, the differ-

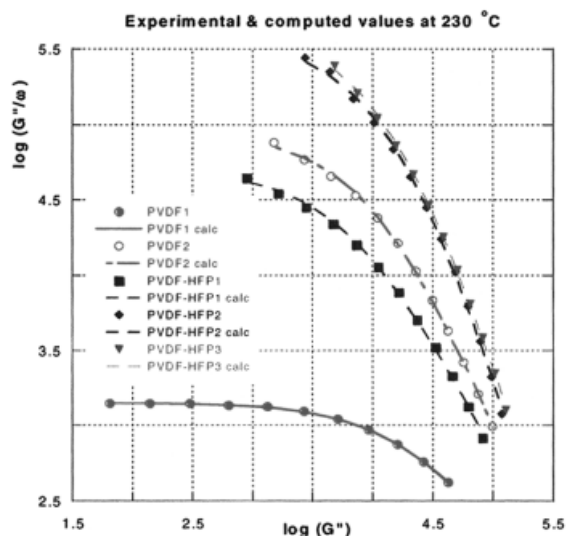
ences extended beyond the statistical error of the measurements. Thus, the PVT behavior, even of supposedly the same PVDF resin, seemed to differ. Evidently, the difference may have originated in the experimental methods and data treatment but also in the resin molecular weight, composition (either by copolymerization or incorporation of additives), and chain configuration.

#### MELT FLOW

The dynamic data for the five resins were measured at  $230^\circ\text{C}$ . In the past,<sup>7</sup> it was shown that zero-shear viscosity ( $\eta_0$ ) or constant-stress viscosity ( $\eta_\sigma$ ) measured at

**Table I** Summary of the PVT Data

Property	PVDF1	PVDF2	PVDF-HFP1	PVDF-HFP2	PVDF-HFP3
$M_w$ (kg/mol)	197	339	321	471	480
$M_w/M_n$	2.0	2.6	2.9	3.3	3.3
HFP (%)	0	0	10.5	11.1	3.1
$P^*$ (bar)	$8,319 \pm 151$	$8,235 \pm 143$	$8,540 \pm 76$	$8,352 \pm 80$	$8,289 \pm 105$
$V^*$ (mL/g)	$0.6072 \pm 0.0018$	$0.6084 \pm 0.0017$	$0.5869 \pm 0.0008$	$0.5884 \pm 0.0008$	$0.5908 \pm 0.0011$
$T^*$ (K)	$10,878 \pm 105$	$10,946 \pm 102$	$10,359 \pm 44$	$10,603 \pm 49$	$10,472 \pm 64$
$M_0$ (g/mol)	59.684	60.550	57.274	59.783	59.259
$\sigma$	0.000859	0.000802	0.000681	0.000719	0.000740
$r^2$	0.999998	0.999999	0.999999	0.999999	0.999999
CD	0.997276	0.997626	0.998617	0.998334	0.998318



**Figure 2** Dynamic viscosity versus loss modulus at  $T = 230^\circ\text{C}$  for the five fluoropolymers. Points are experimental; lines were computed from eq. (2) with the parameters listed in Table II.

different  $T$  and  $P$  could be superposed on a single master curve, plotting

$$\ln \eta_{0,\sigma} = a_0 + a_1 Y_S; \quad Y_S \equiv 1/(a_2 + h) \quad (1)$$

where  $a_i$ 's are the equation parameters that characterize the material. For example, in the case of  $n$ -paraffins,  $a_1 = 0.79 \pm 0.01$  and  $a_2 = 0.07$ .<sup>7</sup> For polymers, a greater variation of values was observed. On many occasions,  $a_2 = 0$  was observed, turning eq. (1) into the well-known Doolittle's dependence, with  $h$  replacing his  $f$  parameter:  $\ln \eta_{0,\sigma} \propto 1/f$ .

To determine  $\eta_{0,\sigma}$ , we fitted the dynamic data to

$$\eta' \equiv G''/\omega = \eta_0/(1 + G''\tau)^m \quad (2)$$

where  $G''$  is loss modulus,  $\omega$  is the frequency,  $\eta'$  is dynamic viscosity, and  $\tau$  and  $m$  are equation constants. The goodness of fit can be judged from the data presented in Figure 2 and the statistical fit parameters listed in Table II.

Equation (2) provides a method for interpolating the experimental values of  $\eta'$  to constant shear stress, expressed as  $G'' = \text{constant}$ . In principle, it also makes it possible to extrapolate the higher stress data to zero-shear,  $\eta_0$ . However, as shown in Figure 2, only PVDF1 measurements provided enough data points to have confidence in the extrapolated value. The experimental range of common values of shear stress for all five resins is  $\log G'' = 3.7\text{--}4.9$ .

Above the entanglement point,  $\eta_0$  usually follows the dependence  $\eta_0 = KM_w^a$  with  $K$  and  $M$  being equation constants. As shown in Figure 3, the plot of  $\log \eta_0$

**Table II** Rheological Data for the Fluoropolymers

Parameter	PVDF1	PVDF2	PVDF-HFP1	PVDF-HFP2	PVDF-HFP3
$\sigma$	0.00278	0.01446	0.02060	0.02725	0.02201
$r^2$	0.999999	0.999992	0.999982	0.999974	0.999983
CD	0.9998	0.9996	0.9991	0.9991	0.9994
$\log \eta_0$	$3.1501 \pm 0.0019$	$4.9561 \pm 0.02321$	$4.7008 \pm 0.0306$	$5.5814 \pm 0.0819$	$5.6627 \pm 0.0769$
$m$	$1.0295 \pm 0.14503$	$2.0498 \pm 0.3259$	$1.6270 \pm 0.3752$	$2.8629 \pm 0.9591$	$2.6784 \pm 0.7300$
$\text{Log } \tau$	$-4.2768 \pm 0.0854$	$-4.0905 \pm 0.0768$	$-3.8737 \pm 0.1065$	$-4.2770 \pm 0.1497$	$-4.2137 \pm 0.1105$
$h$ ( $P = 1, T = 230$ )	0.16120	0.15945	0.17542	0.16856	0.17221

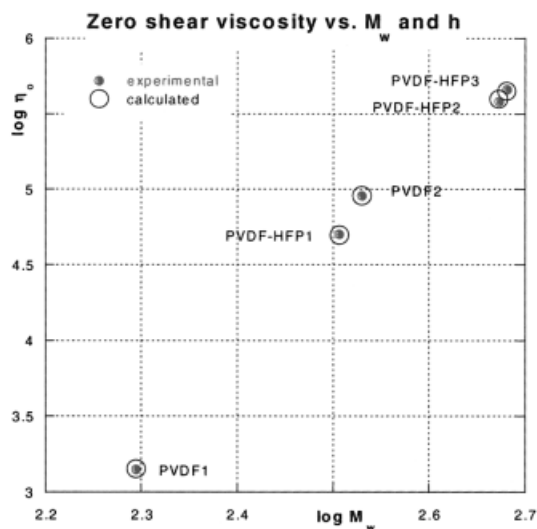
versus  $\log M_w$  followed the line  $\log \eta_0 = -11.39 + 6.3955 \log M_w$ , with large scatter,  $r^2 = 0.983$ . The calculated slope was also higher than what could be expected from a linear polymer (i.e.,  $a = 3.4\text{--}3.5$ ). That the increase was not due to the variation of composition was evident when the two PVDF points were considered, a line connecting them had still a higher slope of  $a = 7.66$ . In short, the viscosity seemed to depend not only on molecular weight.

The last row of Table II lists the  $h$  values computed from the PVT data for  $P = 1$  bar and  $T = 230^\circ\text{C}$ . Evidently, this parameter depended on composition, molecular weight, and possible structural changes introduced during polymerization (the high value of the slope in Figure 3 suggests a long chain branching). Thus, it was tempting to see whether by combining the standard relation between  $\eta_0$  and  $M_w$  with eq. (1) we could obtain a better description of the observed dependence:

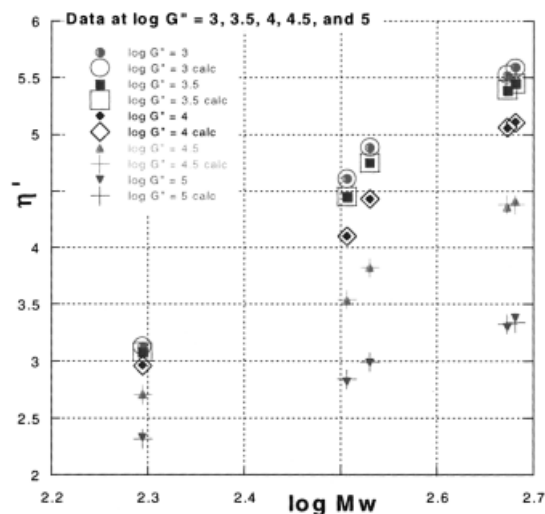
$$\log \eta_0 = b_0 + b_1 \log M_w + b_2 / (b_3 + h) \quad (3)$$

where  $b_i$ 's are equation parameters. The results of this treatment are presented in Figure 3 in the form of large circles centered around the experimental solid points for all resins. The statistics of data fit gave  $\sigma = 0.0213$ ,  $r^2 = 0.999996$ , and  $\text{CD} = 0.99989$ . The values of the four parameters were  $b_0 = -8.938 \pm 0.406$ ,  $b_1 = 5.45 \pm 0.15$ ,  $10^4 b_2 = -1.59 \pm 0.29$ , and  $b_3 = -0.1608 \pm 0.00006$ . Because of uncertainty in the determination of the experimental values of  $\eta_0$  for this application, eq. (3) should be treated as empirical.

Next, eq. (2) was used to obtain constant-stress values of the dynamic viscosity for the five fluoropolymers



**Figure 3**  $\eta_0$  versus molecular weight for the five fluoropolymers. The points represent experimental data extrapolated to zero-shear by means of eq. (2). Large circles were computed from eq. (3).



**Figure 4**  $\eta_\sigma$  versus molecular weight for the five fluoropolymers at  $\log G'' = 3\text{--}5$ . The points represent data interpolated to a constant value of  $G''$  by means of eq. (2). Open symbols and crosses were computed from eq. (3).

in the range of  $\log G'' = 3\text{--}5$ . These values, along with the best fits by eq. (3) are shown in Figure 4. Evidently, the latter equation provided a good description of the observed dependencies. From between the five sets of the constant-stress data, the one for  $G'' = 10^4$  (Pa) was the least affected by the interpolation uncertainties (see Fig. 2). The four parameters of eq. (3) were  $b_0 = -10.199 \pm 0.146$ ,  $b_1 = 5.70 \pm 0.05$ ,  $10^4 b_2 = 2.27 \pm 1.12$ , and  $b_3 = -0.1583 \pm 0.0004$ , with  $\sigma = 0.009$ ,  $r^2 = 0.999999$  and  $\text{CD} = 99997$ .

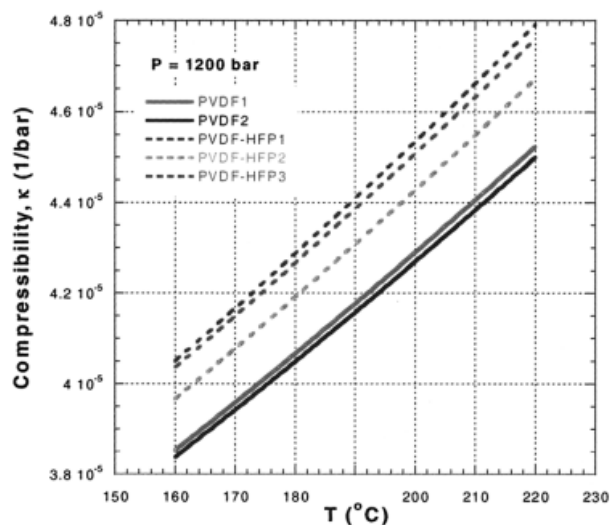
## DISCUSSION AND CONCLUSIONS

The S-S EoS well described the PVT behavior of the five fluoropolymers in the full range of the independent variables:  $P$ ,  $T$ , and composition. As the data in Table I show, incorporation of HFP affected the reducing parameters values:  $P^*$  increased with HFP content, whereas  $V^*$  and  $T^*$  were reduced. The change in  $V^*$  on incorporation of 3.1% HFP was the most dramatic. However, it seemed that in addition to the composition, these parameters were also affected by molecular weight (slightly!) and by some configurational differences.

As published recently,<sup>4</sup> the S-S EoS can be approximated by an analytical expression:

$$\ln \tilde{V} = a_0 + a_1 \tilde{T}^{3/2} + \tilde{P} [a_2 + (a_3 + a_4 \tilde{P} + a_5 \tilde{P}^2) \tilde{T}^2] \quad (4)$$

where  $a_i$ 's are numerical parameters. Their values are listed in the cited publication. Differentiation of eq. (4)



**Figure 5** Compressibility of the five fluoropolymers computed from eq. (4). The reduced parameters from Table I were used.

readily leads to the general expressions for compressibility ( $\alpha$ ) or the thermal expansion coefficient ( $\beta$ ) in reduced variables, respectively:

$$\beta \equiv -\partial \ln V / \partial P|_T = (1/P^*)(-\partial \ln \tilde{V} / \partial \tilde{P})|_{\tilde{T}}$$

$$= (1/P^*)[a_2 + (a_3 + 2a_4\tilde{P} + 3a_5\tilde{P}^2)\tilde{T}^2]$$

$$\alpha \equiv \partial \ln V / \partial T|_P = (1/T^*)(\partial \ln \tilde{V} / \partial \tilde{T})|_{\tilde{P}}$$

$$= (1/T^*)[1.5a_1\tilde{T}^{1/2} + 2\tilde{P}(a_3 + a_4\tilde{P} + a_5\tilde{P}^2)\tilde{T}] \quad (5)$$

Thus, once the reducing parameters of a material are known, the  $\beta$  or  $\alpha$  functions in the liquid state can be calculated for any  $P$  and  $T$ . An example of  $\beta$  versus  $T$  dependence at 1200 bar is presented in Figure 5.

Finally, the scatter in the  $\eta_{0,\sigma}$  versus  $M_w$  dependence vanished once the small differences in  $h$  were taken into account. Because  $h$  was affected by the molecular weight, chain configuration and composition, it seems that these factors modified the thermodynamic and dynamic behavior through the free-volume contribution. In the past, eq. (1) has been used to account for the variation of  $\eta_{0,\sigma}$  with  $P$  and  $T$ . The parameter  $b_3$  was positive, indicating that under stress, the accessible free volume was larger than at the equilibrium thermodynamics. In this analysis,  $b_3$  was small and negative, turning eq. (1) into an expression resembling the Doolittle formula.

## REFERENCES

1. Mekhilef, N. *J Appl Polym Sci* 2001, 80, 230.
2. Simha, R.; Somcynsky, T. *Macromolecules* 1969, 2, 342.
3. Rodgers, P. A. *J Appl Polym Sci* 1993, 48, 1061.
4. Utracki, L. A.; Simha, R. *Macromol Chem Phys Mol Theory Simul* 2001, 10, 17.
5. Schmidt, M. PhD Thesis, Chalmers University of Technology, Göteborg, Sweden, 2000.
6. Jain, R. K.; Simha, R. *J Colloid Surf Sci* 1999, 216, 424.
7. (a) Utracki, L. A. *Polym Eng Sci* 1983, 23, 446; (b) *Polym Eng Sci* 1985, 25, 655; (c) *Can J Chem Eng*, 1983, 61, 753; (d) *J Rheol* 1986, 30, 829.
8. Utracki, L. A.; Simha, R. *J Polym Sci Part B: Polym Phys* 2001, 39, 342.
9. Simha, R.; Utracki, L. A.; Garcia-Rejon, A. *Compos Interfaces* 2001, 8, 345.
10. (a) Curro, J. G.; Lagasse, R. R.; Simha, R. *J Appl Phys* 1981, 52, 5892; (b) *Macromolecules*, 1982, 15, 1621.
11. Rodgers, P. A. *J Appl Polym Sci* 1993, 50, 2075.