# Viscoelastic and Pressure–Volume–Temperature Properties of Poly(vinylidene fluoride) and Poly(vinylidene fluoride)–Hexafluoropropylene Copolymers

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**ABSTRACT:** The relationship between the pressure, volume, and temperature (PVT) of poly(vinylidene fluoride) homopolymers (PVDF) and poly(vinylidene fluoride)–hexafluoropropylene (PVDF–HFP) copolymers was determined in the pressure range of 200–1200 bar and in the temperature range of 40°C–230°C. The specific volume was measured for two homopolymers having a molecular weight ($M_w$) of 160,000–400,000 Da and three copolymers containing between 3 and 11 wt % HFP with a molecular weight range of 320,000–480,000 Da. Differential scanning calorimetry (DSC) was used to simulate the cooling process of the PVT experiments and to determine the crystallization temperature at atmospheric pressure. The obtained results were compared to the transitions observed during the PVT measurements, which were found to be pressure dependent. The results showed that the specific volume of PVDF varies between 0.57 and 0.69 cm$^3$/g at atmospheric pressure, while at high pressure (1200 bar) it varies between 0.55 and 0.64 cm$^3$/g. For the copolymers, the addition of HFP lowered its melting point, while the specific volume did not show a significant change. The TAIT state equation describing the dependence of specific volume on the zero-pressure volume ($V_0,T$), pressure, and temperature has been used to predict the specific volume of PVDF and PVDF–HFP copolymers. The experimental data was fitted with the state equation by varying the parameters in the equation. The use of the universal constant, $C$ (0.0894), and as a variable did not affect the predictions significantly. © 2001 John Wiley & Sons, Inc. J Appl Polym Sci 80: 230–241, 2001

**Key words:** PVDF; PVDF copolymers; PVT; viscoelastic properties; specific volume

## INTRODUCTION

The determination of the specific volume of polymeric materials as a function of pressure and temperature is a major step toward modeling the flow of non-Newtonian fluids in processes such as

extrusion and injection molding.[1,2] The key parameters for predicting such flows are the viscosity–shear rate behavior of the polymer, the variation of the melt density with temperature and pressure, and the thermal properties (heat capacity and thermal conductivity). It is possible to measure accurately the changes in the state of polymers that occur between room temperature and well beyond the melting point at pressures between 20 and 2000 bar, which are temperatures and pressures typically encountered in processes such as injection molding. Instruments for accom-

plishing this type of work could be either a high-pressure capillary rheometer using a plug die or a true PVT instrument based on the confined liquid (usually Mercury) principle.[3,4] The PVT instrument has some advantages compared to a capillary rheometer that makes it the instrument of choice if accurate numbers are desired (0.0001 cm[3]/g).[5] From a theoretical standpoint, several approaches are used to predict the specific volume as a function of temperature and pressure. The ability to perform such a task allows a more accurate and realistic flow simulation of non-Newtonian liquids.

### Theoretical Background

Among the models used to describe the specific volume of polymers in the literature, the TAIT equation is the most convenient and the most widely used for polymers in the molten state, although it has only been used to describe the PVT behavior at temperatures above the melting point for semicrystalline polymers. The TAIT equation is expressed as

$$\frac{V(0,\ T) - V(P,\ T)}{V(0,\ T)} = C\ \ln\left[1 + \frac{P}{B(T)}\right] \quad (1)$$

The TAIT equation only describes the specific volume of a polymer along an isotherm. This is not sufficient to fully describe the PVT diagram of a polymer. It is also necessary to estimate the zero-pressure specific volume that can be expressed as a polynomial or an exponential function of temperature in the form

$$V(0,\ T) = A_0 + A_1 T + A_2 T^2 + \ldots + A_n T^n \quad (2)$$

The zero-pressure specific volume is often well described with a third-order polynomial. It can also be expressed in an exponential form, although not commonly used:

$$V(0,\ T) = A_0 \exp(A_1 T) \quad (3)$$

The TAIT parameter $B(T)$ has also an exponential form:

$$B(T) = B_0 \exp(B_1(T) \quad (4)$$

The TAIT equation also uses a universal constant, $C$, in eq. (1), which has a typical value of 0.0894 for several polymers. However, a non-standard value could be used, as is the case for several other polymers.[2]

Determining the PVT relationships of glassy polymers such as polystyrene[6] and poly(dimethylsiloxane)[7] provides better data and better assessment of the theoretical approaches because the only transition that occurs within a reasonable temperature range (usually between room temperature and well beyond the softening point) is the glass transition, while for crystalline polymers, the crystallization effect, which is dependent on both pressure and the thermal history of the material tested, must be confronted. The complexity of the crystallization and its interpretation at high pressures make this region preferably to be avoided when doing PVT studies. In addition, determination of the crystallization temperature at high pressure is limited to 1000 psi only, with the current thermal-analysis techniques (high-pressure DSC). Therefore, interpretation becomes even more complicated and often speculative.[5,7]

Poly(vinylidene fluoride) (PVDF) is an engineering resin made by the addition of 1,1-difluoroethylene ($CH_2 = CF_2$) in emulsion or suspension polymerization to produce a semicrystalline polymer that contains 59.4 wt % fluorine, 3 wt % hydrogen, and 37.6 wt % carbon. This polymer is primarily used in architectural coatings and the chemical process industry (CPI) for the manufacture of high-purity pipes, injection-molded fittings, electrical and electronic devices, and weather-resistant binders for exterior applications.[8] The crystallinity of PVDF may vary between 35% and 70% depending on the thermomechanical history and exhibits both lamellar and spherulitic structures. Like other crystalline polymers, PVDF exhibits four main transitions observable in a typical DMA curve depending on the treatment of the sample. The $\gamma$-relaxation is attributed to chain rotation in the amorphous phase and is typically seen around −80°C. The $\beta$-relaxation is taken as the glass-transition temperature usually observed at −40°C. The $\beta'$-relaxation occurs in the amorphous phase of PVDF and is attributed to fold motion and usually observed around 40°C. The last transition is defined as the $\alpha$-relaxation and is believed to occur in the crystalline region. These crystalline forms have different densities, ranging from 1.97 g/cm^{3} for the $\beta$-crystal to 1.92 g/cm^{3} for the $\alpha$-form, while the amorphous part of PVDF has a density of 1.68 g/cm^{3}. The overall density of the resin is in the 1.75–1.78 g/cm^{3} range, which is based on a typical

crystallinity of 40%. Another special feature of PVDF is the "chain" defects caused by the reverse addition of vinylidene fluoride in the chain. These head-to-head and tail-to-tail units can be determined using ^{19}F-NMR and are found to be in the range of 3–8 mol % depending on the polymerization temperature.[10] These defects are mainly responsible for the solution behavior of PVDF rather than the melt. However, the presence of a small amount of reverse units would lower the melting point and the crystallization temperature because of the breakage of the crystallinity, although the defects could be seen within the crystalline phase. The peculiar behavior caused by the chemical nature of PVDF makes it a very interesting material in terms of structure–property relationships. As to melt processing, a lack of information prevents a clear understanding of how the state variables affect the flow behavior and moldability of this resin.

In the present article the pressure–temperature–volume relationships of PVDF and PVDF–HFP have been determined in the temperature range of 40–230°C and in the pressure range of 200–1200 bar. The results were used with the TAIT state equation to predict specific volume as a function of temperature and pressure. State parameters such as $B(T)$ and thermal compressibility, $K(T)$, were also determined.

## EXPERIMENTAL

### Materials

The materials selected were commercial resins of poly(vinylidene fluoride) (PVDF) homopolymers and poly(vinylidene fluoride)–hexafluoropropylene (PVDF–HFP) copolymers manufactured by ATOFINA Chemicals, Inc. (Philadelphia, PA). The samples were used as received without further purification.

### Characterization

The samples were characterized by size-exclusion chromatography (SEC) for molecular-weight determination ($M_w$ and $M_w/M_n$) in dimethyl sulfoxide (DMSO) at 100°C using a Waters high-temperature SEC and a PMMA standard calibration. Solution-state ^{19}F-NMR, using a Brucker instrument equipped with a 300-MHz/89-mm magnet, was performed to determine the amount of reverse units in each sample as well as the amount

of HFP contained in the copolymers. Differential scanning calorimetry (DSC) was carried out using a PerkinElmer 7 series for the determination of the crystallization and melting temperatures of each resin upon cooling. The measurements were taken after a second heating at 10°C/min was performed, followed by a cooling process at 5°C/min.

### Viscoelastic Properties

Rheological measurements were done with a Rheometric Scientific ARES-LS strain rheometer to determine the viscosity profile of the resins. The instrument was set up with a 25-mm parallel-plate geometry, and the experiments were conducted in oscillatory mode in the frequency range of 0.01–100 rad/s at 230°C. The oven was heated with a high rate of nitrogen in order to avoid thermal degradation of the resins. All measurements were carried out in the linear viscoelastic region.

The same instrument was used to perform a dynamic mechanical analysis (DMA) on one homopolymer sample and two copolymers containing different amounts of HFP. The DMA was carried out in a temperature range between −50°C and 160°C at an oscillating frequency of 1 Hz, a heating rate of 2°C/min, and a shear–strain amplitude of 0.1%, according to ASTM D5279-95. The storage modulus ($G'$), the loss modulus ($G''$) and tan ($G''/G'$) were recorded as a function of temperature.

### PVT Measurements

The PVT measurements were carried out on a PVT instrument model 100 currently offered by Haak Company (New Jersey). The temperature range considered was 40–220°C, while the pressure range was 200–1200 bar. A sample size of about 1 g was used for each experiment. The measurements were taken during the cooling process, which occurred at 5°C/min. All measurements were carried out under isobaric conditions.

## RESULTS AND DISCUSSION

The physicochemical characteristics of the resins are depicted in Table I. These resins differ in their molecular weight ($M_w$), slightly in molecular-weight distribution, and in HFP content. The NMR analysis showed that the percent reverse

**Table I  Physicochemical Properties of PVDF and PVDF–HFP Copolymers**

| Resin | $M_w$ (kg/mol) | $M_w/M_n$ | HFP (%) | $T_m$ (°C) | $\Delta H$ (J/g) | $T_c$ (°C) |
|---|---|---|---|---|---|---|
| PVDF1 | 197 | 2.0 | 0 | 167.1 | 65.0 | 134.7 |
| PVDF2 | 339 | 2.6 | 0 | 166.5 | 61.1 | 133.8 |
| PVDF–HFP1 | 321 | 2.9 | 10.5 | 142.6 | 37.4 | 103.8 |
| PVDF–HFP2 | 471 | 3.3 | 11.1 | 140.6 | 36.0 | 105.1 |
| PVDF–HFP3 | 480 | 3.3 | 3.1 | 150.4 | 39.6 | 125.6 |

units as 4.8% for all homopolymers. This is in agreement with the percent of reverse units being predominantly controlled by the polymerization temperature.[10]

**Viscoelastic Properties**

The rheological properties of the different resins are presented in Figure 1 as complex viscosity versus frequency of oscillation. The viscosity profiles confirm the validity of the SEC data in that the major difference between the resins lies in the weight-average molecular weight rather than in their distribution. This is shown by the large difference in viscosity in the low-frequency region and a similar slope in the non-Newtonian region. In addition, the viscosity of PVDF–HFP2 is similar to that of PVDF–HFP3, which allows for a better comparison between the two, based on their HFP content. Since molecular weight has only a slight effect on DMA, only samples with a difference in molecular architecture will be discussed.
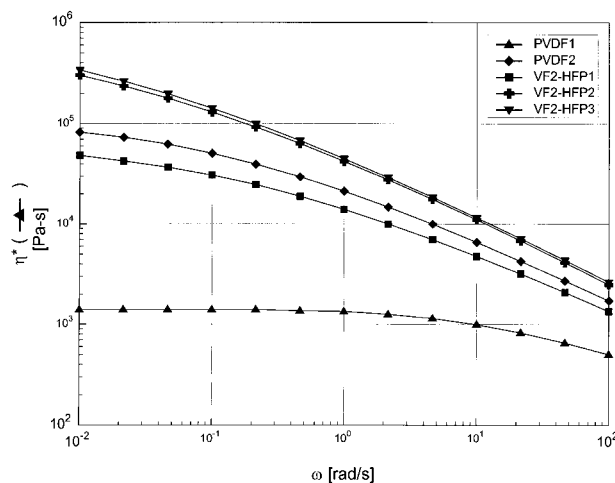


**Figure 1** Complex viscosity as a function of frequency of PVDF homopolymers and VF2–HFP copolymers at 230°C.

Figure 2(a–c) shows the DMA scans of the PVDF2 homopolymer and two copolymers containing different amounts of HFP in the temperature range of −150°C to 160°C. PVDF exhibits four relaxations. The major ones are the $\beta$-relaxation, which corresponds to the glass transition at −37.1°C. The $\beta'$ appears to be around 15°C, while the $\alpha$-transition is observed at 85.4°C. These three transitions are well described in the literature based on various techniques such as dielectric and dynamic mechanical analyses as well as NMR and are reported by Lovinger.[11] The results obtained here vary slightly from those reported in the literature (a shift in the temperature axis) because of the mode of deformation (shear versus tension and flexion) as well as the experimental conditions, mainly the frequency of oscillation and heating rate effects. Figure 2(b,c) shows the DMA curves of PVDF–HFP2 (11%) and PVDF–HFP3 (3%), which have the same molecular weight but differ in their HFP content. For PVDF–HFP2, the $\beta$ transition, which corresponds to the glass transition in the amorphous phase, is shifted to higher temperatures by 2.9°C, whereas the $\beta'$ relaxation remains unchanged in temperature but is more pronounced in amplitude. The $\alpha$ transition appears about 28°C lower than in the homopolymer. For the third copolymer, PVDF–HFP3, the $\beta$ transition occurs at −35.9°C and the $\beta'$ appears at 17.2°C with a smaller tan $\delta$ amplitude than in PVDF–HFP2. The $\alpha$-relaxation occurs at 71.5°C, 3.9°C lower than does the homopolymer PVDF2. Although the interpretation of the $\beta'$ relaxation is not well understood, the $\beta$ transition shows that $T_g$ increases with the amount of HFP in the copolymer. This is a result of the miscibility of the amorphous phase of both the homopolymer and the copolymer. Hypothetically, poly(HFP) has a $T_g$ close to room temperature, based on the Fox equation. The $\alpha$ relaxation, which occurs mostly in the crystalline region, does not show surprising results since the crys-
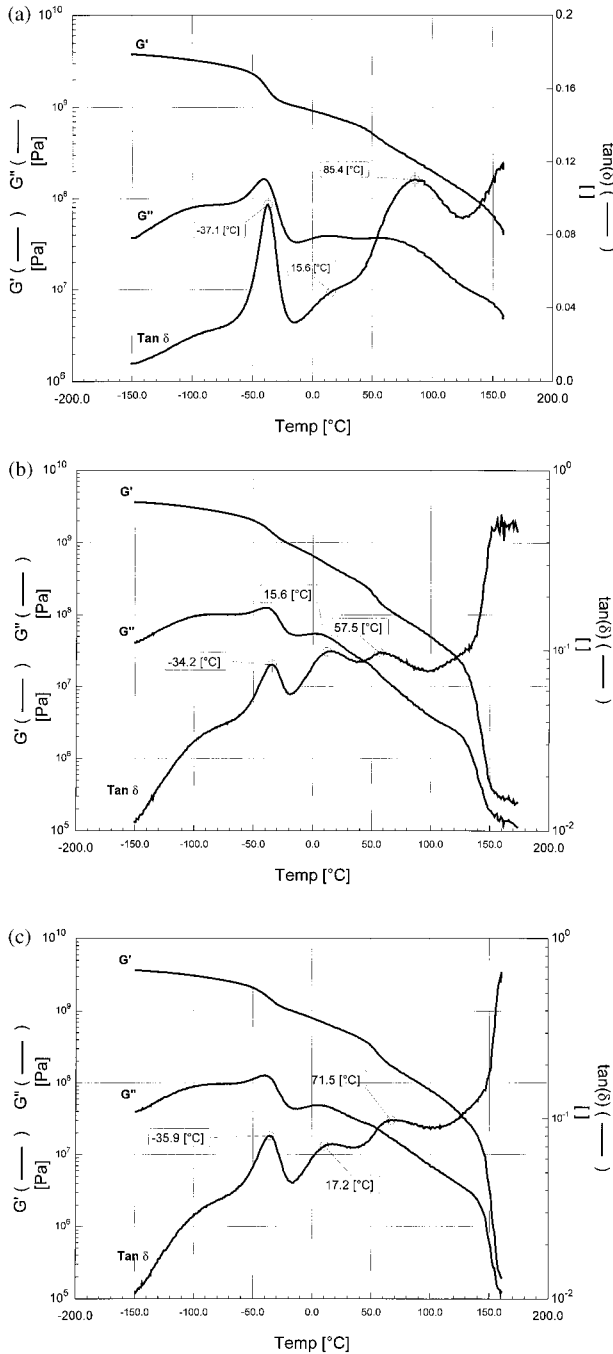
**Figure 2** Dynamic mechanical analysis of PVDF homopolymers and VF2–HFP copolymers: (a) PVDF2, (b) PVDF–HFP2 (11% HFP), and (c) PVDF–HFP3 (3% HFP).

tallinity would be expected to diminish with an increasing amount of HFP in the copolymer.

## PVT Experiments (Isobaric Mode)

These measurements were performed by maintaining the pressure constant and decreasing the

temperature at a rate of 5°C/min. The determination of the specific volume at 1 bar was made by extrapolating the data at elevated pressures (200 bar) to the zero pressure. The specific volume at zero pressure is assumed to be equal to that of atmospheric pressure and will be used as such for curve-fitting purposes. Although it is preferable for the measurements to be taken under isothermal conditions, this is not an issue here since the specific volume is independent of the measurement mode in a phase equilibrium and may be considered the same. Several samples were run to determine the accuracy of the technique. Under these conditions, the experimental error was found to be 0.25% at atmospheric pressure and 0.1% at 1200 bar regardless of the temperature.

Figure 3(a,b) shows the dependence of specific volume on temperature and pressure for PVDF1 and PVDF2. At atmospheric pressure the density of PVDF1 varies between 1.753 g/cc at 40°C and 1.456 g/cc at 220°C, a change of 17%. At 1200 bar the density variation is smaller and ranges be-
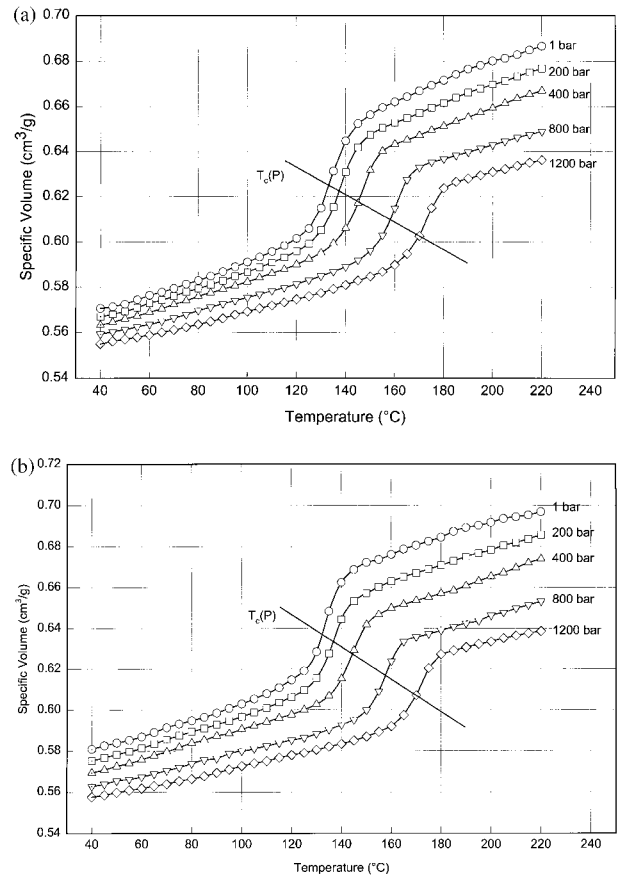


**Figure 3** PVT diagram of the homopolymers (a) PVDF1 and (b) PVDF2.

**Table II   Density of Poly(vinylidene fluoride) and Poly(vinylidene fluoride-hexafluoropropylene) Copolymers as a Function of Temperature and Pressure**

| Materials | Temperature (°C) | Pressure (bar) | Density (g/cc) |
|---|---|---|---|
| PVDF1 | 40 | 1 | 1.753 |
| | 40 | 1200 | 1.802 |
| | 220 | 1 | 1.456 |
| | 220 | 1200 | 1.572 |
| PVDF2 | 40 | 1 | 1.721 |
| | 40 | 1200 | 1.793 |
| | 220 | 1 | 1.435 |
| | 220 | 1200 | 1.566 |
| PVDF–HFP1 | 40 | 1 | 1.745 |
| | 40 | 1200 | 1.806 |
| | 220 | 1 | 1.477 |
| | 220 | 1200 | 1.607 |
| PVDF–HFP2 | 40 | 1 | 1.750 |
| | 40 | 1200 | 1.810 |
| | 220 | 1 | 1.487 |
| | 220 | 1200 | 1.614 |
| PVDF–HFP3 | 40 | 1 | 1.752 |
| | 40 | 1200 | 1.815 |
| | 220 | 1 | 1.476 |
| | 220 | 1200 | 1.604 |

tween 1.802 g/cc at 40°C and 1.572 g/cc at 220°C, a difference of 13%. In the molten state the change in melt density between 1 and 1200 bar is 7.4%, while at 40°C it is only 2.7%. For the second homopolymer, PVDF2, the same trend can be observed; the variation in specific volume within the experimental conditions $(T, P)$ is similar to PVDF1. The density values at extreme conditions are also shown in Table II. Based on the molecular-weight difference, as might be expected, the density of PVDF1 is higher that of PVDF2, although the difference in molecular weight is not that significant. Under normal conditions $(T_{room}, P_{atm})$, the difference is about 2%. In the molten state the difference is less than 2%. Under extreme conditions, where only the free-volume effect is accounted for, the difference is less than 0.5%, which is above the experimental error. Under these conditions $(T_{room}, P_{atm})$, the difference in the specific volume of the homopolymers is mainly due to the difference in crystallinity (65 J/g for PVDF1 and 61.1 J/g for PVDF2). This results in a difference in the free volume contained within the amorphous phase. At room temperature and high pressure the same interpretation is valid. However, because extreme pressures

were used, and the experiments were done in the cooling mode, the free volume within the amorphous phase is reduced. Therefore, the molecular-weight effect can be assessed properly. From a practical standpoint, the specific volume dependence on molecular weight seems to be less significant than originally thought. Whether this resin is used in injection molding or extrusion will
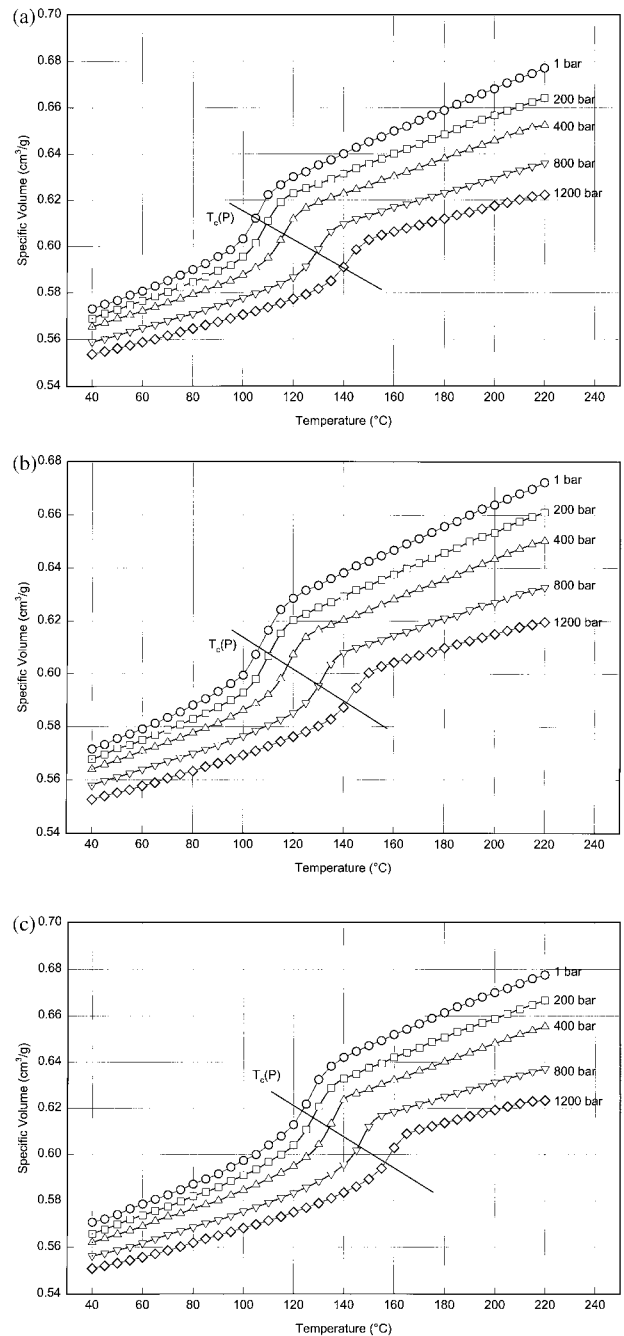


**Figure 4**   PVT diagram of the copolymers (a) PVDF–HFP1, (b) PVDF–HFP2, and (c) PVDF–HFP3.

not have a significant impact on shrinkage and/or warpage.

Furthermore, at atmospheric pressure the specific volume–temperature scan shows a major transition occurring at around 135°C. This transition corresponds to the crystallization temperature ($T_c$) of PVDF1 from the melt. This is in agreement with the crystallization temperature measured by DSC (134.7°C) at a cooling rate of 5°C/min. Although it is trivial that the ideal technique to measure the crystallization temperature is DSC, it was interesting to investigate the pressure dependence since pressure cells in DSC are limited to 1000 psi. At 1200 bar this transition occurs at about 172°C, 37°C higher than at atmospheric pressure. This is commonly known as pressure-induced crystallization. Between the extreme pressures this transition seems to correlate well with the pressure, even though the interpretation of the data in this region is not trivial (phase change and/or equilibrium). As is shown in Figure 5, the crystallization temperature dependence on pressure can be written in the following form:

$$T_c = 0.036P + 137 \tag{5}$$

For PVDF2 the same comments and interpretation are applicable. The crystallization temperature obtained by DSC is 133.8°C. This can also be seen in Figure 3(b) as a slight shift in the $y$-axis because of a molecular-weight difference. As a result, the variation in specific volume, considered in the pressure–temperature window, is slightly smaller than that for PVDF1. At the highest pressure the crystallization temperature appears around 175°C. The crystallization temperature correlation with pressure is also shown in Figure 5. The equation describing this correlation is

$$T_c = 0.035P + 135.2 \tag{6}$$

The dependence of crystallization temperature on pressure is of tremendous advantage, since from a practical standpoint the service temperature of the material is increased by about 40°C if the material is cooled under pressure. This leads to a better mechanical performance of PVDF when subjected to various stresses in a relatively high-temperature environment.

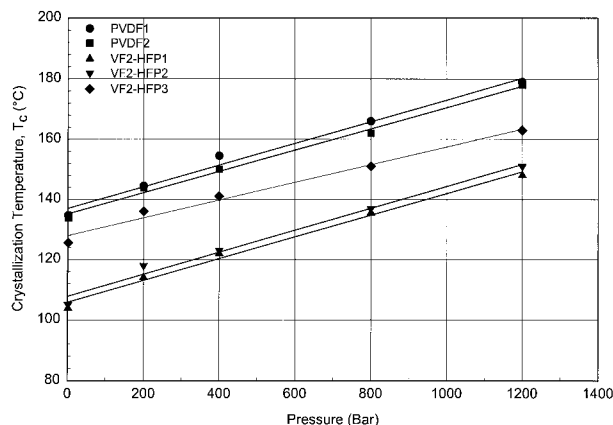Figure 4(a,c) shows the PVT diagrams of the three copolymers, PVDF-HFP1 to 3 respectively.



**Figure 5**  Crystallization temperature dependence on pressure of PVDF and PVDF–HFP copolymers.

For PVDF–HFP1 (low $M_w$ and 10.5% HFP), the change in specific volume within the temperature-pressure window studied is roughly 18%. The density of PVDF–HFP1 at atmospheric pressure and 40°C is 1.745 g/cc, while at 1200 bar and 220°C the density is 1.607. Similarly, the temperature effect is apparently more significant than the pressure effect because of the phase change that occurs in this temperature range (Table II). This phase change occurs at 105°C at 1 bar, which is also in agreement with the DSC data (103.8°C). At 1200 bar the crystallization temperature occurs at 142°C, 37°C higher than at atmospheric pressure. Again, this transition correlates well with pressure. Extracting this information from Figure 5 yields

$$T_c = 0.036P + 105.9 \tag{7}$$

Figure 4(b) shows the PVT data for PVDF–HFP2 (high $M_w$, 11% HFP). The same variation in density with temperature and pressure was obtained (~18%). However, the crystallization temperature shifted toward higher temperatures by about 2–3°C, which was also observed by DSC. The crystallization temperature at high pressures seems to have shifted by the same amount as in the previous case. However, an opposite molecular-weight effect can be seen when the two copolymers are compared: the higher the molecular weight, the lower the density. The pressure dependence on the crystallization point is found to be of this form:

$$T_c = 0.037P + 107.8 \tag{8}$$

The PVT scan of PVDF–HFP3, which contains 3.1% HFP, is shown in Figure 4(c). In the solid state this copolymer has a density of 1.752 g/cc at atmospheric pressure and 1.815 g/cc at 1200 bar (Table II). The crystallization point measured by PVT is approximately 126°C, while at the highest pressure it is 158°C. Again, the crystallization temperature is in agreement with the DSC data, and a similar pressure dependence was also obtained. The crystallization temperature correlation with pressure is

$$T_c = 0.03P + 128 \qquad (9)$$

For eqs. (5)–(9), temperature is expressed in °C and pressure in bar.

For the copolymers the results are quite interesting. The introduction of HFP to the VF2 backbone disturbs the crystallinity of PVDF, leading to a reduction in the melting point that correlates well with the amount of HFP added. In addition, the amount of crystallinity diminishes, as shown by the heat of fusion data (Table I). Consequently, an increase in the fraction of the amorphous phase would be expected, which would diminish significantly the density of the material depending on the HFP content. Our results did not show this effect, however. On the contrary, the density of the copolymers was found in some cases to be equal to or higher than that of the homopolymers, which was attributed to the comonomer added. Indeed, the addition of HFP increases the number of fluorine per unit volume, resulting in a higher total number of fluorine units per unit volume for the copolymer and a higher density. The molecular-weight effect for the first two copolymers cannot be clearly assessed. The two copolymers contain slightly different HFP content (10.5 and 11.1%, respectively). This can be confirmed by the higher melting point of the first copolymer as well as by its heat of fusion. This difference is sufficient to suppress the molecular-weight effect, according to an assessment of the data obtained for the homopolymers. For the third copolymer the amount of HFP is 3.1%, which leads to a melting point of 150.4°C and a heat of fusion of 39.6 J/g. The density, however, does not seem to change a lot in comparison to the other copolymers.

## Predictions of the Specific Volume of the PVDF and PVDF–HFP Copolymers

The most commonly used model for the prediction of the specific volume of semicrystalline polymers
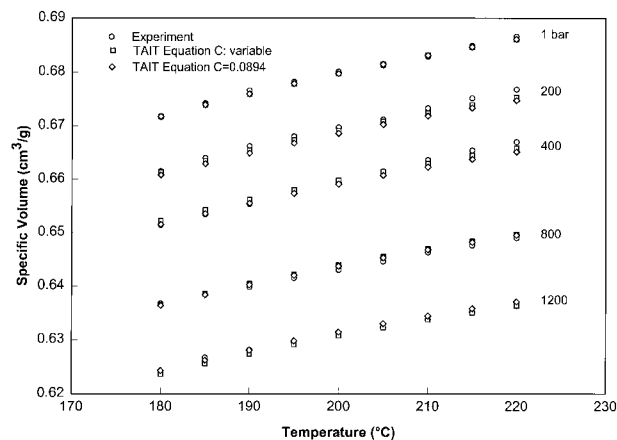


**Figure 6**  Comparison between the experimental data and the theoretical prediction of the TAIT equation for PVDF1.

is the TAIT equation, which describes the change in specific volume as a function of temperature and pressure. However, this model applies to the molten state only, since the prediction of specific volume near crystallization is not trivial and depends on whether phase equilibrium is achieved. For these predictions the zero-pressure specific-volume dependence of temperature $V(0,T)$ was approximated to the values at atmospheric pressure $V(1,T) = V(0,T)$. Then the data was fitted with a polynomial function, which was found to fit better than an exponential function, to achieve a regression coefficient of 0.99, in which case, the specific volume could be predicted with an error of less than 0.1%.

### Predictions for the PVDF Homopolymers

For PVDF1 and PVDF2 the zero-pressure specific volumes were both fitted with a polynomial function. For the first sample a second-order regression was sufficient to describe the variation of the zero-pressure specific volume with temperature with a regression coefficient of 0.99 and in the form

$$V(0, T) = 0.528 + 1.159e^{-3}T - 2e^{-6}T^2 \quad (10)$$

For the second homopolymer (PVDF2) the equation that describes the zero-pressure specific volume with temperature can be written as

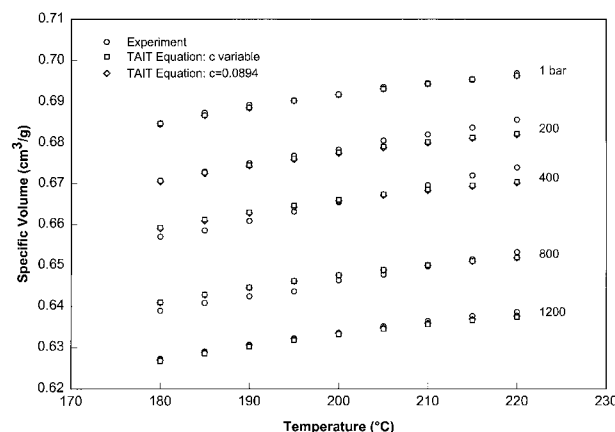$$V(0, T) = 0.508 + 1.547e^{-3}T - 3.139e^{-6}T^2 \quad (11)$$

**Figure 7**   Comparison between the experimental data and the theoretical prediction of the TAIT equation for PVDF2.

In both cases the polynomial functions were used in the TAIT equation to predict the specific volume as a function of temperature and pressure. In addition, we decided to use the universal constant $C$ with a typical value of 0.0894 and also as a variable in the equation for comparison purposes, since other nonuniversal values were reported in the literature for other semicrystalline polymers.[2]

Figures 6 and 7 show the superposition of the experimental data with the prediction of the TAIT equation using $C$ as a universal constant and as a variable in the equation. The experimental data used for the predictions were limited to a temperature range between 180°C (well above the melting point) and 220°C at five different pressures ranging between 1 and 1200 bar. With both scenarios the results show a very good agreement between the predictions and the experimental data. The results of the fitting work are summarized in Table III for $C$, $B_0$, $B_1$, and the percent of relative difference. For both homopolymers the

values of $B_0$ and $B_1$ were found to be in the same range as for other semicrystalline polymers whether $C$ was a constant or a variable.[2] In addition, there seems to be no difference in the prediction of the specific volume. In both cases the average percent of difference with the experimental data was well below 0.1%. Therefore, it appears that the universal constant for $C$ (0.0894) can be used to adequately predict the specific volume of PVDF as a function of temperature and pressure.

### Predictions for PVDF–HFP copolymers

The same analysis was carried out for the copolymers—the zero-pressure specific-volume dependence on temperature was predicted with a polynomial function. The order of the polynomial depended on how much precision was desired. We chose to achieve a regression coefficient of 0.99 as was the case for the homopolymers. For VF2–HFP1 (containing 10.5% HFP) the zero-pressure specific volume as a function of temperature had a simple first-order expression with a regression coefficient higher than 0.99:

$$V(0, T) = 0.577 + 4.543e^{-4}T \qquad (12)$$

Using this equation in the TAIT equation with $C$ as a variable and as a constant leads to excellent agreement with the experimental data overlaid with the predictions shown in Figure 8. For the copolymers the comparison between the experimental data and the predictions was carried out on a wider temperature range since the presence of HFP reduces the melting point of the VF2–HFP copolymer by about 30°C. In this case the temperature range is between 160°C and 220°C. The fitting parameters reported in Table III show there is only a slight difference between the two

**Table III   TAIT Parameters for PVDF and PVDF–HFP Copolymers**

| Resins | $C = 0.0894$ | | | $C$ as a Variable | | | |
| | $B_0$ | $B_1$ | % Error | $C$ | $B_0$ | $B_1$ | % Error |
|---|---|---|---|---|---|---|---|
| PVDF1 | 106.6 | 4.2e-4 | 0.060 | 0.1135 | 147.2 | 4.3e-4 | 0.030 |
| PVDF2 | 81.30 | 3.4e-4 | 0.020 | 0.0945 | 80.26 | 2.47e-4 | 0.015 |
| PVDF–HFP1 | 207.1 | 4.15e-3 | 0.005 | 0.089 | 207.1 | 4.15e-3 | 0.008 |
| PVDF–HFP2 | 183.15 | 3.35e-3 | 0.020 | 0.1008 | 212.75 | 3.26e-3 | 0.010 |
| PVDF–HFP3 | 157.7 | 2.83e-3 | 0.005 | 0.0978 | 177.9 | 2.79e-3 | 0.005 |

**Figure 8** Comparison between the experimental data and the theoretical prediction of the TAIT equation for VF2–HFP1 (10.5% HFP).
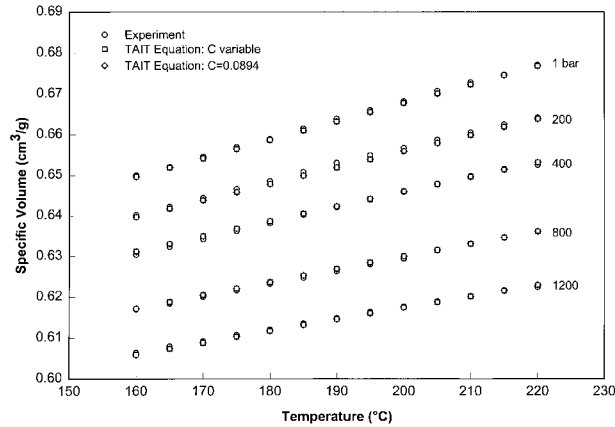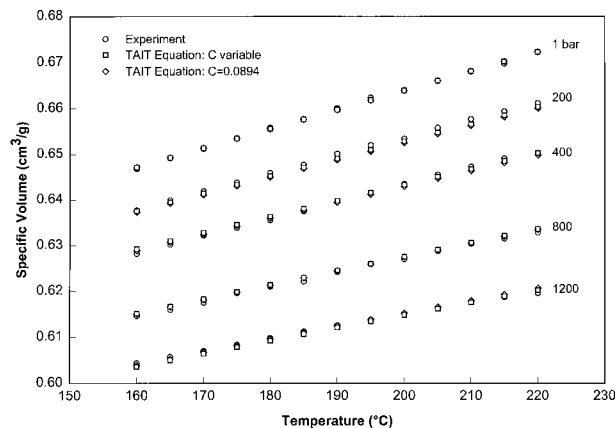


**Figure 10** Comparison between the experimental data and the theoretical prediction of the TAIT equation for VF2–HFP3 (3% HFP).

cases, and the average relative difference with the experimental data is less than 0.01%.

For the second VF2–HFP sample, containing the same HFP content as the previous sample but with a higher molecular weight, the correlation function of the zero-pressure specific volume is also a first order and has the form:

$$V(0, T) = 0.58 + 4.201e^{-4}T \qquad (13)$$

Using this equation in the TAIT equation for the prediction of the specific volume as a function of temperature and pressure leads to the results shown in Figure 9. The superposition of the experimental data and the theoretical predictions turned out to be very good, with an average relative differ-



**Figure 9** Comparison between the experimental data and the theoretical prediction of the TAIT equation for VF2–HFP2 (11% HFP).
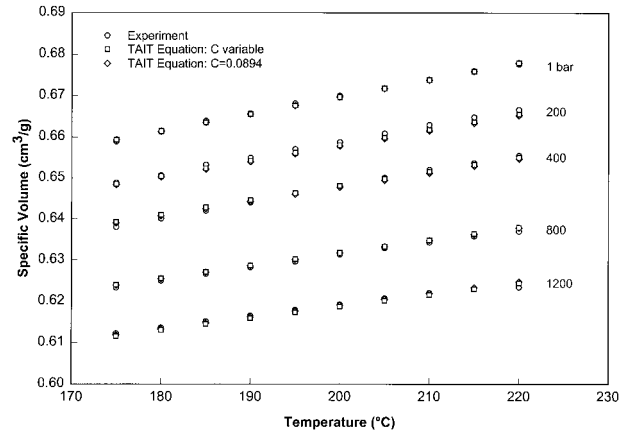
ence between the experimental data and the predictions of 0.01–0.02% whether $C$ was a constant or a variable. The third copolymer, VF2–HFP3, has a lower HFP content and therefore a higher melting point, with a narrower temperature range (175°C–220°C) used for comparing the experimental data with the theoretical predictions. In this case the fitting of the polynomial to the zero-pressure specific volume was also found to be of a first order, with a regression coefficient higher than 0.99. The equation has the form

$$V(0, T) = 0.587 + 4.138e^{-4}T \qquad (14)$$

The predictions of the TAIT equation and the experimental data for this sample are shown in Figure 10. Here also is excellent agreement, with an average relative error of less than 0.01%. The use of the universal constant $C$ leads to the same results as for the variable—no difference in the predicted specific volume.

In summary, it appears that in the molten state the specific volume of both the homopolymers and copolymers can be adequately described by the TAIT state equation using the universal constant $C$ with a value of 0.0894. The specific volume can be predicted with an accuracy of less than 0.1%, which is well within the experimental error. In the molecular-weight range studied, it is apparent that the specific volume does not change significantly. Therefore, within the range of commercial PVDF, the change in specific volume with molecular weight is less than 5%. This is because below a molecular weight of 100 kg/mol, in practice, PVDF loses its mechanical properties and does not have
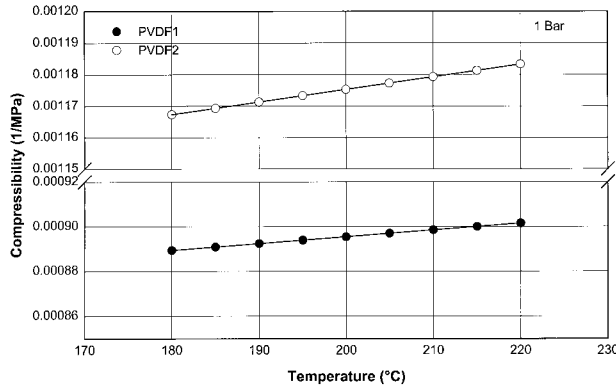
**Figure 11** Isothermal compressibility of PVDF homopolymers at 1 bar.

any significant application in melt processing at the least. Since this polymer can be made by emulsion or suspension polymerization, the highest molecular weight for a melt-processible resin does not exceed 600 kg/mol as measured by our GPC method (relative to a PMMA calibration). In addition, in our case these resins were made by emulsion polymerization, which involves the addition of a surfactant to stabilize the polymerization. Once the reaction is completed, the polymer latex is coagulated and then washed to remove any residues. Unfortunately, the efficiency of the washing process is only as good as the industrial process, which does not eliminate totally all the residues. Extraction work combined with NMR analysis showed that the polymer may contain 100–300 ppm of residual surfactant. Although in small amounts, the surfactant plays a role during the pressurization and the PVT measurements. If it is desired to perform a more theoretical work, the resin needs to be purified; however, in practice, the resin is processed in pellet form, which may contain small amounts of residues.

In melt processing and specifically in injection molding, one aspect not typically considered is the compressibility of a polymer in the molten state. From a theoretical standpoint and in order to facilitate the calculations, it is common that polymer melts are considered incompressible. However, in some cases this assumption may lead to disastrous products, resulting from a poor mold or die design. Knowledge of the compressibility as well as the PVT data of the molten resin allows a correction of the packing pressure to avoid defects such as warpage, shrinkage, and sink marks.

The combination of the TAIT equation describing the dependence of the specific volume on pressure and temperature with the expression of the

specific volume at zero pressure, $V(0,T)$, can be used to calculate the compressibility, $K(P,T)$, of both the homopolymers and copolymers in the liquid state or the inverse of the compressibility, defined as the bulk modulus. The expression for the compressibility can be derived from

$$K(P, T) = -\left[\frac{1}{V}\right] \cdot \left[\frac{dV}{dP}\right]_T \quad (15)$$

Using the expression for $B(T)$ in eq. (4), this will lead to

$$K(P, T) = \frac{C}{P + B(T)}\left[1 - C\ln\left(1 + \frac{P}{B(T)}\right)\right] \quad (16)$$

The compressibility of the homopolymers and copolymers was calculated as a function of temperature at the extreme pressures, in the liquid state, and reported in separate figures for the sake of clarity (Figs. 11–14). For the homopolymers PVDF1 and PVDF2, the compressibility is higher at the highest pressure. Although the difference in molecular weight is not significant, it is apparent that for PVDF1, the compressibility is lower. This is supported by the same interpretation discussed for the PVT data. Moreover, the temperature does not seem to have a significant effect on compressibility. For the copolymers the results are shown in Figures 13 and 14 for, respectively, atmospheric pressure and 1200 bar. The copolymers with similar HFP content seem to have the same slope, while the slope of the third copolymer, with the lowest amount of HFP, has a steeper slope. Here again the compressibility is not affected much by the molecular weight, while the HFP content dominates this effect. Overall, it seems that the compressibility of
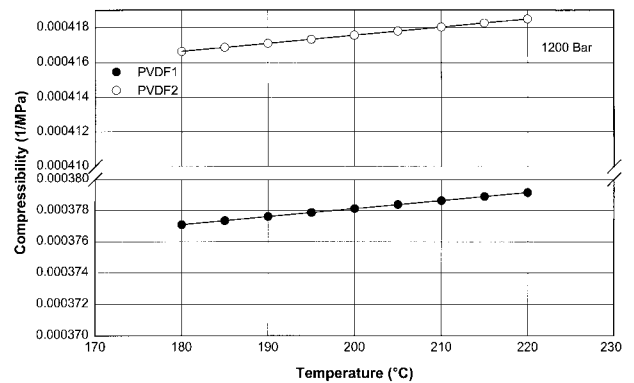


**Figure 12** Isothermal compressibility of PVDF homopolymers at 1200 bar.

PVDF does not vary significantly, at least within the experimental conditions studied.

## CONCLUSIONS

In this work the viscoelastic properties and the PVT relationship of poly(vinylidene fluoride) and its copolymers was studied in the temperature range of 40–220°C and in the pressure range of 1–1200 bar. The effect of molecular weight and HFP content for the copolymers was investigated. A slight effect of molecular weight on specific volume was found for the homopolymers, while for the copolymers the effect of molecular weight could not be properly assessed because of the differences in their HFP content. Introducing HFP to $VF_2$ resulted in a lower melting point of the copolymer and also a lower specific volume compared to the pure homopolymers. The main transition between the liquid and the solid states, which corresponded to the crystallization point, correlated well with the DSC results, at least at atmospheric pressure. The crystallization temperature was also found to correlate well with pressure for both the homopolymers and the copolymers.

The TAIT state equation was used to predict specific volume as a function of temperature and pressure in a temperature range well above the melting and 220°C. Fitting the experimental data with the TAIT equation was performed using $C$ as a universal constant (0.0894) and also as a variable. The results suggest that the use of the universal constant is sufficient to describe the dependence of the specific volume on temperature and pressure with an error of less than 0.1%, which is well within the experimental error of the PVT
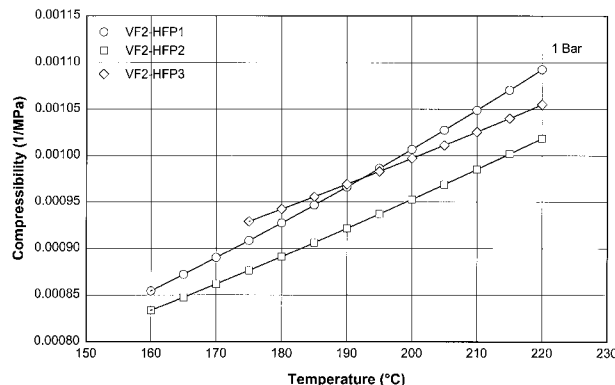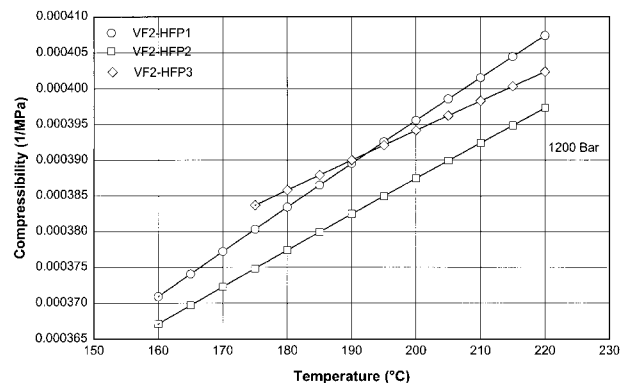


**Figure 14**  Isothermal compressibility of VF2–HFP samples at 1200 bar.

analyses. These results were used to calculate the compressibility of the samples in the liquid state, which were also found to depend slightly on molecular weight and strongly on HFP content.

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**Figure 13**  Isothermal compressibility of VF2–HFP samples at 1 bar.