

Crystallization Kinetics and PVT Behavior of Poly(vinylidene fluoride) in Process Conditions

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ABSTRACT: The so-called fluoropolymers have gained, in recent years, considerable industrial success, and the increasing industrial interest in this class of materials has caused a need for better characterization of the properties of interest for processability, for instance, for injection molding or extrusion. In this work, the pressure–volume–temperature (PVT) relationship of a poly(vinylidene fluoride) is described by combining specific volumes of amorphous and crystalline phases present in the material. The volumes of the two phases are described simply by thermal expansion and compressibility coefficients drawn from standard PVT data below and above the crystallization range. Within the crystallization range, the material volume is assumed to change from amorphous to crystalline according to the evo-

lution of an overall crystallinity degree, which is described by the Nakamura nonisothermal formulation of an Avrami crystallization kinetic model. Model parameters are identified by comparison with standard calorimetric results, PVT data, and final densities of thin samples solidified during quenches conducted with cooling rates of several hundreds of Kelvins/second. The resulting model allows the description of the PVT behavior of PVDF in the pressure- and cooling-rate ranges of interest for processing. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 89: 3396–3403, 2003

Key words: crystallization; fluoropolymers; density; kinetics (polm.)

INTRODUCTION

The so-called fluoropolymers in recent years have gained considerable industrial success in many sectors due to an excellent range of properties. This class of materials offers, in fact, the advantages of high-temperature endurance, outstanding chemical resistance, excellent fire-propagation resistance, and weathering resistance. Basically, fluoropolymers are adopted for special applications, and their use is limited, in part, because of a lack of information about the main parameters influencing processability, principally, the crystallization kinetics and volume change during processing.

This is a wide topic involving many new materials, whose behavior under process conditions is not completely characterized: A good description of density changes is indeed one of the basic challenges for the polymer processing industry to predict important variables during an injection-molding cycle (such as, for instance, pressure curves, final product characteristics, and performance in terms of shrinkage, distribution of internal stresses, dimensional accuracy, and

stability).^{1–3} Polymer density is strongly influenced by cooling conditions such as the cooling rate and pressure history, and this is particularly true for semicrystalline polymers. In fact, during cooling from the molten state, this class of materials undergoes a transition from a completely amorphous to a partially crystalline state, which results in a major change of all material characteristics, including volumetric parameters.

Standard tests to describe volume changes during cooling are confined to unreasonably low cooling rates and/or pressures, if compared with those experienced by the material during processing. In this work, the pressure–volume–temperature (PVT) behavior of a poly(vinylidene fluoride) (PVDF) is described over a wide range of cooling rates. The crystallization kinetics was analyzed by standard calorimetric tests and data, on crystallization attained after cooling procedures, carried out with cooling rates as high as several hundreds degrees per second and under pressures to 120 MPa, adopting techniques already described elsewhere.^{4,5} Knowing the crystallization kinetics, it is possible to obtain not only the specific volume evolution from the cooling history during processing, but also the evolution of the macroscopic crystallinity degree, which influences all the properties of the final object and other features of interest to polymer processing

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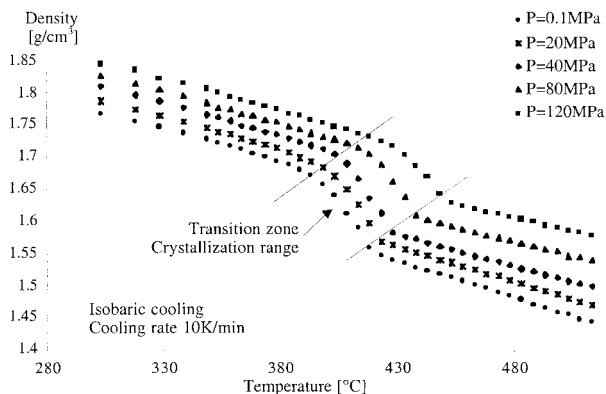


Figure 1 PVT data obtained by piston-die technique in isobaric cooling at a rate of 10 K/min.

such as the distribution of melt–solid transition temperatures and enthalpic effects.

EXPERIMENTAL

Material

A semicrystalline fluorinated polymer (Hylar PVDF MP10), kindly supplied by Ausimont (Bollate-MI, Italy), was selected as the test material. With respect to other fluoropolymers, PVDF has a relatively low melting temperature (438–441 K), which allows processing with conventional machinery. A review of many relevant properties of PVDF can be found elsewhere.⁶

PVT behavior at low cooling rates

Material PVT data were provided by Ausimont and are reported in Figure 1. Data were obtained by a piston-die technique in isobaric cooling at a nominal cooling rate of 10 K/min. The data show that, on increasing pressure, the crystallization range shifts toward higher temperatures, with a slope of about 0.25 K/MPa. Furthermore, outside the crystallization range, the material density change is roughly linear with the temperature at all pressures.

Calorimetry

Some samples of the material were solidified in a DSC apparatus (Mettler, with liquid nitrogen as the cooling fluid) under constant cooling rates (in the range 0.5–80 K/min). All samples were kept at a temperature of 503 K for 30 min and then cooled according to the test procedure. Calorimetric curves obtained under constant cooling rates are shown in Figure 2(a). As expected, by increasing the cooling rate, all curves shift toward lower temperatures and crystallization develops over a wider temperature range. The overall heat released during solidification does not change significantly by changing the cooling rate (at least in the range of the experiments) and was scattered between 42 and 45 J/g .

The final crystallinity degree, x , in the samples solidified with DSC ramps, was found from calorimetric curves using $\lambda = 105$ J/g (ref. 7) as the latent heat of crystallization. In the range of the cooling rates explored, the crystallinity degree was found to be always between 40 and 43%, as shown in Figure 2(b), this value being in line with that normally reported in the literature.⁸

Some samples were also analyzed under isothermal conditions. Also, in this case, the samples were kept for about 30 min at 503 K before lowering the temperature at a rate of 1.7 K/s to the test value. The material was tested at five temperatures: 415, 416, 417, 418, and 419 K. At temperatures higher than 419 K, testing times were very high and output signals too low, whereas temperatures lower than 415 K could not be reached due to the limited apparatus cooling rate, which was not sufficient to prevent samples from crystallizing during cooling to the set temperature. Isothermal calorimetric curves are shown in Figure 3(a). The overall energy released during each test was found to be always between 42 and 45 J/g. This implies that equilibrium crystallinity is essentially constant below 420 K. Half-crystallization times (i.e., times at which crystallinity reaches one-half of the

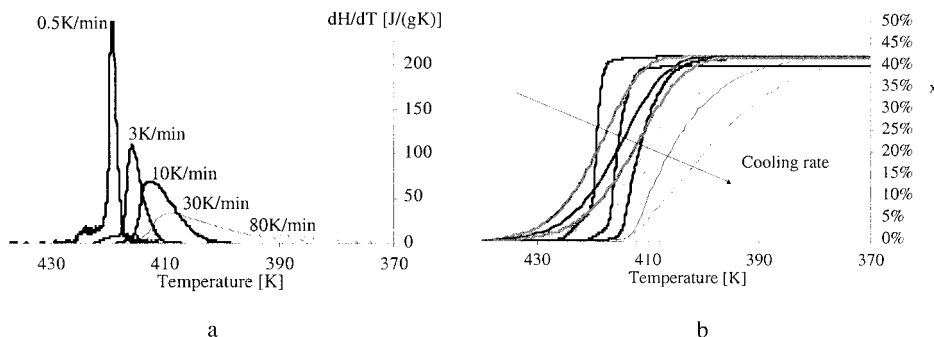


Figure 2 Calorimetric curves measured during solidification of PVDF samples in a DSC apparatus at different cooling rates. Gray lines refer to model predictions.

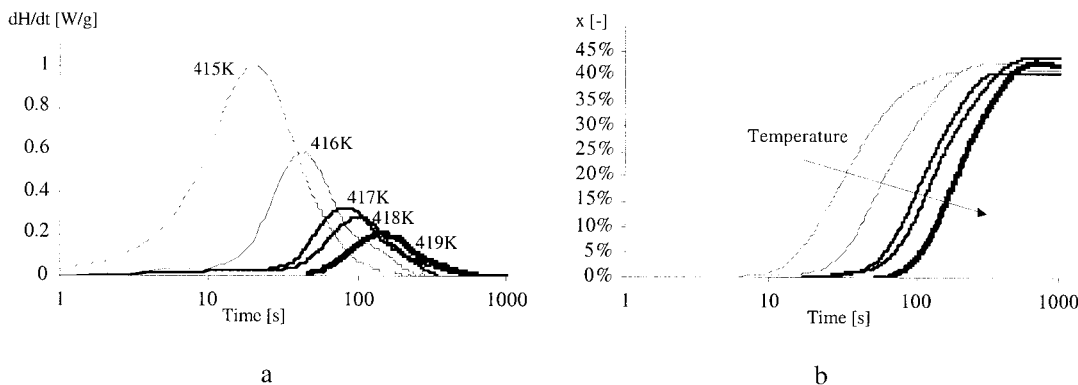


Figure 3 Calorimetric curves obtained during isothermal analysis at different temperatures of samples of PVDF in a DSC apparatus.

equilibrium value) increase with the temperature of the isothermal test [Fig. 3(b)].

Quenching of thin samples

A procedure of analysis was already presented elsewhere⁵ and was adopted to carry out the characterized solidification quenches of thin molten polymer films. The thermal history experienced by the sample was measured during the quench using a thin thermocouple connected to a fast data acquisition system.

Before each quenching test, samples were kept in the temperature-controlled chamber of the quenching apparatus at 503 K for 30 min and then cooled to room temperature. The detected cooling rate decreased during the test with the decreasing temperature: This is consistent with the cooling procedure as also is the difference between the sample temperature and the temperature of the cooling medium which decrease with the temperature decrease. The cooling rate at the temperature of 373 K (close to crystallization temperatures at the cooling rates adopted) was chosen as representative of the quenching effectiveness. According to this choice, the obtained cooling rates ranged from 0.4 to 420 K/s depending on the flow rate and on the nature of the cooling medium (air or water).

Density measurements

The densities of samples solidified in different conditions (either by DSC or during quenching experiments) were measured at 298 K by flotation in solutions of bromoform and carbon tetrachloride. The dependency of the density (measured at 298 K) on the cooling rate is shown in Figure 4. As is evident, the material density after solidification decreases with an increasing cooling rate from a value of about $1.775 \times 10^{-3} \text{ kg/m}^3$ to a value of $1.745 \times 10^{-3} \text{ kg/m}^3$.

ANALYSIS OF RESULTS

The material PVT behavior, as characterized by standard procedures, is accounted for only at low cooling rates. Indeed, the Tait equation normally adopted for the description of the PVT data, apart from some recent manipulations,^{8–10} does not even account for the cooling rate. On the other hand, it is well known that the density of all polymeric materials is determined by the complete thermomechanical history starting from the melt. The effect on the specific volume of the thermal history, experienced during solidification from the melt, is particularly relevant for semicrystalline polymers because this class of materials undergoes partial crystallization during solidification and crystals have densities larger than those of the corresponding amorphous phases. Depending upon the crystallization kinetics, not only is the temperature range over which crystallinity develops dependent upon both the pressure and the cooling rate (as shown by the data reported in Figs. 1 and 2), but also the final crystallinity degree (and thus the final density) is influenced by the thermomechanical history (as shown in Fig. 4). These effects are obviously in

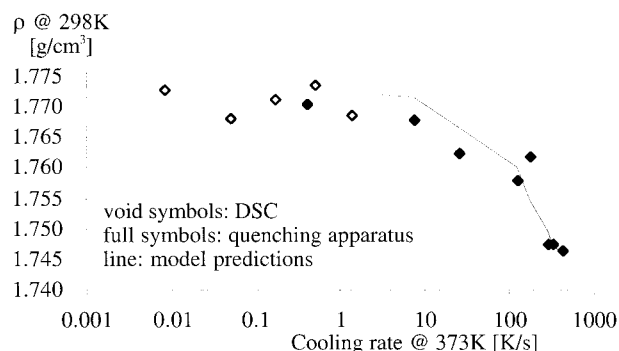


Figure 4 Dependency of the density on cooling rates (measured at 373 K). Measurements (symbols) were taken at 298 K. The line refers to predictions performed by the model.

parallel to the effect of the thermomechanical history on the amorphous phase-density contribution, which, however, has a normally much smaller relevance.

Outside the crystallization range, where the dependence of the density upon the crystallinity becomes linear, as shown in Figure 1, the crystallinity can be considered constant and the analysis of the PVT behavior is simplified; obviously, the crystallization determines the main features of the density evolution inside the crystallization temperature range. Therefore, a reliable description of the PVT behavior must rely on the description of the crystallinity evolution.¹⁻³ Consequently, the analysis of the density evolution will be split here into three parts:

1. Linear combination of densities of amorphous and crystalline phases into the polymer density.
2. Description of the specific volume behavior outside the temperature range where crystallization takes place, that is, the fitting of isobaric cooling data as reported in Figure 1 at high and low temperatures.
3. Description of the crystallization kinetics and of the specific volume behavior of the material also in the crystallization range on the basis of both the density of quenched samples and some features of the calorimetric thermograms.

Contribution of phases to specific volume

For the purpose of determining the volume dependence upon the thermomechanical history, it is sufficient to consider only one crystalline phase. Under this simplification, an overall crystallinity degree can be calculated using the following equation:

$$x = (\rho - \rho_A) / (\rho_C - \rho_A) \quad (1)$$

where ρ_A , ρ_C , and ρ are the amorphous, crystalline, and total densities, respectively.

The material density, as a function of the pressure, temperature, and crystallinity degree, can be thus written as

$$\rho(T,P,x) = \rho_C(T,P)x + \rho_A(T,P)(1-x) \quad (2)$$

To a first approximation, the dependencies of amorphous and crystalline densities upon temperature and pressure can be described as

$$\rho_A(T,P) = \rho_A^0 (1 - \alpha_A (T - T^0) + \beta_A P) \quad (3)$$

$$\rho_C(T,P) = \rho_C^0 (1 - \alpha_C (T - T^0) + \beta_C P) \quad (4)$$

TABLE I
Volumetric Parameters for PVDF MP10
to be Used in Eqs. (1)–(4)

	Units	Value
T^0	K	298
ρ_A^0	g/cm ³	1.68
ρ_C^0	g/cm ³	1.9
α_A	1/K	6.50×10^{-4}
α_C	1/K	4.00×10^{-4}
β_A	1/MPa	6.10×10^{-4}
β_C	1/MPa	1.00×10^{-4}

where T^0 is a reference temperature and ρ_A^0 and ρ_C^0 are specific volumes of the amorphous and crystal phases, respectively, at $T = T^0$ and $P = 0$.

The values of the parameters of eqs. (3) and (4) were found by a best fit of the calorimetric and density results. In particular, schematically, the following steps were made:

- (a) ρ_C^0 , α_A , and β_A were identified by the description of the density data at high temperatures (from Fig. 1): For temperatures above the transition zone (i.e., $T > 450$ K), the volumetric curves of PVDF found from eq. (2) with $x = 0$ [i.e., from eq. (3)] should be able to describe the experimental data of the PVDF melt as given in Figure 1.
- (b) ρ_C^0 , α_C , and β_C were identified by the description of the density data at low temperatures (i.e., below 370 K) shown in Figure 1 and of the density measurements of the samples solidified in the DSC apparatus (of which the crystallinity degree had been identified by calorimetry to be about 42%).

Values of the reference densities, thermal expansion coefficients, and compressibilities, obtained as described above, are reported in Table I and are reasonably close to those reported in the literature.⁸ It is worth pointing out that a density for the crystal phase of 1.9 g/cm³ would suggest that the α -form is present mainly in samples solidified at low cooling rates (10 K/min), the β -form being much heavier (1.97 g/cm³). This is normally the case in PVDF samples solidified from the melt, when a low percentage of constitutive defects are present.¹¹

The high- and low-temperature descriptions identified above, that is, those related to the parameters reported in Table I, are shown in Figure 5, with reference to the lowest and highest considered pressures, namely, 0.1 and 120 MPa, together with the density evolution of the amorphous and crystalline phases. The comparison with the data, shown in the same figures, is satisfactory both in the high- and in the low-temperature limits.

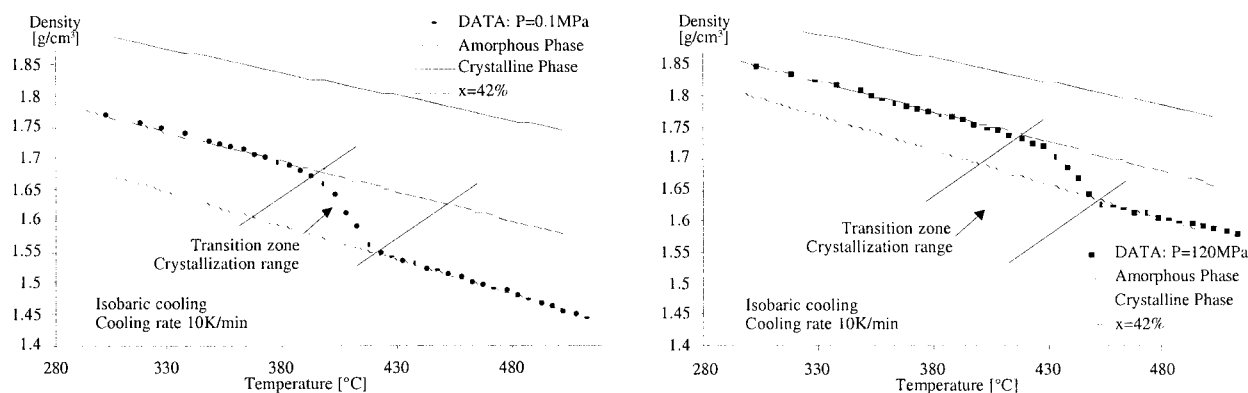


Figure 5 High- and low-temperature descriptions of the density of the PVDF. Densities of amorphous and crystalline phases [as described by eqs. (3) and (4)] are also shown.

The density description in the transition temperature range is related to the crystallization and its kinetics. This will be considered in the next section together with calorimetric results and densities of the quenched samples as functions of the quenching cooling rates.

Crystallization kinetics

As mentioned above, PVDF is a polymorphic material, and in the wide range of cooling rates analyzed in this work, it should be expected that different crystalline phases can develop. However, the main goal of this work was to describe the PVT behavior: To this purpose, it is sufficient to consider the presence of only one equivalent crystalline phase. Crystallization kinetics will be considered here mainly with reference to calorimetric results and densities of quenched samples as functions of the quenching cooling rates, and it is expected that details of the crystallization kinetics will not be captured by the model. The PVT description in the crystallization temperature range, reported in Figure 1, will be considered at the end as a check of the model identified.

The crystallization kinetic model adopted here is the nonisothermal formula due to Nakamura et al.¹² of the Avrami–Evans model, which can be written as

$$x = xe \left(1 - \exp\left\{ - \ln 2 \left[\int_0^t K(T) dt \right]^n \right\} \right) \quad (5)$$

where xe is the equilibrium crystallinity value (here taken to be constant with the temperature); n , the so-called Avrami index; and $K(T)$, the kinetic constant, which, according to eq. (5), is equal to the reciprocal of crystallization half-time when the temperature is constant. $K(T)$ is a bell-shaped curve having a maximum

between the melting temperature, T_m , and the glass transition temperature, T_g . The equation

$$K(T) = K_0 \exp\left(\frac{-4 \ln 2 (T - T_{\max})^2}{D^2} \right) \quad (6)$$

which is symmetric with respect to the temperature of the maximum, T_{\max} , is often adopted for $K(T)$. D and K_0 are the half-width of the Gaussian curve and the maximum value reached, respectively. Obviously, eq. (6) holds below the melting temperature T_m , which is 438 K, as mentioned above.

The effect of the pressure on the crystallization kinetics can be taken into account by assuming that

$$T_{\max} = T_{\max}^0 (1 + \gamma P) \quad (7)$$

Under constant cooling rates, eq. (7) describes a rigid shift of the crystallization range toward higher temperatures with increasing pressure, as described by the PVT data reported in Figure 1. The value of the parameter γ can be thus taken as 0.25 K/MPa, as shown by the PVT data reported in Figure 1.

The evolution of crystallinity for any of the experimental tests can be evaluated by coupling eqs. (5)–(7) with the proper thermal history. The following experimental features will be considered as references for the identification of the kinetic parameters:

TABLE II
Values of the Parameters for Crystallization Kinetics Model [Eqs. (5)–(7)]

xe [–]	42%
n [–]	0.35
K_0 [1/s]	148.4
D [K]	22
T_{\max}^0 [K]	376.3
γ [K/MPa]	0.25

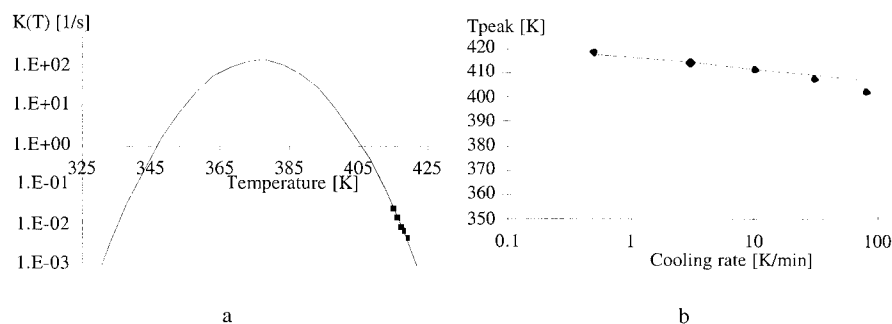


Figure 6 (a) Kinetic constant as expressed by eq. (6) with parameters listed in Table II. Experimental data refer to the reciprocal of the crystallization half-time, drawn from curves depicted in Figure 3; (b) description of the peak of calorimetric curves during DSC ramps at different cooling rates, performed using the parameters listed in Table II.

- (i) The curve of crystallization half-times during the calorimetric isothermal tests as a function of temperature;
- (ii) The temperatures of the peaks during calorimetric cooling ramps; and
- (iii) The final densities [linked to crystallinity by means of eq. (2)] of the solidified samples, either using DSC or the quenching apparatus.

The five parameters (χ_e , n , K_0 , T_{\max}^0 , D) of the crystallization kinetic model were optimized with the objective of describing the data mentioned above all together. The values of the parameters obtained by this optimization are reported in Table II. A low value of the Avrami index n is normally found when kinetic parameters of eqs. (5) and (6) are tuned on the basis of data referring to a wide range of cooling rates.^{5,13,14} This is mainly because different phases, nucleation rates, and growth regimes are considered simultaneously by a limited number of kinetic parameters, which, therefore, lose part of their physical meaning.

A comparison between model predictions and the chosen features of the calorimetric data (both the crystallization half-time during the calorimetric isothermal tests and the temperature of the peak as a function of the cooling rate in the calorimeter) is shown in Figure 6; since, when the temperature is constant, $K(T)$ is equal to the reciprocal of the crystallization half-time, the latter is reported in the plot of $K(T)$, shown in Figure 6(a). A comparison of the crystallinity evolution during the calorimetric cooling ramps is also reported in Figure 2(b) (gray lines).

The final specific volume of the solidified samples compares satisfactorily, in Figure 4, with the model predictions over about five orders of magnitude of the cooling rate change. The kinetics identified gives a reasonable description of the very wide and diversified set of data, including results of the analysis of samples solidified under cooling rates of a few hundreds Kelvins/seconds.

Calculations of the specific volume evolution under arbitrary solidification conditions can be performed

by coupling the thermal history with eqs. (2)–(4) and (5)–(7). Evolution during the cooling ramps at 10 K/min under different pressures, calculated adopting the parameters reported in Tables I and II, are compared with the experimental data in Figure 7. For all pressures, the calculated transition takes place at higher temperatures with respect to the experimental data and is slightly sharper. This is known to be due to the presence of a thermal gradient inside the sample during PVT measurements.² The comparison is thus satisfactory, confirming the consistency of the applied method.

Of course, using the model applied in this work, it is possible to describe the material density evolution during cooling at an arbitrary cooling rate. This is shown in Figure 8, with reference to solidification under room pressure at cooling rates ranging from those reachable in a DSC apparatus to those encountered during processing.

Indeed, consistent with the data reported in Figure 2, as cooling rates increase, crystallization (and thus density changes) takes place over a wider temperature interval. A peculiarity of the method applied in this work is that it naturally predicts the reduction of the final density on an increasing cooling rate (consistent with data reported in Fig. 4), whereas PVT equations of state (and their modifications), even if accounting for the effect of cooling rate and pressure on the transition zone, neglect that phenomenon¹⁰ or assume a specific volume corrected for high pressures and high cooling rates.¹⁵ It should be mentioned that if parameters of the kinetic equations are tuned only on standard (calorimetric) data, the extrapolation to cooling rates of the order of those experienced by the polymer during processing can lead to incorrect results.⁵

The evolution of crystallinity during solidification of the quenched samples would, of course, be a very valuable piece of information to identify details of crystallization kinetics and thus of the total density evolution in process conditions. Unfortunately, at the moment, apart from some attempts,¹⁶ cooling ramps at these cooling rates are not available to experimental

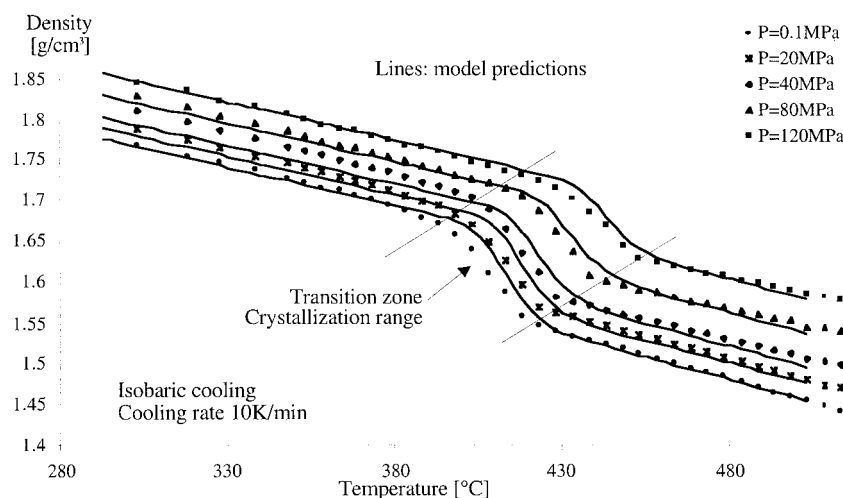


Figure 7 Description of PVT data of PVDF performed of coupling thermal histories with eqs. (2–4) and (5–7). Symbols refer to data reported in Figure 1.

real-time observation and the analysis of the effect of high cooling rates can only rely on results of a final density analysis.

CONCLUSIONS

A procedure of analysis was suggested to describe the PVT behavior of a fluorinated polymer over a wide range of cooling rates and pressures. The experimental procedure is based on the combination of the specific volume of amorphous and crystalline phases into the specific volume of the polymer, the description of specific volume behavior outside the temperature range where crystallization takes, and the modeling of crystallization kinetics.

Standard PVT data at high and low temperatures allowed us to identify thermal expansion coefficients and the compressibility of amorphous and crystalline

phases. The crystallization kinetics and the specific volume behavior of the material (also in the solidification temperature range) were analyzed and described on the basis of both the density of the quenched samples and some features of the calorimetric thermograms. In particular, polymer crystallization kinetics was described by the nonisothermal formulation due to Nakamura et al. via the Avrami–Evans model, whose parameters were identified on the basis of a very wide and diversified set of data, including results of the analysis of samples solidified under cooling rates of a few hundreds Kelvins/second. Following this path, a complete description of polymer PVT behavior over an extremely wide range of cooling rates and pressures was obtained.

Using the model applied in this work, it was possible to describe the material density evolution during cooling under cooling rates and pressures of interest

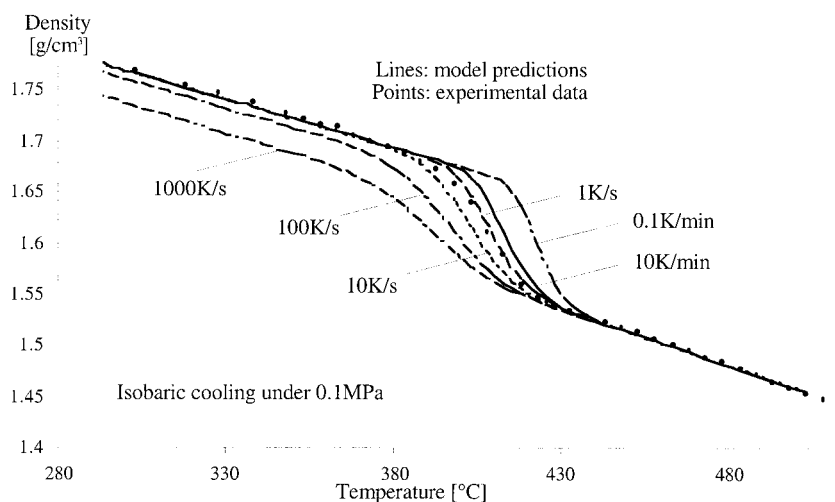


Figure 8 Density of PVDF during solidification at different cooling rates and under room pressure. Symbols refer to PVT data reported in Figure 1.

for polymer processing. It was shown that the model applied in this work naturally predicts the reduction of the final density with an increasing cooling rate, whereas PVT equations of state (and their modifications), even if accounting for the effect of cooling rate on the transition zone, neglect the phenomenon.

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