NOTE

Maintaining Hydrostatic Conditions During Solidification of Polymers in a High-Pressure Dilatometer

INTRODUCTION

Pressure–volume–temperature (PVT) measurements have established themselves as a useful technique for polymer physical studies.[1,2] Their utility lies in the inclusion of pressure as a variable and in the highly quantitative nature of the results. Equations of state of equilibrium liquids (melts, solutions) can readily be obtained by a variety of techniques,[2,3] although the accuracy of the different techniques is not uniformly excellent. When measurements in the solid state are desired, or transitions from a liquid to the solid state (glass formation, crystallization) need to be studied, all known techniques are unable to maintain a hydrostatic state of stress on a sample as it solidifies.[4] We wish to point out, however, that PVT equipment using the "confining-fluid" principle (see below) can measure the solid-state PVT properties of a solid sample prior to its first melting. Here we report on a very simple modification to the confining-fluid PVT technique, which is able to maintain hydrostatic pressure during solidification and in the solid state itself.

There are two principal techniques[2,3] used for obtaining PVT relationships of polymers: the confining-fluid method and the "piston" method. In the latter (see Ref. 5 for a representative example), a polymer is placed in a closed cylinder, and a "pressure" is applied to it by a piston from one end. Volume changes are calculated from the motion of the piston. Before measurements can begin, solid polymers must be melted in order to fill the space in the cylinder completely. This can only be done for thermoplastics and erases the structure and formation history of the sample, which is normally undesirable. For a melt (or another liquid sample), there are no objections in principle to using this technique. When a sample solidifies by crystallization or glass formation, on the other hand, the state of stress in the solid sample is no longer hydrostatic, and the motion of the piston (if indeed it does not get stuck in place by the solidifying melt) is no longer a measure for the volume changes under hydrostatic pressure. We have analyzed this situation mathematically.[4] There are also significant practical problems (friction and leakage), which make data obtained from this technique (even in the melt) much less accurate than those obtained using the confining-fluid technique.

The PVT technique preferred by us,[6] and realized in a commercial machine,[7] involves using a confining fluid to surround the sample. The confining fluid is usually mercury, but oils, water, and other fluids can and have been used. The role of the confining fluid is to provide a hydrostatic state of stress even for a solid sample. The motion of the bellows is used to calculate volume changes of the sample, making use of the known PVT properties of the confining fluid. The bellows motion is not subject to friction, and there is no leakage past it, thus avoiding the shortcomings of the piston method. The confining-fluid technique clearly allows the measurement of the PVT properties of a sample in the (solid or liquid) state in which it was filled into the cell, as well as measurements in the melt.

When a sample melts in the piezometer cell of the GNOMIX PVT apparatus, it generally collects at the top or bottom of the cell, depending on the sample density relative to that of the confining fluid. If mercury is the confining fluid, the melt rises to the top of the cell and forms a "melt" plug against the end piece of the piezometer cell. As the melt is cooled and solidifies, one ends up with a situation very similar to that in a piston PVT apparatus, insofar as mercury generally does not surround the sample completely any longer, but rather presses on it from one side, a situation functionally identical to using a piston. In addition, the solidified sample might adhere to the cell walls, constraining the volume change and leading to elastic or inelastic deformations of the piezometer cell itself, further complicating the situation.

MAINTAINING HYDROSTATIC PRESSURE DURING COOLING AND IN THE SOLID STATE

In the following, we will discuss a very simple modification to the confining-fluid PVT technique that makes it possible to keep a sample under hydrostatic pressure at all times during solidification and in the solidified state itself.

The technique we have developed involves placing a solid sample (in the form of pellets, pieces of a molding, etc.) inside an open cup formed of thin nickel foil. When the sample pieces melt, they coalesce to form a melt plug against the end of this cup, rather than against the walls of the (rigid) piezometer cell. As the sample solidifies, hydrostatic pressure surrounds this sample cup at all times, and because of the very thin foil used to form the cup, the

sample is also subjected to (very nearly) hydrostatic pressure.

Naturally, the material used to surround the sample must be inert to the confining fluid used. Mercury is the most common fluid used, and aluminum or tin foil are not suitable for use with mercury because they readily form alloys with mercury. We found 0.001 in. (0.025 mm) thick nickel 200 foil to be an excellent material for our purpose. It can be formed into a cup by folding, very much like the familiar aluminum foil, is readily available at reasonable cost, and has very low solubility in mercury (less than 5 × 10^{-3} wt % to 400°C).[8]

We pre-form the open sample cup by wrapping the nickel sheet around a mandrel with a diameter about 1 mm less than the sample cell, and folding over one end to form the bottom of a cup. The nickel cup is placed into the piezometer sample cell, and the sample is placed into the nickel cup. The sample cell is vacuum-filled with mercury in the usual manner. Mercury occupies all free space in the piezometer cell (including the free space in the sample cup). Using a nickel sample cup offers the additional advantage that the cleanup procedure is much simplified: Instead of the sample sticking to the piezometer wall, and needing to be dissolved or burned off, it is neatly packaged in its nickel cup, which simply drops out of the piezometer cell when it is opened.

The commercial GNOMIX PVT apparatus has a provision in its data acquisition and control software to make automatic corrections to the calculated sample volume for the presence of a "second material" in the cell. All that
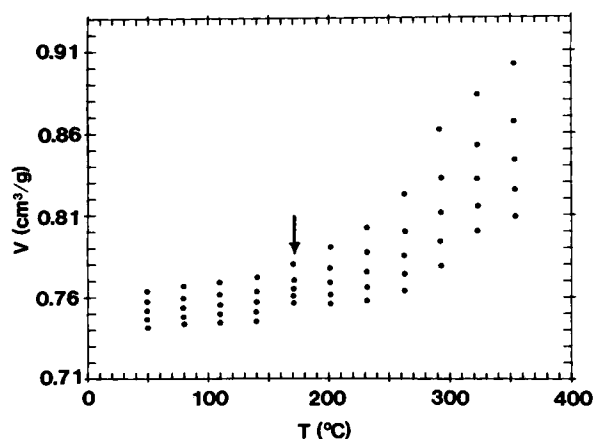
Figure 1   PVT data of a poly(aryl ether ketone) polymer taken without the use of a nickel sample cup. Isotherms were measured from high to low temperatures. Points along each isotherm are plotted in 50-MPa increments from 0 to 200 MPa. The arrow points to the file that is obviously affected by adhesion to the cell and/or non-hydrostatic pressure conditions. Closer analysis (in comparison to the data in Fig. 3, for which a sample cup was used) reveals that isotherms at higher temperatures (but already in the solid state) are also affected, but less obviously so.
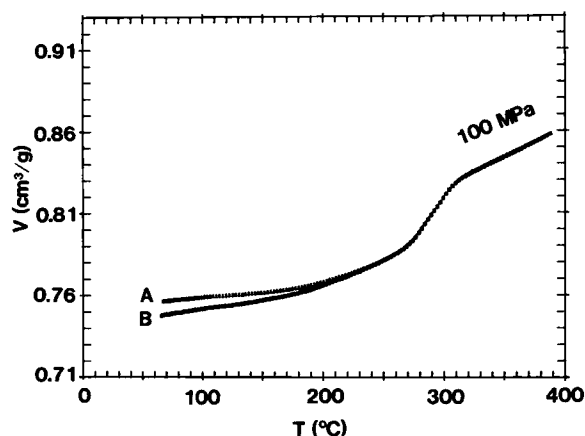

Figure 2   Isobaric cooling data (rate: 2.5°C/min) at a pressure of 100 MPa. Curve A without, curve B with, a nickel sample cup. The data shows very good agreement in the melt and transition region, but in the solid state it is clear that the sample not placed in the sample cup is not completely free to shrink.

is required is an expression for the PVT properties of the second material (in this case nickel), which is entered into a file in a prescribed format. Based on literature values of the bulk modulus[9] and the thermal expansivity[10] of nickel, we developed the following expression for its specific volume:

$$V_{Ni}(P, T) = 0.1124 + 0.472 \times 10^{-5}T - 0.555 \times 10^{-6}P$$

(volume in cm^3/g, P in MPa, T in °C). For a typical nickel cup (0.25 g), this expression adds very small corrections (less than 0.0005 cm^3/g) to the sample volumes that would be calculated without it.

We will demonstrate the performance of this modified technique using measurements on a sample of a high melting thermoplastic material from the family of poly(aryl ether ketones). Figure 1 shows data obtained along a series of isotherms without using a nickel sample cup. Starting at about 370°C, data were recorded along isotherms spaced about 30°C apart, at pressures from 10 to 200 MPa in increments of 10 MPa. Data are plotted in Figure 1 in intervals of 50 MPa only, in order not to crowd the picture. The two highest isotherms are clearly in the melt; the third shows crystallization occurring during its measurement. Once the sample is in the solid state, an obvious irregularity occurs at the isotherm marked by an arrow. The volume change along this isotherm is much smaller than along the next lower one, or the next higher one. We believe that this is due to the influence of non-hydrostatic pressure and adhesion of the sample to the cell wall. The volume change goes back to what is apparently a more normal value in the isotherm just below the marked file. This can be explained by the assumption that the sample plug released from the wall at this point and started shrinking and responding to pressure more freely. Although it is not immediately obvious from Figure 1, a
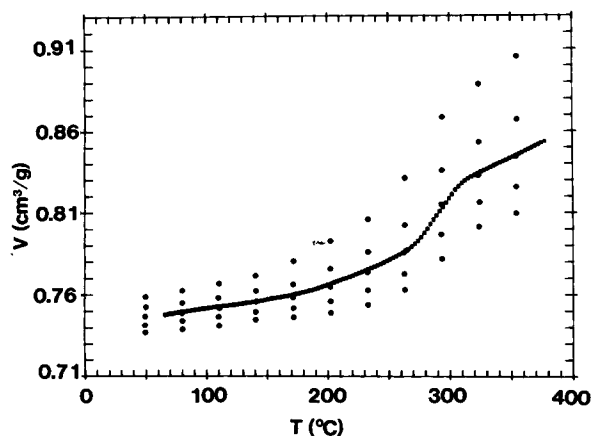
Figure 3 Solid circles: PVT data of poly (aryl ether ketone) polymer, taken under the same conditions as the data in Fig. 1, but using a nickel sample cup. Also shown is a cooling isotherm at 100 MPa (line B from Fig. 2). No anomalies are seen, and the isothermal and isobaric data agree, not only in the melt regions (as they should) but also in the solid state.

detailed comparison with data taken using a sample cup (see Fig. 3) reveals that the apparent compressibility along the other isotherms in the solid state above the marked file is also lower, while the agreement in the melt is excellent, as it should be. We have observed similar effects in a variety of materials, but not in all. According to the mathematical treatment,[4] the ratio of the shear relaxation modulus of the material to its bulk modulus determines the magnitude of the volume changes measured in uniaxial (constrained) compression, but adhesion (not considered in Ref. 4) also plays an important role.

Next we will discuss isobaric cooling runs at 2.5°C/ min and P = 100 MPa, starting from the melt at about 390°C. In Figure 2, curve A was obtained without, curve B with, a nickel cup. It may be noted that the data from both runs superimpose perfectly in the melt, as they should, and through the crystallization region. It is only below the crystallization region that curves A and B separate, presumably as the shear modulus increases rapidly, and adhesion to the cell wall becomes a factor. Curve B (with nickel sample cup) is lower than curve A, indicating that the sample not enclosed in a nickel sample cup was not able to shrink freely and assume its full volume change. In some runs without a sample cup, we have occasionally seen a sudden drop in volume, which we now interpret as a transition from curve A to B, coinciding with the sudden breaking free of the sample from the piezometer walls (subjecting it to hydrostatic pressure once again).

Finally, Figure 3 shows another series of isotherms. The conditions were the same as for the run in Figure 1, except that a nickel sample cup was used. The anomaly seen in Figure 1 is now absent, and when we superimpose the corresponding cooling isobar (curve B from Fig. 2), we get excellent agreement between isothermal and isobaric data both in the melt and in the solid state. We

would like to point out, however, that data in the solid state obtained isobarically and isothermally are not necessarily expected to superimpose, since different formation histories (solidification pressures, cooling rates, etc.) may very well lead to different solid states, having different volumes.

In conclusion, these newly refined PVT techniques enable us to expand the scope of our PVT studies to the solidification process under strictly hydrostatic pressures (to 200 MPa). Examples of work in progress include studies of the effect of formation pressure on the volume of glassy polymers, and studies of the dependence of crystallization kinetics on pressure.

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