Specific Volume of Molten Thermoplastic Polymer Composite at High Pressure

Y. Z. WANG,[1] W. J. CHIA,[2] K. H. HSIEH,*[,2] and H. C. TSENG[3]

[1]Institute of Materials Science and Engineering, National Taiwan University, Taipei, Taiwan 10764, Republic of China, [2]Department of Chemical Engineering, National Taiwan University, Taipei, Taiwan 10764, Republic of China, [3]Department of Chemical Engineering, National Taiwan Institute of Technology, Taipei, Taiwan 10772, Republic of China

SYNOPSIS

The specific volume of thermoplastic polymers and composites with glass fiber have been measured at high pressure, up to 2000 kg/cm^2, in the molten state by a dilatometer. The specific volume and thermal expansion coefficient of the melts increase with increasing temperature at a constant pressure and decrease with increasing pressure at a constant temperature. The data of specific volume of molten polymers were satisfactorily fitted to an empirical equation of state based on the Tait equation. Furthermore, it is found that the data of specific volume of molten composites were suitably fitted by an additive rule of Tait equation from the volume fractions of specific volume of polymers and the glass fiber in composites. The thermal expansion coefficients of molten polymers and composites are approach to the derivative values of the Tait equation and the additive Tait equation, respectively.

INTRODUCTION

Polymers reinforced with glass fiber are a useful technique to improve mechanical properties of thermoplastic polymer materials. Injection molding used for polymer processing increases the product amount and reduces the product price. The choices of suitable processing conditions for injection molding are essential to obtain optimum properties. The computer-aided design of injection molding is a powerful tool. However, computer simulation of injection molding needs a large amount of quantitative equations relating to polymer physical properties. Hence, pressure–volume–temperature (PVT) properties of polymers and composites will be helpful for the computer-aided design of injection molding.

Equations of state provide us with a suitable quantitative description of molten polymer systems and valuable thermodynamic information to predict other important thermolphysical properties. Up to the present, there have been some equations of state including theoretical model and empirical equations reported in the literature.[1-18] The widely used theoretical equation of state on polymer liquid systems are the Flory–Orwoll–Vrij (FOV) equation, the lattic fluid theory of Sanchez and Lacombe (SL), and the Simha and Somcynsky (SS) hole theory. These theoretical model derivations are based on the cell model of Prigogine.[1] The SS hole theory has been successful in predicting the PVT relation of single and multiconstituent fluids and has also been applied to the polymer and compatible polymer blend systems.[19-21] Recently, Nies and Stroeks defined the external contact fraction, which is different from the SS site fraction, to modify the hole theory of polymer liquids and succeeded in describing the influence of pressure on phase diagrams.[22,23] In empirical equations, the Spencer–Gilmore equation, the Hartmann–Haque equation, and the Tait equation are proposed. Among these equations, the SS equation and Tait equation are most widely used. The former is composed of two relative equations and solved by the aid of numerical method. The latter is feasible to derive. The Tait equation is expressed as follows:

$$V_p(T, P) = V_p(T, 0)\{1 - C(T)\ln[1 + P/B(T)]\}$$

$$V_p(T, 0) = V_0 \times \exp(\alpha_0 \times T)$$

$$B(T) = B_0 \times \exp(-B_1 \times T)$$

$$C(T) \cong 0.0894 \qquad (1)$$

where $V_p(T, P)$ is the specific volume of polymer at T and P, $V_p(T, 0)$ is the specific volume of polymer at T and $P = 0$, and V_0, α_0, B_0, and B_1 are parameters.

Among the measurement methods of the specific volume during high pressure reported in the literature, the dilatometer method is the most popular. In the present study the dilatometer based on the design published in the literature has been developed and employed to measure the specific volume of polymers and their composites at high temperature and pressure.[5,24]

Polymers have much larger thermal expansion coefficients than glass fiber. The mismatch in the coefficients of thermal expansion of the component making up a composite produces several important characteristics, particularly in the mechanical properties. Many equations there have been proposed to calculate the thermal expansion coefficients of composites from the components of formed composites. The various equations always predict quite different values for a given composite. The Kerner equation, the Thomas equation, or the "rule of mixture"[25] are often adopted.

This paper will focus on the factors that influence the specific volume and thermal expansion coefficient of polymers and their composites, such as temperature, pressure, and filler content. Furthermore, the quantitative description of thermal expansion coefficients of the polymers and composites will also be suggested in the paper.

EXPERIMENTAL

Materials and Sample Preparation

Isotactic polypropylene (i-PP) (Yung Chia Chem. Ind. Co.), poly(methyl methacrylate) (PMMA), nylon 6, nylon 6,6 (Taiwan Nylon Ltd. Co.), and glass fiber (Ta Lai Glass Co.) were mainly used as testing materials. The above polymers were dried approximately at 80°C in a vacuum oven. The nylon 6 and nylon 6,6, were compounded twices with various amount of untreated glass fiber through a twin screw extruder to prepare the composites. The spec-

imens (about 1–3 g) for the PVT measurements were cut into pellets.

Measurements of Specific Volume

The PVT measuring technique has been described in detail.[26-29] The samples of polymers or their composites were immersed within a high pressure cell with full of mercury. The system was then evacuated to remove the air in the cell. In the period of testing, the isothermal mode was adopted. The specific volume measurements were performed at a pressure increment of 500 kg/cm². The volume changed due to increased pressure at each isothermal mode could be calculated from the change of the height level of the mercury in the central channel of the cell. The height of the mercury in the central channel was detected by an onset of electric current when the moving mental probe came into contact with the top surface of the mercury in the channel. The glass fiber content in the composite was determined by thermogravimetry (TGA, DuPont 951) from the residue content after heating above 600°C.

RESULTS AND DISCUSSION

In the research, the operation temperature and pressure ranged from room temperature to 300°C and atmospheric pressure to 2000 kg/cm², respectively. Dilatometry data of molten i-PP and the values of the fitted parameters in the Tait equation are similar to the results in the literature.[30]

Figures 1 and 2 show the variation in the specific volume of molten i-PP, PMMA, and molten nylon 6 and nylon 6,6, respectively, with the temperature at a constant pressure. From those results, the specific volume increases with temperature with about a 3–8% increase in the processing temperature at a constant pressure. From molecular concepts, the thermal expansion of molten polymers are explained solely by the change in cell volume according to FOV theory, but the SL theory explains thermal expansion phenomena by allowing empty sites on the lattice while the cell volume is assumed to be constant. Finally, the SS hole theory allows both cell and lattice vacancy expansion and the major part of the thermal expansion is due to holes. Previously, the PVT data of molten PP have been measured and discussed by Zoller and Leute et al. and the scaling parameters based on SS equation are to be obtained.[31] It is found that a satisfactory agreement between experiment and estimated values calculated with the SS or Tait equation ensues in all operation
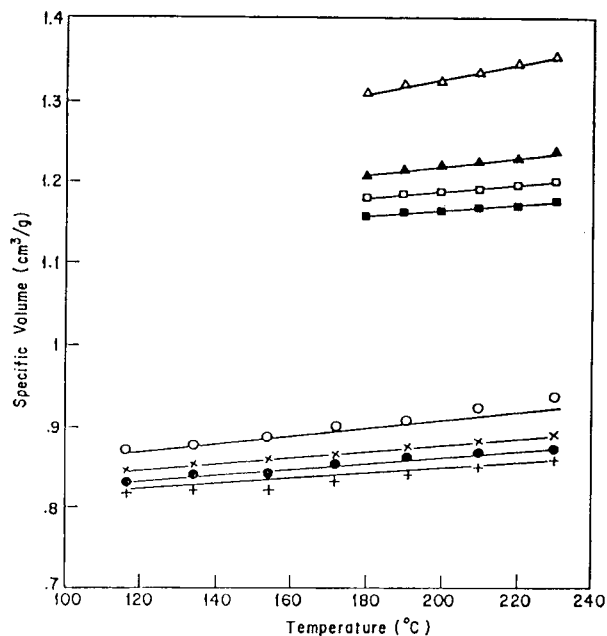
Figure 1 Temperature dependence of specific volume of isotactic polypropylene and polymethacrylate at constant pressure: ($\triangle$) polypropylene at 1 atm; ($\blacktriangle$) polypropylene at 1000 kg/cm^2; ($\square$) polypropylene at 1500 kg/cm^2; ($\blacksquare$) polypropylene at 2000 kg/cm^2; ($\bigcirc$) polymethacrylate at 1 atm; ($\times$) polymethacrylate at 1000 kg/cm^2; ($\bullet$) polymethacrylate at 1500 kg/cm^2; ($+$) polymethacrylate at 2000 kg/cm^2; (——) Tait equation.

Figure 2 Temperature dependence of specific volumes of nylon 6 and nylon 6,6 at constant pressure: ($\bigcirc$) nylon 6,6 at 1 atm; ($\bullet$) nylon 6,6 at 1000 kg/cm^2; ($+$) nylon 6,6 at 1500 kg/cm^2; ($\times$) nylon 6,6 at 2000 kg/cm^2; ($\triangle$) nylon 6 at 1 atm; ($\blacktriangle$) nylon 6 at 1000 kg/cm^2; ($\square$) nylon 6 at 1500 kg/cm^2; ($\blacksquare$) nylon 6 at 2000 kg/cm^2; (——) Tait equation.

conditions. The fitted parameters of molten polymers based on the Tait equation are shown in the Table I. These results from the Tait equation are plotted by solid curves in the above figures. It is found that the Tait equation is accurate enough to describe the PVT relation of the tested specimens. In addition, the quantitative description of glass fiber by polynomial is shown in polynomial form as eq. (2). It is found that the specific volume of glass fiber was hardly influenced by temperature and pressure and was considered as a constant in the discussion and calculation because its solid state existed in the processing conditions:

$$V_g(T, P) = 0.3921 + 1.890 \times 10^{-6}$$

$$\times (T - 25) - 1.0211 \times 10^{-7} \times P \quad (2)$$

The effect of pressure on the specific volume of molten polymers are also shown in Figures 1 and 2. The experimental data show that the specific volumes decrease with pressure at a constant temperature. The specific volume of molten polymers at 2000 kg/cm^2 were about 8–14% smaller than those
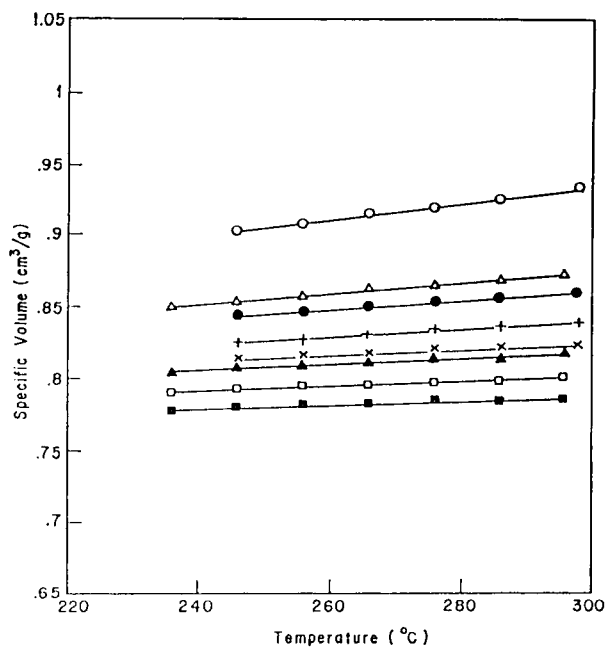
at atmospheric pressure. From Eyring's hole model,[32] with applied pressure, the equilibrium is shifted between the numbers of holes and phonos associated with the liquid lattice. As a result, the number of holes is decreased, i.e., the free volume is decreased by increasing pressure. Therefore, this leads to a decrease in the specific volume. Based on previous concepts, the decrease of specific volume due to increasing pressure is also explained by the decrease of cell volume or hole sizes. Furthermore, it is found that the effect of pressure on specific volume appears more significantly between atmo-

Table I The Parameters of Molten Polymers for Tait Equation

Material	Tait Equation Parameters			
	V_0	α_0	B_0	B_1
i-PP	1.1635	6.599E−4	1505	4.128E−3
PMMA	0.8146	5.231E−4	4362	3.689E−3
Nylon 6	0.7597	4.701E−4	3841	4.660E−3
Nylon 6,6	0.7657	6.600E−4	3226	5.040E−3

spheric pressure and 1500 kg/cm² than that beyond 1500 kg/cm².

Figure 3 shows that the effect of glass fiber content on the specific volume of nylon 6 and nylon 6,6 composites. As shown in the figure, the specific volume of composites is decreased with increasing fiber content. This result is due to the smaller specific volume of glass fiber than of polymers in the composites.

Some studies have investigated the equation of state of polymer blends, such as PPO blending with PS, and some equations have been suggested for this compatible system.[20,21] However, the polymer composites of nylon 6 and nylon 6,6 used in the study are two-phase systems. It is found that the experimental data of the specific volume of the molten polymer composites are well fitted in the study by using a simple additive rule from the volume fractions of the specific volume of polymers and glass fiber in the composites. The additive rule is expressed as eq. (3). As shown in Figure 4, the solid lines show that the specific volumes are calculated according to eq. (3). This simple additive rule being applied well to molten composites is possible due to two reasons: no interaction between polymer and untreated glass fiber and low volume content of glass
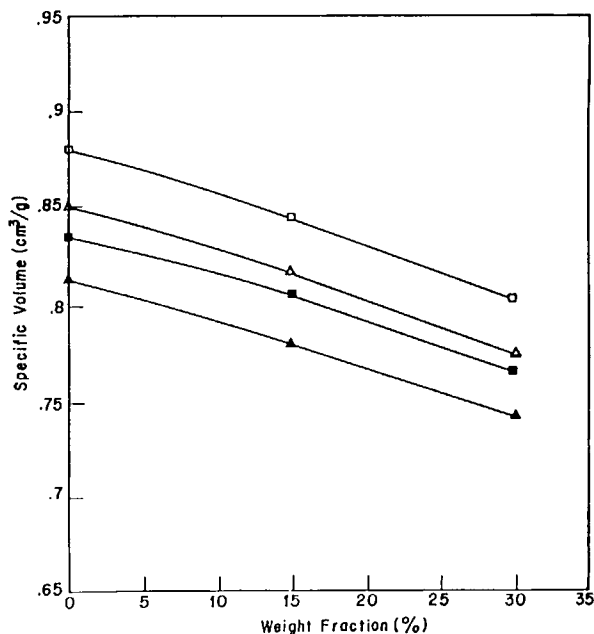

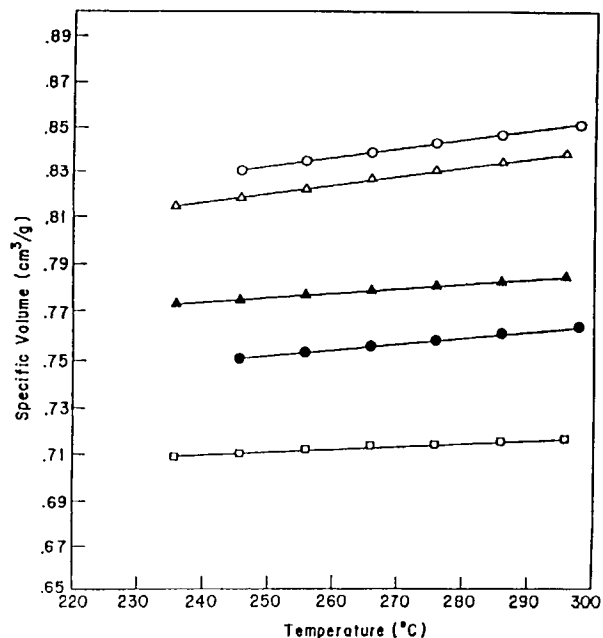**Figure 4** Temperature dependence of specific volume of nylon 6 and nylon 6,6 composites: (△) nylon 6 with 14.94% fiber content at 1 atm; (▲) nylon 6 with 14.94% fiber content at 1000 kg/cm²; (□) nylon 6 with 30.14% fiber content at 2000 kg/cm²; (○) nylon 6,6 with 15.12% fiber content at 500 kg/cm²; (●) nylon 6,6 with 29.95% fiber content at 1500 kg/cm²; (——) by additive rule.

fiber. Therefore, the molten polymer composites can be considered as an ideal condition and the additive rule is suitable for the ideal condition:

$$V_c(T, P) = (1 - \phi_g) \times V_p(T, P)$$
$$+ \phi_g \times V_g(T, P) \quad (3)$$

where $V_c(T, P)$ is the specific volume of molten polymer composite and ϕ_g is the volume fraction of glass fiber.

Analytical equations of state are valuable not only for interpreting purposes for the PVT relationship but also for calculating derivatives. From the first derivatives of volume, the thermal expansion coefficient can be determined. The thermal expansion coefficient is

$$\alpha = (1/V)(\partial V/\partial T)_p \quad (4)$$

From eqs. (1) and (3), these are given by

$$\alpha_p = \alpha_0 - PB_1/([P + B(T)]$$
$$\times \{11.19 - \ln[1 + P/B(T)]\}) \quad (5)$$

Figure 3 Fiber content dependence of specific volumes of nylon 6 and nylon 6,6 composites: (△) nylon 6 at 1 atm and 236°C; (□) nylon 6 at 1000 kg/cm² and 266°C; (■) nylon 6,6 at 500 kg/cm² and 276°C; (▲) nylon 6,6 at 1500 kg/cm² and 286°C.

$$\alpha_c = \left\{ \frac{[(1 - \phi_g) + 2.55 \times (1 - 1/W) \times \phi_g^2 \times \Delta V_{gp}]}{[(1 - \phi_g) \times V_p(T, P) + \phi_g \times V_g(T, P)]} \right\}$$

$$\times \left(\frac{\partial V_p(T, P)}{\partial T} \right)_p + \phi_g$$

$$\times \left\{ \frac{(\partial T_g(T, P)_p / \partial T)_p}{[(1 - \phi_g) \times V_p(T, P) + \phi_g \times V_g(T, P)]} \right\} \quad (6)$$

where, α_p is the thermal expansion coefficient of polymer, α_c the thermal expansion coefficient of composite,

$$\left(\frac{\partial V_p(T, P)}{\partial T} \right)_p = V_p(T, P) \times \alpha_p$$

$$\Delta V_{gp} = V_p(T, P) - V_g(T, P)$$

and W the weight of glass fiber in composite base on unit mass of the composite.

Figures 5 and 6 show that the thermal expansion coefficients based on eqs. (5) and (6), respectively, change with temperature at the isobar. From Figure 5, the experimental results show that the changes of the thermal expansion coefficients of polymers are small and the calculated values by eq. (5) de-
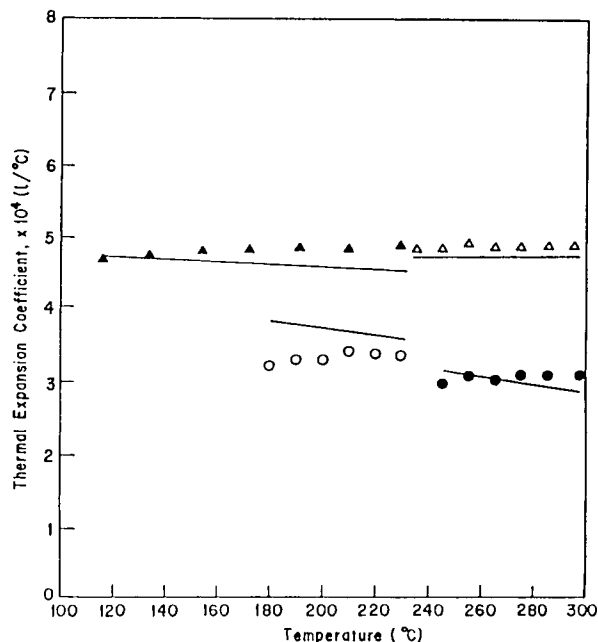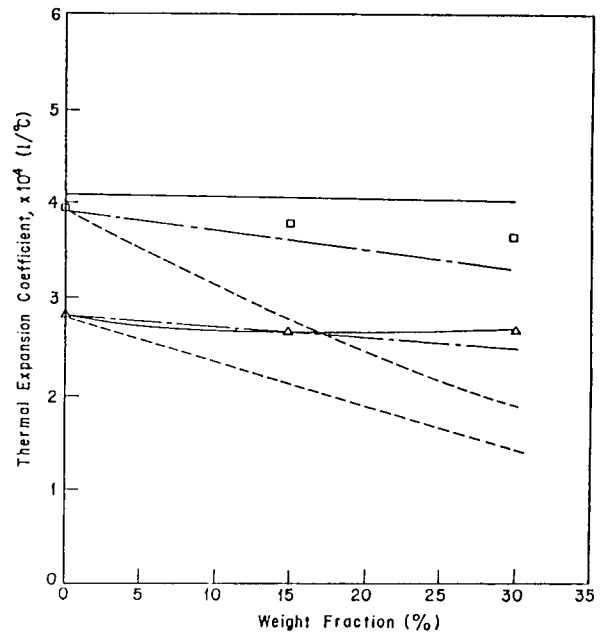

Figure 6 The thermal expansion coefficient calculated by different equations: (△) nylon 6 at 1000 kg/cm² and 256°C; (□) nylon 6,6 at 1000 kg/cm² and 256°C; (———) eq. (6); (– –) eq. (7); (———·) eq. (8).

crease with temperature. The dependence of temperature of the thermal expansion coefficients is due to the second derivatives and changes depending on the variation of specific volume and changing rate of specific volume from eq. (4). The overall changing tendencies with temperature are determined by the competition of the above two factors.

In the literature, some famous quantative equations have been proposed to calculate the thermal expansion coefficients of polymer composites and are expressed as follows:

The Thomas equation:

$$\log \alpha_c = \phi_p \times \log \alpha_p + \phi_g \times \log \alpha_g \quad (7)$$

The "rule of mixtures":

$$\alpha_c = \phi_p \alpha_p + \phi_g \alpha_g \quad (8)$$

If the filler particles are rodlike in shape, and are randomly oriented in three directions, it is believed that the Thomas equation gives a better estimation. Figure 6 shows the different equations for thermal expansion coefficients of the molten polymer composites. It is found that the "rule of mixtures" and eq. (6) are more accurate than the Thomas equation for the randomly dispersed composites containing

Figure 5 Temperature dependence of thermal expansion coefficient at constant pressure: (△) nylon 6 at 1 atm; (▲) PMMA at 500 kg/cm²; (○) *i*-PP at 1500 kg/cm²; (●) nylon 6,6 at 2000 kg/cm²; (———) eq. (5).

rodlike short glass fibers. It is noticeable that the additive rule is not only accurate enough to calculate the specific volume of polymer composites but also suitable to calculate the thermal expansion coefficients of molten polymer through its first derivative.

CONCLUSION

The specific volume of molten polymers and their composites were measured by the self-designed dilatometer. The results show that the specific volume increases with temperature and decreases with pressure or the fiber content. The Tait equation for molten polymers and the additive rule from the fractions of specific volume of two individual components in composites will provide a quantative description of the PVT relationships for the molten polymer composites. The derivation of equations will enable calculation of the thermal expansion coefficients of the molten polymers and polymer composites.

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