

Effect of Compatibility on Specific Volume of Molten Polyblends

Y. Z. WANG,¹ K. H. HSIEH,^{2,*} L. W. CHEN,² and H. C. TSENG³

¹Institute of Materials Science and Engineering, National Taiwan University, Taipei, Taiwan 106, ²Department of Chemical Engineering, National Taiwan University, Taipei, Taiwan 106, and ³Department of Chemical Engineering, National Taiwan Institute of Technology, Taipei, Taiwan 106

SYNOPSIS

The specific volume of polymer blends with different degree of compatibility has been measured at high pressure, up to 2000 kg/cm², in the molten state by a dilatometer. The specific volume and thermal expansion coefficient of the molten homopolymers at zero pressure were satisfactorily fitted to a simplified Simha–Somcynsky equation. The specific volume of styrene–butadiene (SBR) random copolymer, which is considered to be a compatible system, at a constant styrene composition can be calculated by an semiempirical equation based on the Tait equation. The temperature dependence of excess specific volume of SBR with different styrene content at zero pressure was estimated by a combining rule in terms of self- and cross interactions. The concentration-dependent equation is derived to estimate the specific volume of SBR with various styrene contents. Both the thermal and dynamic mechanical analysis of the blend from the two polystyrene (PS) and polybutadiene (BR) homopolymers show a low degree of compatibility. The weight fractions of each domain consisting of PS blending with BR and those of the components in each domain can be calculated from the mass balance on the two domains and the rearranged Couchman equation. The specific volume of PS–BR composed of two phases obeys the principle of additivity from the weight fractions of the specific volume of the corresponding phases. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

In recent years, polymer blends and composites have been studied to elucidate the factors influencing phase behavior of the polymer blends and composites because of their widely technological importance, as a simple method of formulating new materials with tailored properties. Injection molding used for polymer processing increases the productivity and therefore reduces the price of the product. The suitable processing conditions for injection molding are essential to obtain optimum properties. The computer-aided design for injection molding is a powerful tool. However, computer simulation of injection molding needs a lot of quantitative physical properties of the molten materials. Pressure–vol-

ume–temperature (PVT) property of polyblends and composites is one of the physical properties, which are useful for the computer-aided design of injection molding.

PVT equation of state provides us not only a suitable quantitative description of the molten polymer blends and but also a valuable thermodynamic equation to derive other important thermophysical properties, such as excess properties and phase behavior. Up to the present, several equations of state based on theoretical model or empirical equations have been reported in the literature.^{1–18} The widely used theoretical equations on polymer liquid systems are the Flory–Orwoll–Vrij (FOV) equation, the lattice 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 in

* To whom correspondence should be addressed.

application to the homopolymer and compatible polyblend 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} Hamada suggested a mixing rule based on the properties of pure component alone and succeeded in estimating the phase diagrams of polymer blends and polymer solutions.^{24,25} For empirical equations, the Spencer-Gilmore, the Hartmann-Haque, and the Tait equations have been proposed. The Tait equation has been applied successfully to a large number of polymer melts and glasses.²⁶⁻³⁰ Among these equations, the SS equation and Tait equation are widely used. The SS equation is composed of two relative equations and solved by the aid of numerical method. The reduced SS equation has the following form:

$$\tilde{P}\tilde{V}/\tilde{T} = (1 - \eta)^{-1} + (2y/\tilde{T})Q(1.011Q - 1.2045) \quad (1)$$

where $\eta = 2^{-1/6} y(y\tilde{V})^{-1/3}$ and $Q = (y\tilde{V})^{-2}$. The excess free-volume fraction $1 - y$ satisfies the following equation:

$$s/3c[(s-1)/s + y^{-1}\ln(1-y)] = (\eta - \frac{1}{3}) \times (1 - \eta)^{-1} + y/6\tilde{T}Q(2.409 - 3.033Q) \quad (2)$$

The Tait equation is generally written as:

$$V(P, T) = V(0, T) \times \{1 - C(T)\ln[1 + P/B(T)]\} \quad (3)$$

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

$$C(T) \cong 0.0894 \quad (4)$$

where $V(0, T)$ is the specific volume at T and $P = 0$; B_0 and B_1 are parameters.

Among the measurement methods of the specific volume under high pressure reported in the literature, the dilatometer method is the most popular one. In the present study a dilatometer based on the design published in the literature has been developed and employed to measure the specific volume of polymers and polyblends at high temperature and pressure.^{5,31}

The phase behavior of polymer blends can provide information related to the degree of compatibility. Miscible blends have been widely studied; However, only few studies have been developed to determine

the degree of compatibility for the phase-separated polyblend systems. Thermal and dynamical analysis may be the most convenient method to determine the phase behavior of polymer blends. Recently, the technique has been extensively used for some partially compatible polymer blends.³²⁻³⁴ The compatibility of polymer blends can be estimated from the experimental values of glass transition temperature shift (ΔT_g) and heat capacity increment (ΔC_p) by using differential scanning calorimetry (DSC). The glass transition temperature (T_g) of miscible polyblends or random copolymers can usually be described by the following equations:

Wood equation³⁵

$$T_{g,b} = W_1 T_{g,1} + W_2 T_{g,2} \quad (5)$$

Fox equation³⁶

$$1/T_{g,b} = W_1/T_{g,1} + W_2/T_{g,2} \quad (6)$$

Gordon and Taylor equation³⁷

$$T_{g,b} = (W_1 T_{g,1} + \gamma W_2 T_{g,2})(W_1 + \gamma W_2) \\ \gamma = \Delta\alpha_2/\Delta\alpha_1 \quad (7)$$

Couchman equation³⁸

$$\ln T_{g,b} = (W_1 \Delta C_{p,1} \ln T_{g,1} + W_2 \Delta C_{p,2} \ln T_{g,2}) / (W_1 \Delta C_{p,1} + W_2 \Delta C_{p,2}) \quad (8)$$

where Δ denotes transition increments; $T_{g,i}$, α_i , and W_i are the T_g , thermal expansion coefficient, and weight fraction of component i , respectively; $T_{g,b}$ is the T_g of the miscible polyblend or random copolymer.

The blend of PS and BR is an important material, being a widely used impact-resistant plastic. In addition, it serves as a model material for the blending of two linear polymers. Our recent papers³⁹⁻⁴² were devoted to finding some simple and useful quantitative empirical equation to describe thermal physical properties of molten polymers and composites. In our present research, the DSC method is applied to examine the degree of compatibility of polymer blends. Furthermore, this study expands on our previous studies of polymers and their composites to develop a suitably quantitative description of specific volume of polymer blends with different degree of compatibility. The excess specific volume of SBR at zero pressure based on a combining rule will be estimated in the study.

Table I Characteristics and Sources of Materials

	PS	BR	SBR-10	SBR-23.5	SBR-25	SBR-60	SBR-85
<i>cis</i> -1,4 BR	0	96	35	30	30	30	30
<i>trans</i> -1,4 BR	0	2	52	47	47	47	47
Vinyl-1,2 BR	0	2	13	23	23	23	23
SM/BDM	100/0	0/100	10/90	23.5/76.5	25/75	60/40	85/15
M_w	330,000	600,000	650,000	720,000	960,000	820,000	730,000
M_w/M_n	3.38	5.16	5.82	5.72	6.07	6.41	6.04

EXPERIMENTAL

Materials

The primary characterization and sources of polystyrene (PS), polybutadiene (BR), and styrene-butadiene (SBR) samples, which are purified twice with methanol as a nonsolvent, used in our research are provided by suppliers and summarized in Table I. Molecular weights and polydispersities are measured by gel permeation chromatography in tetrahydrofuran (THF) at 22°C.

Preparation of Polymer Blends

Polymer blends were prepared by using a two-roll mill, 0.1-m diameter and 0.2 m length, at a roll surface temperature of 147°C for 20 min and quenched rapidly with liquid nitrogen. The rotation velocity was 10 rpm for both front and back rolls. The polymers were dried in a vacuum oven at 110°C overnight before blending. The compositions of polymer blends by weight ratio are listed in Table II.

Thermal and Dynamic Mechanical Measurements

The T_g 's were determined with a DuPont DSC (Mode 9900). In each run about 15 mg of the samples were used. During each T_g measurement, the quenched sample was heated to 147°C in a nitrogen environment for about 30 min to eliminate the previous thermal history and to reach thermodynamic equilibrium. It was then quenched to -140°C with a liquid nitrogen cooling supply and scanned with a heating rate of 10°C/min from -140 to 250°C. Temperature calibration was performed using *n*-heptane

($T_m = -90.4^\circ\text{C}$) and indium ($T_m = 156.6^\circ\text{C}$). The T_g was also determined with a DuPont DMA (Mode 983) using hot pressed samples (50 × 10 × 30 mm) to measure storage modulus (E'), loss modulus (E''), and $\tan \delta$. The amplitude and frequency were set at 0.2 mm and 0.1 Hz, respectively. The T_g was determined from the peak value of the diagram of E'' against temperature.

Measurements of Specific Volume

The PVT measuring technique has been described in detail elsewhere.^{41,42} The samples of polymers or polymer blends were immersed in a high pressure cell filled with 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 level change 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 metal probe came into contact with the top surface of the mercury in the channel. The specific volume at room temperature was determined with a pycnometer (Model Accupyc 1330).

RESULTS AND DISCUSSION

Degree of Compatibility of SBR and PS/BR Polyblends

The T_g and C_p values of the PS and BR homopolymers were measured by using DSC. The results show that the T_g value of PS and BR is 107 and -98°C, respectively. The heat capacity increment (ΔC_p) value of 0.268 kJ/kg × °C and 0.536 kJ/kg × °C was found from the T_g increment of PS and BR, respectively. Figure 1 shows the specific volume of PS and BR with increasing temperature at at-

Table II Weight Ratio of PS/BR Blends

Polymer Blend	Compositions (Weight Ratio)					
PS-BR	10/90	24/76	40/60	60/40	70/30	90/10

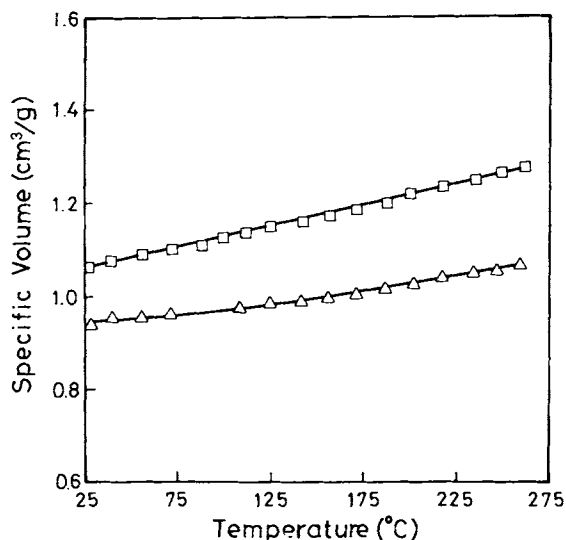


Figure 1 Temperature dependence of specific volume of polystyrene and polybutadiene at atmospheric pressure: (Δ) polystyrene, (\square) polybutadiene.

atmospheric pressure. The thermal expansion coefficient (α) of PS calculated from the slopes of the curve is $5.69 \times 10^{-4} \text{ 1/}^\circ\text{C}$ above T_g and $2.84 \times 10^{-4} \text{ 1/}^\circ\text{C}$ below T_g . For the BR, the α is $6.59 \times 10^{-4} \text{ 1/}^\circ\text{C}$ above T_g . The α of the BR below T_g , found from the literature,³⁵ is $2.0 \times 10^{-4} \text{ 1/}^\circ\text{C}$. The γ value is calculated to be 1.61. The SBR random copolymer is assumed to be a miscible system because of its random arrangement in the chain, and only one T_g was observed. The T_g 's calculated by using Eqs. (5)–(8) for the SBR with various styrene contents are plotted in Figure 2. The T_g 's evaluated by the Couchman equation were found to be in agreement with the experiment results.

It is well known that incompatibility exists for the blend of PS and BR, and therefore two T_g 's were observed. The degree of compatibility of one polymer in another for a partially compatible polymer blend is dependent on the shift values of the two T_g 's of blending polymers related to each component and is defined empirically by the following form:

DC (degree of compatibility)

$$= (T_g^0 - T_{g,b}) / (T_g^0 - T_{g,c}) \times 100\%$$

where T_g^0 and $T_{g,b}$ are the T_g of the homopolymer in pure state and blends, respectively. The $T_{g,c}$ is the T_g , calculated by the Couchman equation, of the miscible polyblend. For PS–BR blend, the T_g 's are shown and the phenomenon implies that two domains in the PS–BR blend existed, that is, PS-enriched domain (PS-rich) with a high T_g (T_{gh}) and

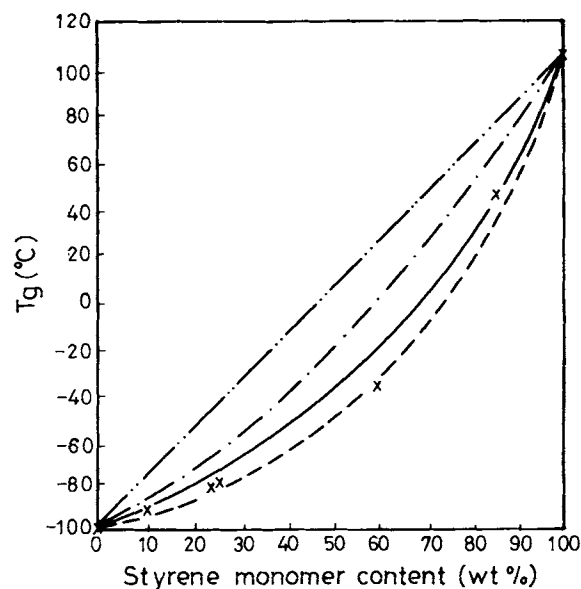


Figure 2 Composition dependence of glass transition temperature of SBR random copolymers with various PS content (wt %): (x) experimental data, (– · –) Eq. (5); (· · ·) Eq. (6); (—) Eq. (7); (– – –) Eq. (8).

the other BR-enriched domain (BR-rich) with a low T_g (T_{gl}). In Figure 3, the T_g 's of PS-rich domain and BR-rich domain as a function of the PS–BR ratio in the PS–BR blend are presented. It is found that the T_g decreases about 2–7°C for the PS-rich domain and increases about 2–4°C for the BR-rich domain as the PS content increased. The tendency of T_g shift of the PS–BR blend measure by DSC or dy-

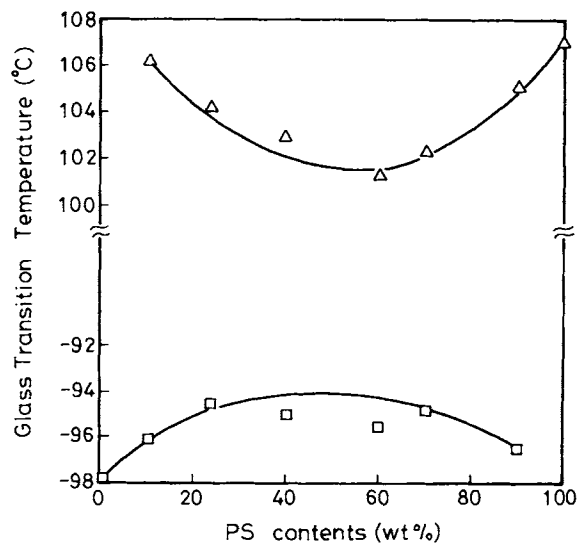


Figure 3 Composition dependence of glass transition temperature of PS–BR blends: (Δ) PS-rich domain (T_{gh}); (\square) BR-rich domain (T_{gl}).

dynamic mechanical analysis (DMA) are quite similar. From the definition described above, the degree of compatibility of PS and BR in the PS-BR blend is calculated and listed in Table III. A low degree of compatibility is found for the PS-BR blends.

Specific Volume of the Polymers

In this research, the operation temperature and pressure ranged from room temperature to 270°C and atmospheric pressure to 2000 kg/cm². Figures 4 and 5 show the variation in the specific volume of molten PS and BR, with temperature, at a constant pressure, respectively. From those figures, it can be seen that the specific volume increases with temperature about 6–12% in the processing temperature at a constant pressure. From molecular concepts, the thermal expansion of molten polymers are solely explained 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. The effect of pressure on the specific volume of molten polymers are also shown in Figures 4 and 5. The experimental data show that the specific volume decreases with pressure at a constant temperature. The specific volume of molten polymers at 2000 kg/cm² were about 4–8% smaller than those at atmospheric pressure. From Eyring's hole model,^{43,44} with applied pressure, the equilibrium is shifted between the numbers of holes and phonons 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. Furthermore, it is found that the effect of pressure on specific volume appears more significantly between atmospheric pressure and 1500 kg/cm² than that beyond 1500 kg/cm².

Fits of various theories were made with the PVT data of PS. We performed a nonlinear least-squares fit of the aforementioned equations. The criterion

Table III Degree of Compatibility of PS/BR Blends

Blend Composition (PS-BR)	DC (PS) (%)	DC (BR) (%)
40/60	2.98	8.01
60/40	4.78	3.41
70/30	5.67	3.75

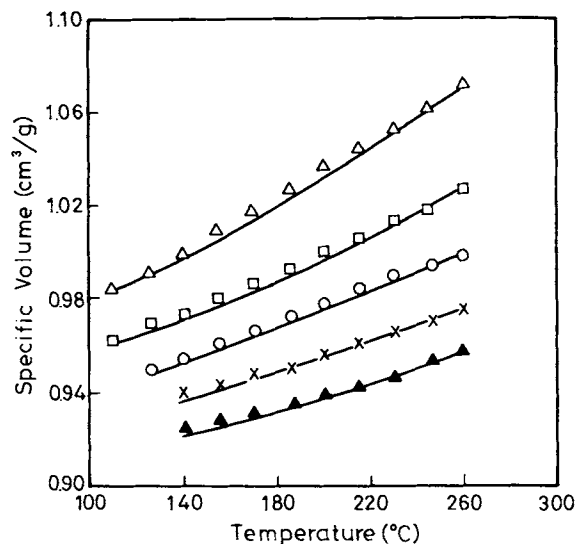


Figure 4 Temperature dependence of specific volume of polystyrene: (Δ) 1 kgf/cm²; (\square) 500 kgf/cm²; (\circ) 1000 kgf/cm²; (\times) 1500 kgf/cm²; (\blacktriangle) 2000 kgf/cm²; (—) Eq. (12).

for choosing a particular function [root mean square (RMS)] is its deviation

$$\% \text{ RMS} = \sum_{i=1}^N \left[\frac{[P_i(\text{exptl}) - P_i(\text{fit})]^2}{N} \right]^{1/2}$$

where $P_i(\text{exptl})$ is the experimental pressure and N is the number of data points. Table IV shows the

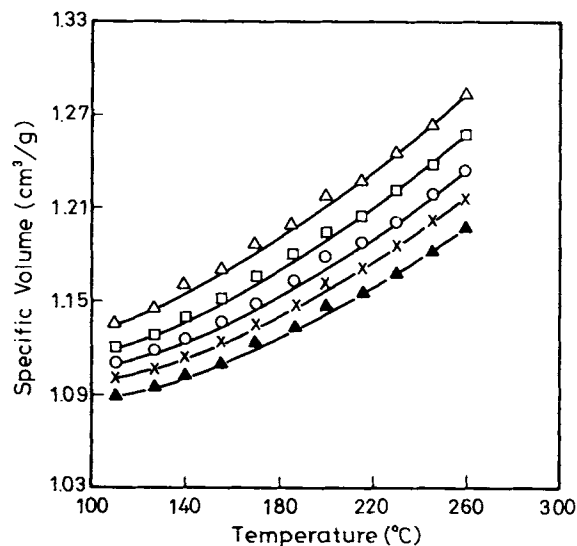


Figure 5 Temperature dependence of specific volume of polybutadiens: (Δ) 1 kgf/cm²; (\square) 500 kgf/cm²; (\circ) 1000 kgf/cm²; (\times) 1500 kgf/cm²; (\blacktriangle) 2000 kgf/cm²; (—) Eq. (12).

Table IV Values of Fit Characteristic Parameters of PS

	P^* (kgf/cm ²)	V^* (cm ³ /g)	T^* (K)	RMS (kgf/cm ²)	T Range (°C)	P Range (kgf/cm ²)
FOV	4843.7	0.8307	8097	3.29	110–260	0–2000
SL	3874.9	0.9059	747	5.33	110–260	0–2000
SS	7788.6	0.9627	12713	1.13	110–260	0–2000

fitting results. It is found that the SS equation provides the best fit to the experimental data because of the minimum RMS value. Meanwhile, the dilatometry data of the molten BR and the values of the fitted parameters in the SS equation are similar to the results in the literatures.^{45–47} Furthermore, the solution of the coupled Eqs. (1) and (2), starting with atmospheric pressure $\bar{P} \cong 0$, can then be approximated by the equation⁴⁸

$$\ln \bar{V}|_{\bar{p}=0} = A + B\bar{T}^{3/2} \quad (9)$$

Therefore, for the melt specific volume we adopted an expression suggested by the theory of Simha¹⁹,

$$\ln V(0, T) = C + DT^{3/2} \quad (10)$$

Analytical equations of state are valuable not only for interpreting purpose for the PVT relationship but also for calculating derivatives. From the first derivatives of volume, the thermal expansion coef-

ficient can be determined. The thermal expansion coefficient at zero pressure can be obtained by differentiating Eq. (10) with temperature, and expressed as the following form:

$$\alpha(0, T) = (\frac{3}{2}D)T^{1/2} \quad (11)$$

In our previous paper⁴¹, the molten specific volume of many thermalplastic polymers has been reported. For those molten polymers, specific volume values reported for $P = 0$ were obtained by extrapolation along each isotherm. Equation (10) is fitted with the zero pressure volume. Thus, thermal expansion coefficients can be calculated from Eq. (11). Figures 6 and 7 show the specific volumes and the thermal expansion coefficients based on Eqs. (10) and (11) at various temperatures and at zero pressure. As shown in Figures 6 and 7, it is found that Eqs. (10) and (11) are suitable to predict the specific volumes and the thermal expansion coefficients of the polymer melts. Therefore, the Tait equation modified

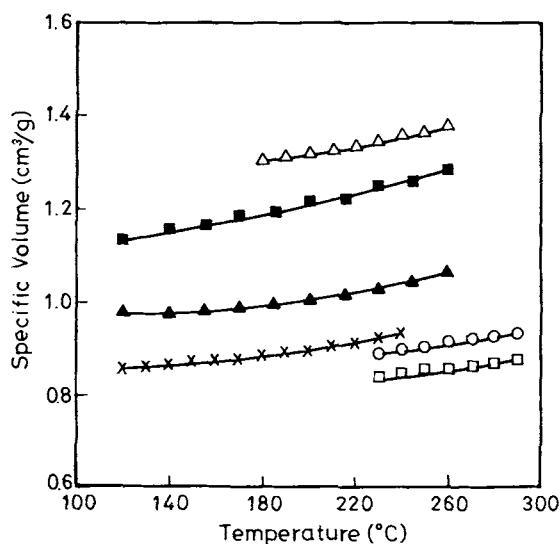


Figure 6 Temperature dependence of specific volume of molten polymers at zero pressure: (Δ) polypropylene; (□) nylon 6; (○) nylon 6.6; (X) PMMA; (▲) polystyrene; (■) polybutadiene; (—) Eq. (10).

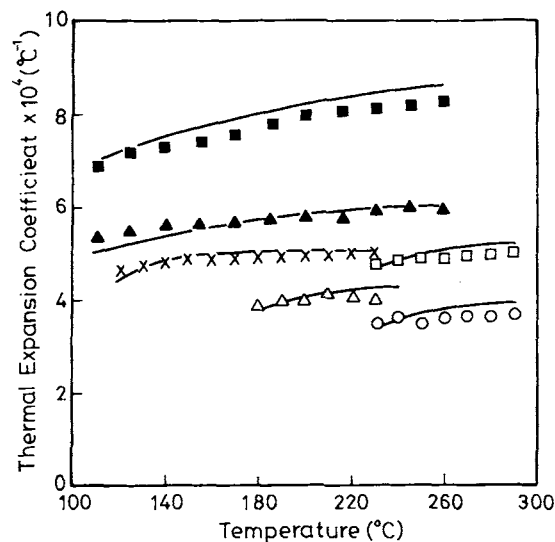


Figure 7 Temperature dependence of thermal expansion coefficients of molten polymers at zero pressure: (Δ) polypropylene; (□) nylon 6; (○) nylon 6.6; (X) PMMA; (▲) polystyrene; (■) polybutadiene; (—) Eq. (11).

Table V Parameters Obtained for the Semiempirical Equation of State, Eq. (12)

	BR	SBR-10	SBR-23.5	SBR-60	SBR-85	PS
V_0	0.9411	0.9053	0.8986	0.8812	0.8704	0.8605
$D \times 10^5$	2.514	2.437	2.317	2.031	1.846	1.740
B_0	5112	5408	5625	4956	3637	2569
$B_1 \times 10^3$	3.82	3.99	4.17	4.34	4.24	4.11

with the above equation provides a convenient and accurate means to calculate the specific volume of molten polymer blends as a function of temperature and pressure by means of the following expression:

$$V(P, T) = V_0 \exp(DT^{3/2}) \times \{1 - 0.0894 \ln[1 + P/B(T)]\} \quad (12)$$

where $V_0 = \exp(C)$. The parameters of molten PS and BR based on the Eq. (12) are listed in the Table V. These results from the Eq. (12) are plotted as solid curves in Figures 4 and 5. It is found that Eq. (12) is accurate enough to describe the PVT relation of the tested specimens, and the RMS value is 1.24 for PS, which approaches to the RMS value of SS equation.

Specific Volume of Compatible System

Based on previous DSC results, the SBR random copolymers (SBRs) with various styrene content have been identified as compatible mixtures. Values of the coefficients of Eq. (12) for SBRs are listed in Table V. Figure 8 shows that the specific volumes of SBRs at each fixed styrene content and at 1000 kg/cm² can be suitably evaluated by using Eq. (12). At the same time, it is found that the parameters in Eq. (12) are dependent on the compositions of SBRs. In addition, the accurate description for the PVT relation of SBRs will be improved if the microstructure effect of BR in the SBRs is considered.⁴⁹

Sachez and Lacombe¹⁰ have emphasized the importance of excess volumes of mixing on the polymer thermodynamics. However, due to the experimental difficulty to measure excess volumes in polymer-polymer mixtures, few experiments have been carried out for miscible blends. The importance of this type of measurements has been highlighted by the theoretical approaches intending to explain the mixture with specific interactions.

Experimental results have been expressed in the form of $V^E = V - V^0$, where V^0 is the additive specific volume of the mixture

$$V^0 = \phi_1 V_1^0 + \phi_2 V_2^0 \quad (13)$$

where ϕ_i is the volume fraction of the components in the blends, and V_i^0 is the specific volume of the pure component i . Hence, V^E is the difference between true specific volume (V) of the blends and the additive one (V^0). Figure 9 shows the results obtained from five various styrene blend compositions of SBRs at zero pressure and molten state. The specific volume change due to mixing at 110 and 140°C, where the polyblends are in equilibrium liquid state, is shown a negative value over the whole composition range. It is suggested that a larger negative V^E value obtained means much more closed intermolecular arrangement when the weight fraction of PS is approximately 45%. In order to estimate the excess volume of the compatible system at zero pressure, the combing rule of polymer blend systems was assumed:

$$V = \sum_{i=1}^2 \sum_{j=1}^2 \phi_i \phi_j V_{ij}^0 (1 - k_{ij})$$

$$V_{ij}^0 = V_i^0 \quad k_{ij} = 0 \quad \text{for } i = j$$

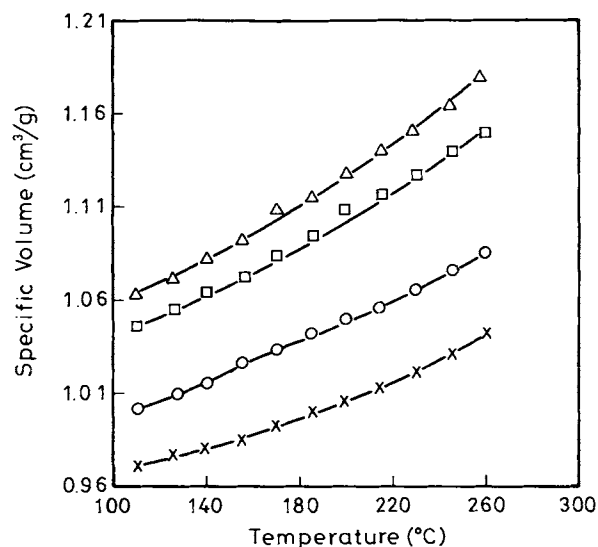


Figure 8 Temperature dependence of specific volume of SBR random copolymers with various PS content (wt %) at 1000 kgf/cm²: (Δ) SBR-10; (\square) SBR-23.5; (\circ) SBR-60; (\times) SBR-85; (—) Eq. (12).

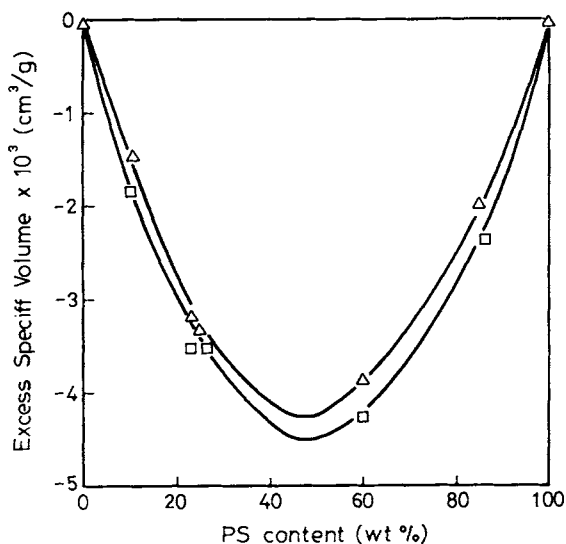


Figure 9 Concentration dependence of excess specific volume of SBR random copolymers with various PS content (wt %) at 1000 kgf/cm²: (Δ) 110°C; (□) 140°C; (—) predict excess specific volume with $k_{ij} = 0.0063$.

and

$$V_{ij}^0 = \left[\frac{(V_i^0)^{1/3} + (V_j^0)^{1/3}}{2} \right]^3$$

$$k_{ij} = k_{ji} \quad \text{for } i \neq j \quad (14)$$

where k_{ij} is a parameter accountable for compatibility and V_{ij}^0 is the specific volume of self- and cross interactions. The subscripts 1 and 2 represent neat BR and PS, respectively.

Substituting the V^E and V_i^0 from experiments for a certain blend composition into Eq. (14), k_{ij} characteristic of the polymer blend, independent of composition of the polymer blend, can be evaluated. Fortunately, the k_{ij} is almost constant and equals 0.0063. It shows that the V^E of SBRs in the melt state evaluated by using Eqs. (13) and (14) with $k_{ij} = 0.0063$ as shown in Figure 9 is in close agreement with the experimental data. A positive K_{ij} is in response to the existence of compatibility in the blend. The mixing volumes resulted in a negative excess specific volume of the polyblend and are usually related to the existence of strong intermolecular interactions between the blend components. Meanwhile, the symmetric curve of V^E vs. the weight fractions of PS demonstrates the suitability of the combining rule.

From Table V, it is found that the parameters B_0 and B_1 in Eq. (12) are dependent on blending compositions. Therefore, we express B_0 and B_1 of polymer blends in a polynomial function of composi-

tion. Polynomials are fitted with Eqs. (14)–(16) to the experimental data, and the parameters in B_0 and B_1 are obtained. The coefficients of B_0 and B_1 are shown on Eqs. (15) and (16).

$$B_0(\phi_2) = (5.112 + 3.576\phi_2 - 6.119\phi_2^2) \times 10^3 \text{ (kg/cm}^2\text{)} \quad (15)$$

$$B_1(\phi_2) = (3.82 + 1.71\phi_2 - 1.42\phi_2^2) \times 10^{-3} \text{ (}^\circ\text{C}^{-1}\text{)} \quad (16)$$

B_0 and B_1 calculated from Eqs. (15) and (16) are within 0.32% of the values deviated from that of the Eq. (12). Therefore, the specific volume of polymer blends at any temperature and pressure can be calculated through Eqs. (14)–(16). In Figure 10, the specific volumes of SBRs are shown at 1000 kg/cm² and increase with temperature. The solid curves from Eqs. (14)–(16) indicate that they are in good agreement with the experimental data. The deviations in specific volume are within 0.5%.

Specific Volume of Incompatible System

In the previous research,⁴⁷ the specific volumes of composites consisting of polypropylene and untreated glass fiber have been measured. The polymer composites of polypropylene used in the study are considered an incompatible two-phase system. For the two-phase system, additivity of the component

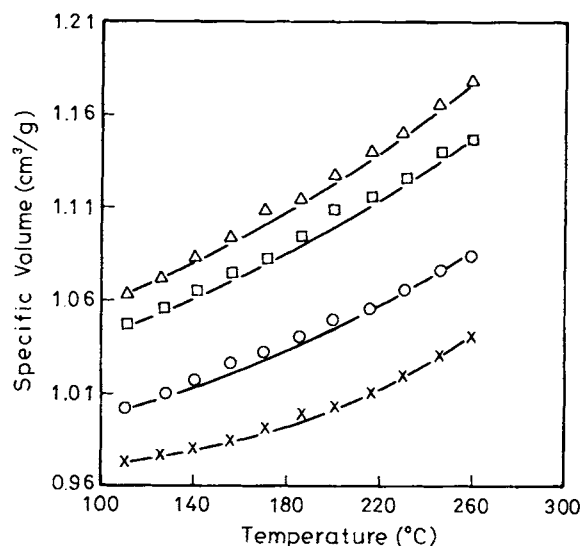


Figure 10 Temperature dependence of specific volume of SBR random copolymers with various PS content (wt %) at 1000 kgf/cm²: (Δ) SBR-10; (□) SBR-23.5; (○) SBR-60; (X) SBR-85; (—) Eqs. (14)–(16).

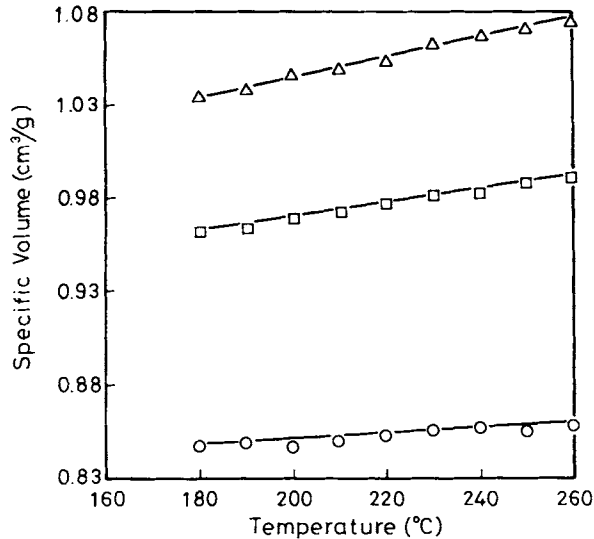


Figure 11 Temperature dependence of specific volume of polypropylene (PP) composites: (Δ) PP with 30% fiber content at atmospheric pressure; (\square) PP with 30% fiber content at 1000 kg/cm³; (\circ) PP with 40% fiber content at 2000 kg/cm³; (—) additive rule based on weight fraction.

mass and volume should be followed to find the specific volume of the composite. Thus, the specific volume of the composites was calculated, according to the following equation, $V_{sp}(\text{composite}) = W_p V_{sp}(\text{polymer}) + (1 - W_p) V_{sp}(\text{glass fiber})$.⁵⁰ As shown in Figure 11, the specific volume according to the above equation is coincident with experimental data. The reason that this simple additive rule is also applied to the molten composites is possibly due to no interaction between the polymer and the untreated glass fiber.

Specific Volume of Partially Compatible System

In order to estimate the composition of PS-rich and BR-rich domains in this partially compatible systems, it is essential to assume that the blending of the PS and the BR could reach an equilibrium state and form two independent domains, that is, a PS-rich domain and a BR-rich domain. According to the previous results, the Couchman equation can predict the T_g 's of the compatible SBR. For the partially compatible blend of the PS and BR, it is reasonable to divide those two domains into domain a , associated with a PS-rich SBR, and domain b , associated with a BR-rich SBR. Moreover, two pseudo-SBR domains can be individually described by the Couchman equation. Hence, the apparent weight fraction of each component in domain a can be cal-

culated from the arrangement of the Couchman equation:

$$W_1^a = \frac{\Delta C_{p,2}(\ln T_g^a - T_{g,2})}{\Delta C_{p,1} \times (\ln T_{g,1} - T_g^a) + \Delta C_{p,2} \times (\ln T_g^a - T_{g,2})} \quad (17)$$

$$W_2^a = 1 - W_1^a \quad (18)$$

A similar equation for domain b can also be derived. The overall apparent weight fractions of PS-rich SBR, W^a , and BR-rich SBR domain, W^b , can be calculated through the following material balance:

$$W^a + W^b = 1 \quad (19)$$

$$W_1^a W^a + W_1^b W^b = W_{1T} \quad (20)$$

where, W_{1T} is the total weight fraction of component 1 before blending. Following the above procedures, the overall apparent weight fractions of each domain and apparent weight fractions of each component in each domain are obtained and listed in Table VI.

Based on the above assumptions, the blend of PS and BR in its equilibrium state is separated into two domain, a PS-rich and a BR-rich domain. For a two-phase system, such as a polymer composite, the specific volume can precisely be predicted by an additive rule from the weight fractions of the specific volume of each component in the blending system. Hence, the specific volumes of the PS-BR blends similar to the composite of two separated phases, can be predicted by the following equation:

$$V_{sp}(\text{blend}) = W^a V_{sp}(\text{PS-rich}) + (1 - W^a) V_{sp}(\text{BR-rich}) \quad (21)$$

Table VI Overall Weight Fraction of Each Domain in PS-BR Blends and Apparent Weight Fraction of Each Component in Each Domain

Compositions	Weight Fractions					
	Overall		Apparent			
	W^a	W^b	W_1^a	W_1^b	W_2^a	W_2^b
10/90	0.104	0.896	0.987	0.013	0.013	0.987
24/76	0.242	0.758	0.990	0.010	0.014	0.986
40/60	0.406	0.594	0.968	0.032	0.012	0.988
60/40	0.625	0.375	0.954	0.046	0.010	0.990
70/30	0.714	0.286	0.973	0.027	0.011	0.989
90/10	0.908	0.092	0.982	0.018	0.001	0.999

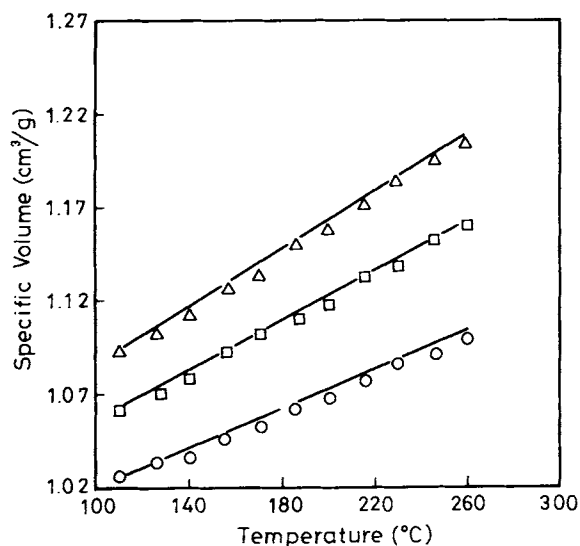


Figure 12 Temperature dependence of specific volume of PS-BR blend: (Δ) PS-BR blend with 24 wt % PS content at 1000 kgf/cm²; (\square) PS-BR blend with 40 wt % PS content at 1000 kgf/cm²; (\circ) PS-BR blend with 60 wt % PS content at 1000 kgf/cm²; (—) Eq. (21).

where, $V_{sp}(i\text{-rich})$ is the specific volume of the i -rich domain.

As shown in Figure 12, it is found that this additive rule is suitable to predict the specific volumes of this partially compatible PS-BR blends.

CONCLUSIONS

The DSC has been successfully applied to determine the phase behavior of polymer blends. It is found that a PS-BR blend has a low degree of compatibility. The T_g 's of the miscible SBR random copolymer can be predicted satisfactorily by the Couchman equation. The PS-BR blend was found partially compatible with two separated domains of compatible phases. The specific volumes and thermal expansion coefficients of polymer melts can be predicted by equations derived from Simha-Somcynsky. The specific volumes of polymer blends are the function of the defined "degree of compatibility." The specific volume of a compatible blend at a constant composition or a homopolymer in the melt state can be calculated by an semiempirical equation derived from the Tait equation. The specific volumes of the partially compatible PS-BR blends can be solved through derived equations. The specific volume of an incompatible blend obeys the principle of additivity from the weight fractions of the specific volume of the corresponding individual domain.

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