

Effect of Compatibility on Heat Capacity of Molten Polyblends

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SYNOPSIS

The heat capacity and phase relation of polymer blends consisting of two homopolymers or a homopolymer with a block copolymer have been investigated by differential scanning calorimetry (DSC). Polystyrene (PS) and polybutadiene (BR) are the two homopolymers, while the styrene-butadiene-styrene (SBS) copolymer is employed as the block copolymer in this study. The heat capacity and specific volume of the PS and BR homopolymers increase with increasing temperature at a constant pressure. The heat capacity of styrene-butadiene (SBR) random copolymer, which is considered a miscible system, can be calculated by an additive rule from the addition of the styrene and butadiene segment number fractions in the random copolymer multiplied by the corresponding heat capacity of PS and BR homopolymers. However, the heat capacity of the immiscible system of the SBS triblock copolymer can be estimated by the addition of the two segment number fractions multiplied by the reciprocal of the corresponding heat capacity of the PS and BR homopolymers. The thermal and dynamic mechanical analysis data of the polyblend from the two PS and BR homopolymers both show a low degree of miscibility. A saturated solubility of the homopolymer dissolved in the SBS block copolymer is proposed and the purification of the styrene and butadiene phases in the SBS copolymer is observed as it blends with either PS or BR homopolymer. The heat capacity of polymer blends composed of two phases obey the principle of additivity from the weight fractions of the heat capacity of the corresponding individual phase. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

In recent years, polymer blends and composites have been the subject of many studies to elucidate the factors influencing phase behavior of polymer blends and composites because of their wide technological importance, as a simple method of formulating new materials with tailored properties, and in academia. In recent research, extensive phase behavior observations of polymer blends, composed of homopolymer-copolymer or copolymer-copolymer, have shown more interesting phenomena.¹⁻⁹ A simple binary interaction model¹⁰ with various extensions and functional integral formalism¹¹⁻¹⁵ provides the

theoretical basis to rationalize phase behaviors of polymer blends.

Our recent papers¹⁶⁻¹⁸ were devoted to finding some simple and useful quantitative empirical equations to describe thermal physical properties during processing of molten thermoplastic polymers and their composites at injection-molding pressure. Those important processing thermophysical properties included heat capacity, thermal conductivity, and specific volume. Heat capacity is one of the most important thermodynamic properties. It is related to the microscopic structure and motion in a polymer blend and is the basic factor for derivation of other thermodynamic properties. Most studies¹⁹⁻²¹ on heat capacities have focused on the solid-state homopolymers. For copolymers and polymer blends, studies on heat capacities related to phase behaviors become more sophisticated.

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The phase behavior of polymer blends can provide important information related to the degree of miscibility and has been determined in terms of mixing Gibbs free energy. Miscible blends have been studied widely; however, only a few studies have been developed to determine the degree of miscibility for phase-separated polymer-blend systems. Thermal and dynamic mechanical analysis may be the most convenient and inexpensive method to determine the phase behavior of polymer blends. Recently, the technique has been used extensively for some partially miscible polymer-blend systems.²²⁻²⁴ These characteristics of miscibility of polymer blends can be estimated using differential scanning calorimetry (DSC) data from the experimental values of glass-transition temperature shift (ΔT_g) and heat capacity increment (ΔC_p).

Traditionally, the glass-transition temperature (T_g) of miscible polymer blends or random copolymers can usually be described by the following equations.

Wood equation²⁵

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

Fox equation²⁶

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

Gordon and Taylor equation²⁷

$$T_{g,b} = (W_1 T_{g,1} + \gamma W_2 T_{g,2}) / (W_1 + \gamma W_2) \quad (3)$$

$$\gamma = \Delta\alpha_2 / \Delta\alpha_1.$$

Couchman equation²⁸

$$\ln T_{g,b} = (W_1 \Delta C_{p,1} \ln T_{g,1} + W_2 \Delta C_{p,2} \ln T_{g,2}) / (W_1 \Delta C_{p,1} + W_2 \Delta C_{p,2}) \quad (4)$$

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 polymer blend or random copolymer.

The blend of polystyrene (PS) and polybutadiene (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. In our present research, the DSC method is again applied to examine the degree of miscibility of the model material. Furthermore, this paper expands on our previous studies of polymers and their composites to develop a suitably quantitative description of heat capacities of PS/BR blends, random styrene-butadiene rubber (SBR), triblock styrene-butadiene-styrene rubber (SBS), PS/SBS blends, and BR/SBS blends.

EXPERIMENTAL

Materials

The characteristics and sources of PS, BR, SBR, and SBS samples used in our research are summarized in Table I. Molecular weights and polydispersities are measured by gel permeation chromatography (GPC) at 295K in tetrahydrofuran (THF).

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 420K for 20 min. The rotation velocity was 10 rpm for both front and back rolls. The polymers were dried in a vacuum oven at 383K overnight before blending. The compositions

Table I Characteristics and Sources of Materials

| | Polymers | | | |
|---------------|----------------------------|------------------------------|--------------------------------|-------------------------------|
| | PS (PG-33) ^a | BR (BR-0150) ^b | SBR (SSBR-375) ^b | SBS (TPE-411) ^b |
| Polybutadiene | | | | |
| <i>cis</i> | 0 | 96 | 30 | 40 |
| <i>trans</i> | 0 | 2 | 47 | 50 |
| <i>vinyl</i> | 0 | 2 | 23 | 10 |
| SM/BDM | 100/0 | 0/100 | 25/75 | 30/70 |
| M_w | 330,000 | 600,000 | 960,000 | 130,000 |
| M_w/M_n | 3.38 | 5.16 | 6.07 | 2.03 |

^a Commercial name, Gue, Meitt. Co.

^b Commercial names, Taiwan Synthetic Rubber Lt. Co.

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 sample was heated to 420K in a nitrogen environment for about 10 min to eliminate the previous thermal history. It was then quenched to 140K with a liquid nitrogen cooling supply and scanned with a heating rate of 10 K/min from 140K to 520K. Temperature calibration was performed using *n*-heptane ($T_m = 182.6\text{K}$) and indium ($T_m = 429.8\text{K}$). The T_g was taken as the temperature at which the heat capacity reached one half of the entire step change. The T_g was also determined with a DuPont DMA (Mode 983) using hot pressed samples ($50 \times 10 \times 30$ mm) to measure storage modulus (E'), loss modulus (E''), and $\tan \delta$. The amplitude and frequency were set at 0.2 mm and 1.0 Hz, respectively. The T_g was determined from the peak value of the diagram of E'' against temperature.

Measurements of Specific Volume (*sp vol*) and Heat Capacity (C_p)

The specific volume measurement was carried out by using a dilatometer designed and tested in our laboratory. Detail descriptions can be found elsewhere.¹⁸ The specific volume at room temperature was determined with a pycnometer (Model Accupyc1330). The heat capacity was measured with a DuPont DSC. Sapphire was taken as a standard. The heat capacity was calculated from the relative absorption heat difference between the sample and sapphire. The samples were scanned at 10 K/min from 350K to 520K.

RESULTS AND DISCUSSION

T_g and C_p of the Polymers

The T_g and C_p values of the PS and BR homopolymers were measured by using DSC. The results

Table II Weight Ratio of Polymer Blends

| Polymer Blends | Compositions (Weight Ratio) | | |
|----------------|-----------------------------|-------|-------|
| PS/BR | 24/76 | 40/60 | 60/40 |
| PS/SBS | 14/86 | 43/57 | 71/29 |
| BR/SBS | 22/78 | 33/67 | |

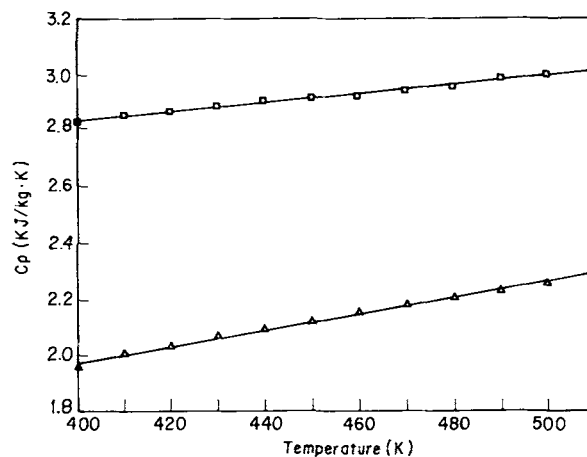


Figure 1 Temperature dependence of heat capacity of PS and BR at atmospheric pressure: (Δ) PS (\square) BR.

show that the T_g value of PS and BR are 380K and 175K, respectively. As shown in Figure 1, the C_p values of the molten PS and BR increased with increasing temperature at atmospheric pressure. The heat capacity increment (ΔC_p) values of 0.268 kJ/kgK and 0.536 kJ/kgK were found from the T_g increment of PS and BR, respectively. The SBR random copolymer is assumed to be a miscible system because of its random mixture and only one T_g at 195K was observed. However, the SBS triblock copolymer exhibits two separated phases because of its block structure and therefore two T_g 's 190K (T_{gl}) and 367K (T_{gh}) were observed. Figures 2 and 3 show the temperature dependence of the heat capacity of

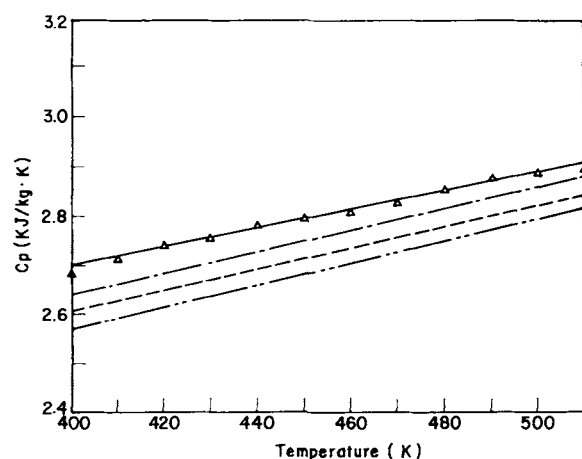


Figure 2 Temperature dependence of heat capacity of SBR at atmospheric pressure: (Δ) experimental data of SBR; (—) eq. (7); (---) additive rule based on weight fraction; (-·-) additive rule based on volume fraction and reciprocals of heat capacities.

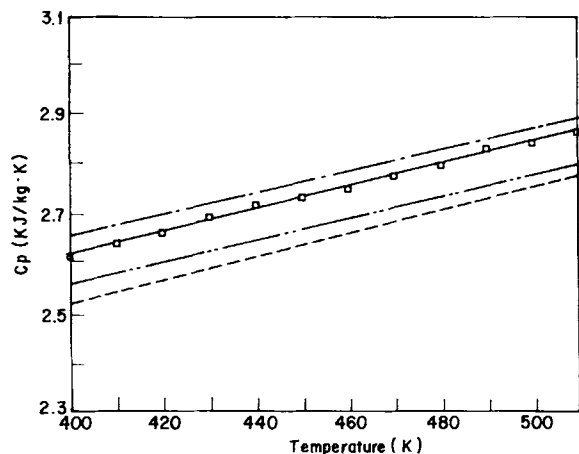


Figure 3 Temperature dependence of heat capacity of SBS at atmospheric pressure: (\square) experimental data of SBS; (—) eq. (8); (---) additive rule based on volume fraction and reciprocals of the heat capacities; (---) additive rule based on segment number fraction; (---) additive rule based on weight fraction.

the molten SBR and SBS, respectively, at atmospheric pressure. It can be seen that the heat capacity increases with increasing temperature.

T_g of PS/BR, PS/SBS, and BR/SBS Polyblends

It is well known that incompatibility exists for blends of PS and BR, and two T_g 's were observed. The degree of miscibility of one polymer in another for a partially miscible polymer blend is dependent on the shift values of the two T_g 's of blending polymers related to each component. For PS/BR blend, the T_g 's are shown and the phenomenon implies that

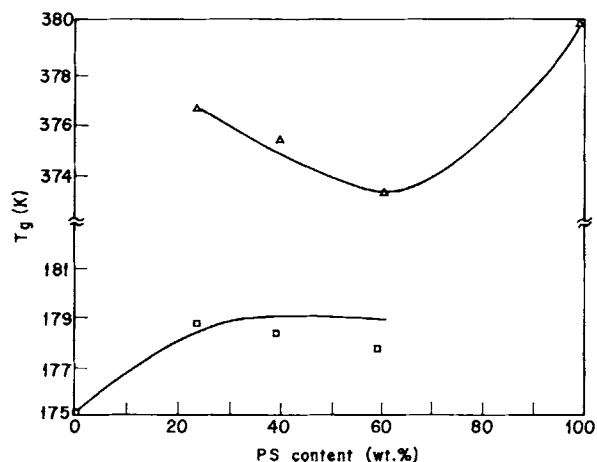


Figure 4 Composition dependence of glass-transition temperature shift of PS/BR blends: (Δ) T_{gh} ; (\square) T_{gl} .

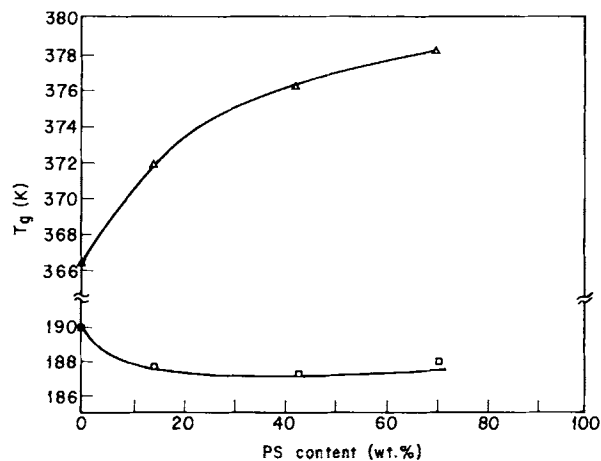


Figure 5 Composition dependence of glass-transition temperature shift of PS/SBS blends: (Δ) T_{gh} ; (\square) T_{gl} .

two domains in the PS/BR blend existed, for example, PS-enriched domain (PS-rich) with a high T_g (T_{gh}) and the other BR enriched domain (BR-rich) with a low T_g (T_{gl}). In Figure 4, the T_g 's of PS-rich domain and BR-rich domain as a function of the PS/BR weight ratio in the PS/BR blend are presented. It is found that the T_g decreases about 2–7K for the PS-rich domain and increases about 2–4K for the BR-rich domain as the PS content varied. In contrast, for the PS/SBS and BR/SBS blends, the T_g shifted in an opposite direction (Figs. 5–7). The T_g of PS-rich domain increased and that of BR-rich domain decreased as the PS and BR contents increased in the PS/SBS and BR/SBS blend system, respectively. This result shows that the T_{gh} (T_g of the PS-rich domain) of PS/SBS blend is higher and broader than that the T_{gh} of SBS and

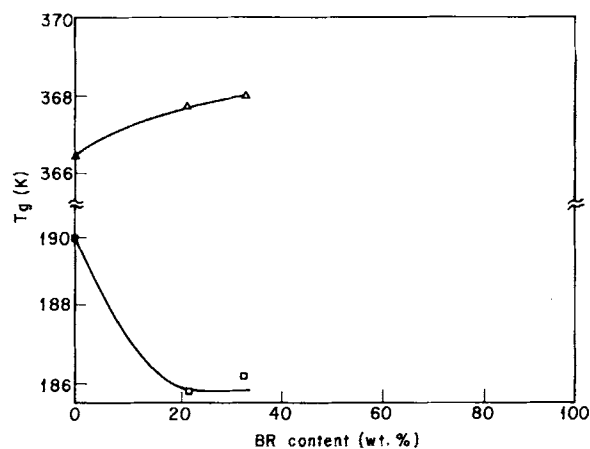


Figure 6 Composition dependence of glass-transition temperature shift of BR/SBS blends: (Δ) T_{gh} ; (\square) T_{gl} .

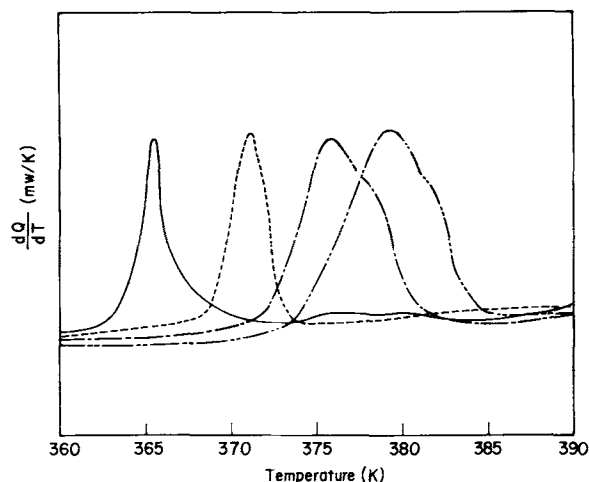


Figure 7 Temperature dependence of endothermal derivative curve of PS/SBS with various added PS content: (—) with 0% PS content; (---) with 14% PS content; (-·-) with 43% PS content; (···) with 71% PS content.

approaches the T_g of PS at high PS content. The T_{gl} (T_g of the BR-rich domain) of PS/SBS blend is shifted to a lower temperature than the T_{gl} of the SBS, and remains at that value in spite of an increase of the PS content in the system. Although a similar trend for the BR/SBS blend system is evident, T_{gh} increased slightly and T_{gl} decreased with an increase of the BR content. The tendency of the T_g shifts of the forementioned three polyblends, measured by DSC or DMA, are quite similar. For the T_g shifts, two important findings are: a low degree of miscibility exists for the PS/BR system and blending of PS or BR with the SBS reduces the degree of miscibility between the block styrene and butadiene of the SBS. The shift tendency of the T_{gh} and T_{gl} for the PS and BR homopolymers blend with the block SBS copolymer can be satisfactorily interpreted as caused by the PS or BR homopolymer only dissolving in the styrene or butadiene block of the SBS, respectively, and therefore a purification effect making two, more "pure," PS-rich and BR-rich domains in the SBS copolymer.²⁹⁻³¹ When a small amount of PS is added to the SBS, the PS is readily dissolved in the styrene block of the SBS. When more PS was added, a broader transition peak was observed (Fig. 7), indicating saturated solubility of the PS in the styrene block of the SBS copolymer (heterogeneous property) resulted. Thereafter, the PS and the PS-saturated styrene block of SBS will co-exist for the PS-rich domain of the SBS. However, more pure BR segments (a lower T_{gl} result) existing in this BR-rich domain are because of the hard PS segments in the SBS copolymer being at-

tracted out of the BR-rich domain by the PS dissolving in the SBS. The experimental results are found to be in close agreement with this reasoning. Similarly, purification of the PS-rich domain of the BR/SBS blend will display similar behavior to that of the BR-rich domain in the PS/SBS blend.

Calculation of the Composition of PS-Rich and BR-Rich Domains in the Blends

In order to estimate the composition of PS-rich and BR-rich domains, 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.

Figure 8 shows specific volumes of PS and BR with increasing temperature at atmospheric pressure. The thermal expansion coefficients (α) of the PS calculated from the slopes of the curve are 5.69×10^{-4} 1/K above T_g and 2.84×10^{-4} 1/K below T_g . For the BR, α is 6.59×10^{-4} 1/K above T_g . The α of the BR below T_g , found from the literature,²⁵ is 2.0×10^{-4} 1/K. The γ value is calculated and equals 1.61. The T_g 's calculated by using eqs. (1)–(4) for the SBR of 25 wt % PS are 229K, 202K, 210K, and 195K, respectively. The Couchman equation can predict the T_g of the SBR. For the blend of 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, the two pseudo SBR domains can be individually described by the Couchman equation. Hence, the apparent weight fraction of each com-

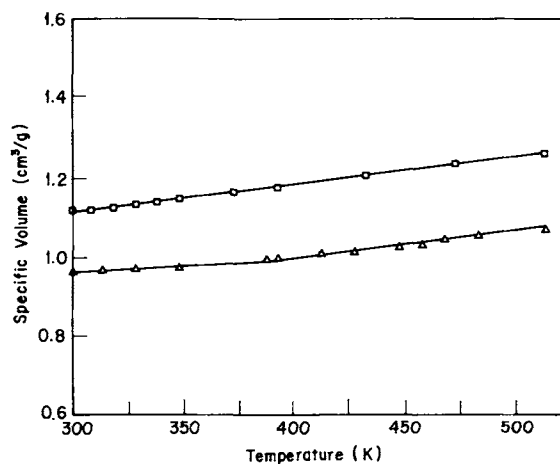


Figure 8 Temperature dependence of specific volume of PS and BR at the atmospheric pressure: (Δ) PS; (\square) BR.

ponent in domain "a" can be calculated from the rearrangement of the Couchman equation:

$$W_1^a = \Delta C_{p,2}(\ln T_g^a - \ln T_{g,2}) / [\Delta C_{p,1} \times (\ln T_{g,1} - \ln T_g^a + \Delta C_{p,2}(\ln T_g^a - \ln T_{g,2}))] \quad (5a)$$

$$W_2^a = 1 - W_1^a. \quad (5b)$$

A similar equation for domain "b" can be made. The overall apparent weight fractions of PS-rich SBR, W^a , and BR-rich SBR domain, W^b , can be calculated by following material balance equations:

$$W^a + W^b = 1 \quad (6a)$$

$$W_1^a W^a + W_1^b W^b = W_{1T} \quad (6b)$$

where, W_{1T} is 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 are listed in Table III.

Equations of C_p for SBR and SBS

Most studies on heat capacities have focused on homopolymers, especially as developed by Wunderlich et al.¹⁹⁻²¹ Only a few papers related to copolymers have been reported.³²⁻³⁴ In the present study, the heat capacities of SBR and SBS have been fitted to the different equations with the addition of weight fraction, volume fraction, or segment number fraction, based on the heat capacities of PS and BR or the reciprocals of heat capacities of PS and BR. It is found that the heat capacity of SBR, assumed to be a compatible system, with melt-state temperatures can be estimated by the following equation, that is, the additive rule of segment-number frac-

tions of the heat capacities of the PS and the BR (Fig. 2):

$$C_p(\text{SBR}) = (Z_{\text{PS}}/Z)C_p(\text{PS}) + (Z_{\text{BR}}/Z)C_p(\text{BR}) \quad (7)$$

$$Z = Z_{\text{PS}} + Z_{\text{BR}}$$

where, Z_i is segment number of component i .

For SBS, an incompatible system, the heat capacities can be fitted more suitably by the following equation (Fig. 3):

$$1/C_p(\text{SBS}) = (Z_{\text{PS}}/Z)[1/C_p(\text{PS})] + (Z_{\text{BR}}/Z)[1/C_p(\text{BR})]. \quad (8)$$

Thus, from Figures 2 and 3, the heat capacities of molten SBR (compatible system) and SBS (incompatible system) closely fit eqs. (7) and (8), respectively.

Equations of C_p for PS/BR, PS/SBS, and BR/SBS Polyblends

Based on the above assumptions, the blend of PS and BR in its equilibrium state is separated into two domains, a PS-rich and a BR-rich domain. In our previous paper,¹⁶ a polymer composite with untreated glass fiber was considered as two independent separated phases, and its heat capacity with various fiber contents can precisely be predicted by an additive rule from the weight fractions of the heat capacity of each component in the composite, even though it was at high pressure. Hence, the heat capacities of the PS/BR blends similar to the composite of two separated phases, can be predicted by the following equation:

$$C_p(\text{blend}) = W^a C_p(\text{PS-rich}) + (1 - W^a) C_p(\text{BR-rich}) \quad (9)$$

Table III 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 |
| PS/BR | | | | | | |
| 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 |

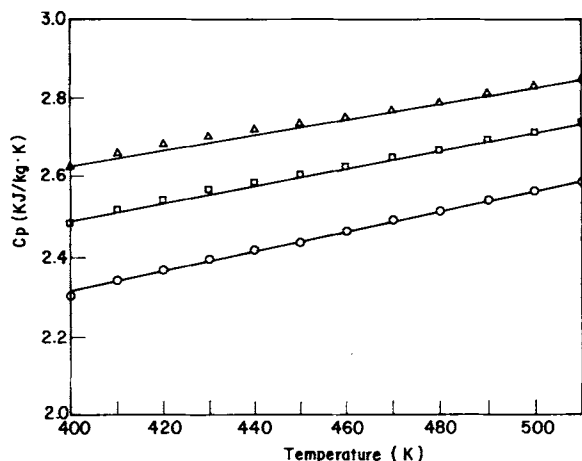


Figure 9 Temperature dependence of heat capacity of PS/BR blends: (Δ) PS/BR blend with 24% PS content; (\square) PS/BR blend with 40% PS content; (\circ) PS/BR blend with 60% PS content; (—) eq. (9).

where, C_p (i -rich) is the heat capacity of the i -rich domain.

As shown in Figure 9, it is found that this additive rule is suitable to predict the heat capacities of the PS/BR blends. The value of a saturation solubility, which is only dependent on the temperature, was assumed as a constant. Similarly, two independent phase domains are formed in the PS/SBS and BR/SBS blends. Therefore, the heat capacity of the blend can be calculated similar to eq. (9) from the weight fraction of the heat capacities of each independent domain when an excess of PS or BR is

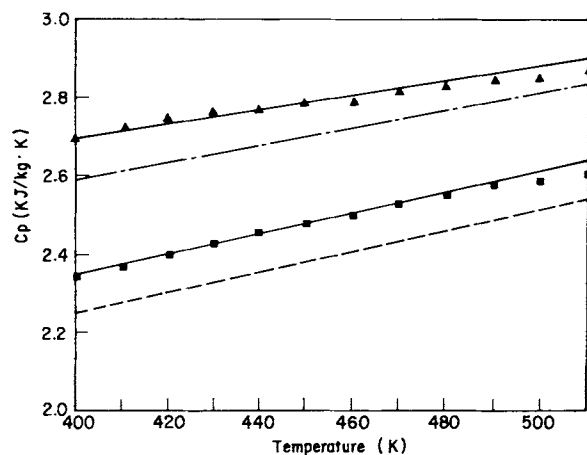


Figure 10 Temperature dependence of heat capacity of PS/SBS and BR/SBS blends: (\blacksquare) PS/SBS blend with 43% PS content, (—) eq. (10) with 43% PS content and $W_c = 0.083$; (---) eq. (10) with 43% PS content and $W_c = W$; (\blacktriangle) BR/SBS blend with 33% BR content, (—) eq. (10) with 33% BR content and $W_c = 0.039$; (---) eq. (10) with 33% BR content and $W_c = W$.

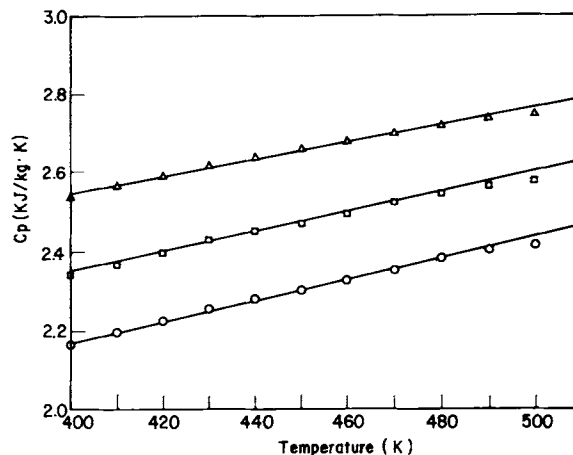


Figure 11 Temperature dependence of heat capacity of PS/SBS blend with various added PS contents: (Δ) PS/SBS blend with 14% PS content; (\square) PS/SBS blend with 43% PS content; (\circ) PS/SBS blend with 71% PS content; (—) eq. (10) with $W_c = 0.083$.

added to SBS. Because of a saturated solubility involved in the SBS domains, the heat capacities of the blends for PS/SBS or BR/SBS are calculated by the following equation:

$$C_p(\text{blend}) = (W - W_c)C_p(\text{homopolymer}) + (1 - W + W_c)C_p(\text{saturated SBS copolymer}) \quad (10)$$

where W is the weight fraction of homopolymer (PS or BR) before blending and W_c is the saturation weight fraction of the homopolymer (PS or BR) dissolved in the SBS block copolymer. The C_p (sat-

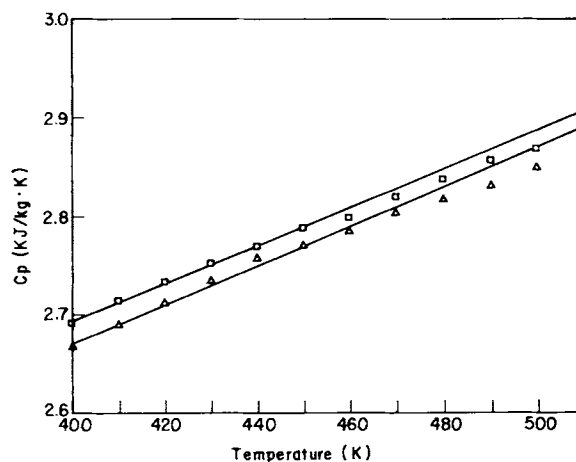


Figure 12 Temperature dependence of heat capacity of BR/SBS blend with various added BR contents: (Δ) BR/SBS blend with 22% BR content; (\square) BR/SBS blend with 43% BR content; (—) eq. (10) with $W_c = 0.039$.

urated SBS copolymer) is the heat capacity of the PS- or BR-saturated SBS domains. Based on the saturation solubility concept and the derived eq. (10), the heat capacities of the PS/SBS and BR/SBS blends are predicted (Fig. 10) more accurately than those with no solubility limitation in the blends' copolymer.

Figures 11 and 12 show that the heat capacities of PS/SBS and BR/SBS with various compositions can be suitably predicted by eq. (10), except at high temperature. The deviation of heat capacities at high temperature may be caused by the presence of only a liquid phase. The value W_c , fitted from experimental data, for PS/SBS is 0.083 and for BR/SBS is 0.039. These low saturation solubilities of PS and BR in the PS/SBS and the BR/SBS blends are caused by the relative molecular weight of comonomer blocks in the SBS and have the same order as Meier's prediction.³⁰

CONCLUSIONS

The DSC method has been successfully applied to determine the phase relation and heat capacities of polymer blends containing two homopolymers or a homopolymer with a copolymer. It is found that a PS/BR blend has a low degree of miscibility. A saturated solubility and the effect of purification of styrene domain and butadiene domain was found in the PS/SBS and BR/SBS blend system, respectively. The T_g of the miscible polyblends or a random copolymer can be predicted by the Couchman equation. The overall weight fractions of each domain in the polymer blends and those of the components in each domain can be calculated from the overall mass balance in the two domains and the Couchman equation. The heat capacities of SBR and SBS are estimated by using the additive rules from the segmental number fraction of styrene and butadiene in the polymers. The heat capacities of polymer blends are also predicted by the additive rule, as polymer composites, from the weight fractions of the two domains of the polyblend.

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