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Glass-transition Temperature and Thermal Expansion Coefficient of a Two-Phase System of Polymers

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The abnormal increase of glass-transition temperature (T_g) and the deviation of thermal expansion coefficient from the simple additivity relationship in a two separate phase system having different T_g 's were explained by the thermal stress originating from the difference of the thermal expansion coefficients of the two component polymers. Among the two T_g 's of the blend system, the higher T_g was increased and the lower T_g was decreased compared with the original T_g 's of the component polymers in some cases.

The spherical shell model composed of three layers was adopted to interpret such phenomena of the blend system. These three layers were numbered 0, 1, and 2 from the outer layer. The component polymer of the layer 0 was assumed to be the same as in the layer 2. In this model, v_s , which is defined as the volume ratio of the sphere 2 to the sphere 1, represents the mixing state of the two component polymers.

The thermal expansion coefficients of the whole system and the layers 0, 1, and 2 were calculated on the basis of this model. The agreement between the calculated and the observed values was rather good for the blend systems of polystyrene(PS)/polybutadiene (PBD), PS/styrene-butadiene rubber (SBR), polymethylmethacrylate(PMMA)/SBR and styrene-acrylonitrile copolymer/PBD.

The blend system of PS/PMMA did not follow the above prediction. It was pointed out that in such a case the molecular interaction between two component polymers should be taken into account.

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1 INTRODUCTION

Polymer blend systems are generally classified into four groups; a perfectly miscible system, a microheterogeneous system, a partially miscible system, and a two separate phase system, according to the extent of miscibility of the component polymers. The effect of mixing on the viscoelastic properties and glass transition temperatures (T_g) differs among their groups.

In the case of the systems such as perfectly miscible, microheterogeneous and partially miscible systems, the T_g of each component shifts with variation of the composition within a temperature range between both T_g s of two component polymers in their unmixed state. The composition dependence of T_g in the case of a perfectly miscible system obeys the same law as given to T_g s of random copolymers.¹ It has been recognized that, in the two separate phase system, two T_g s are observed separately and their locations are very close to the T_g s of two components in their unmixed state.

Recently, it has been reported that the T_g of polystyrene (PS) of a two separate phase system, which contains PS as one component, shifted to a higher temperature than T_g of PS in a monophase system.^{2,3} These shifts of T_g of the plastic phase to the higher temperature side were also observed in the blend systems of polymethylmethacrylate (PMMA) or polyvinylchloride (PVC) and some rubbers. The degree of shifting decreases in the order of PS, PMMA, and PVC. The degree of this shift was related to the impact strength of the plastic component. That is, the smaller the impact strength is, the larger the degree of shift. The plastic, which cannot easily comply with the impact stress or strain followed by some molecular relaxation mechanisms, is considered to show lower strength. It must be presumed that such a plastic having low impact strength would behave more rigidly against the thermal stress caused by expansion of the rubber phase. Thus, it is considered that the shift of T_g may depend on the thermal stress caused by the difference of the thermal expansion coefficients between the two component polymers.³

It was also observed by the authors^{2,3} that the T_g of the rubber of the blend systems, which contain *cis*-polybutadiene (*cis*-PBD) as their rubber component, shifted to the lower temperature side of T_g of the same rubber in a monophase system. This phenomenon was also considered to be due to the thermal stress as mentioned above.³ These considerations coincide with those presented by Wang *et al.*⁴

The increase of T_g of the plastic phase was not described quantitatively in the previous papers.^{2,3,4} For this purpose, it is necessary to calculate the thermal expansion coefficients of each component polymer in the blend system. Although there has been no report about the thermal expansion of the component polymers in the blend systems, there are some equations describing

the thermal expansion coefficient of the composite materials such as Kerner's equation,⁵ Wang's equation,⁶ and the author's equation.⁷ These equations were derived by neglecting the effect of interaction between the dispersed particles and the difference in the mixed state.

In this paper, therefore, the equation of the thermal expansion coefficients of the component polymers will be derived in due consideration of the mixed state. The abnormal phenomena observed in T_g behavior mentioned above will be interpreted using this equation.

2 THEORY

2.1 Derivation of Basic Equations

The dispersed state of the components in a polymer blend is assumed to be the spherical shell model as shown in Figure 1. The shells are denoted by 0,

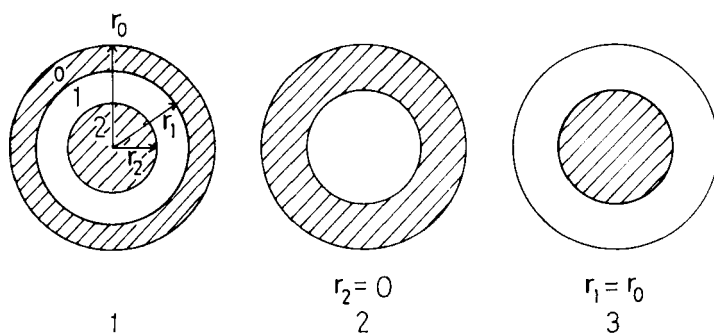


FIGURE 1 Shell models representing the dispersion state of blend system. Cases No. 2 and No. 3 are special cases of No. 1.

1 and 2 from the outer to the inner shell. The shells 0 and 2 are made of the same polymer and the shell 1 is made of the other component polymer of the blend. Figure 1(1) is the generalized model which includes together the models of Figures 1(2) and 1(3) sketched as their special cases of $r_2 = 0$ and $r_1 = r_0$, respectively. r_0 , r_1 , and r_2 are the radii of each sphere as indicated in Figure 1(1). The reasons why the model of Figure 1 was adopted will be easily understood by taking into account the following factors. (1) The interaction between the dispersed particles must be taken into account, and is represented by the existence of the layer 0 symbolizing the neighboring particles against the sphere 2 with the layer 1 symbolizing the medium between the particles. In other words, Figure 1(1) shows the schematic model of phase 1 embedded in the medium of the polymer composing the layers 0 and 2. (2) The thermal expansion coefficient of the matrix phase which lies between the neighboring

particles is different from those of the parts of the outer shells in Figures 1(2) and 1(3). (3) In order to express the change of the dispersed state of particles from variation of the composition, the parameter characterizing the dispersed state of particles is necessary. Judging from the experimental results of the composition dependence of elastic modulus, the actual dispersed state may be similar to the intermediate state between Figure 1(2) and Figure 1(3). Therefore, it may be desirable to adopt the model as shown in Figure 1(1) which includes together dispersed states of Figure 1(2) and Figure 1(3) exhibited as its special cases.

The interpolymers of PS and styrene-butadiene rubber (SBR) and the ABS resin are the examples corresponding to the dispersed state of Figure 1(1) in which layer 1 corresponds to the rubber phase. According to recent electron microscopic observation of the polymer texture of ABS resin using the osmic acid-staining method it was revealed that the rubber particles include many plastic particles in themselves (cellular structure) and are dispersed in the plastic medium.¹¹ Such a texture is in accordance with the model represented in Figure 1(1) if the layer 1 is taken as the rubber phase.

The stress applied to the inner shell 2 from the outer shell can be approximated by hydrostatic pressure. σ_r represents the radial stress at the place of the distance r from the center of the sphere. The following equation is obtained from the theory of mechanics.⁸

$$\frac{d^2\sigma_r}{dr^2} + \frac{4}{r} \frac{d\sigma_r}{dr} = 0 \quad (1)$$

From Eq. (1) we obtain

$$\left. \begin{aligned} \sigma_r &= 3BK - 4GA r^{-3} \\ u &= A r^{-2} + Br \end{aligned} \right\} \quad (2)$$

where u is the radial deformation, and K and G are bulk and shear moduli, respectively. A and B are the constants determined by the boundary conditions. When the temperature of this system is higher by an amount of T than the critical temperature where the system is free from the thermal stress, A and B can be obtained under the following boundary conditions:

- (1) Each shell contacts with the others at the whole parts of the boundary.
- (2) The stresses of the two shells at their boundary are the same.
- (3) The stress at the boundary of an atmosphere is zero.

These boundary conditions are expressed by the following equations. The suffixes denote the corresponding layers.

$$\left. \begin{aligned} 3K_0 B_0 - 4G_0 A_0 r_1^{-3} &= 3K_1 B_1 - 4G_1 A_1 r_1^{-3}, \\ A_0(1 + \beta_2 T)^{-2} r_1^{-2} + (1 + \beta_2 T) B_0 r_1 + (1 + \beta_2 T) r_1 \\ &= A_1(1 + \beta_1 T)^{-2} r_1^{-2} + (1 + \beta_1 T) B_1 r_1 + (1 + \beta_1 T) r_1 \end{aligned} \right\} \quad (3)$$

$$\left. \begin{aligned} 3K_1 B_1 - 4G_1 A_1 r_2^{-3} &= 3K_2 B_2, \\ A_1(1 + \beta_1 T)^{-2} r_2^{-2} + B_1(1 + \beta_1 T)r_2 + (1 + \beta_1 T)r_2 \\ &= B_2(1 + \beta_2 T)r_2 + (1 + \beta_2 T)r_2 \end{aligned} \right\} \quad (4)$$

Further,

$$3K_0 B_0 - 4G_0 A_0 r_0^{-3} = 0 \quad (5)$$

Eq. (4) represents the boundary conditions between the shells 1 and 2, and is correct only when the strain caused by the thermal stress and the thermal expansion is sufficiently small compared with unity. β is the linear thermal expansion coefficient. The β_2 equals β_0 because the components of the shell 0 and 2 are the same as assumed before. Thus, the following equations are obtained from Eqs. (3), (4), and (5) under the condition of $\beta T \ll 1$.

$$A_0 = \frac{3K_1 K_0 (\beta_0 - \beta_1) T (3K_0 + 4G_1) (r_1^{-3} - r_2^{-3})}{D} \quad (6)$$

$$B_0 = \frac{4G_0 r_0^{-3} (\beta_0 - \beta_1) T K_1 (3K_0 + 4G_1) (r_1^{-3} - r_2^{-3})}{D} \quad (7)$$

$$A_1 = \frac{3(\beta_0 - \beta_1) T K_0 K_1 r_1^{-3} (4G_0 + 3K_0)}{D} \quad (8)$$

$$B_1 = \frac{4(\beta_0 - \beta_1) K_0 T \{ (r_2^{-3} - r_1^{-3}) G_0 (3K_0 r_1^{-3} - 3K_0 r_0^{-3} - 4r_0^{-3} G_1) + r_1^{-3} G_1 (4G_0 r_2^{-3} + 3K_0 r_1^{-3}) \}}{D} \quad (9)$$

$$B_2 = \frac{4(\beta_0 - \beta_1) K_1 T (r_1^{-3} - r_2^{-3}) \{ r_0^{-3} (3K_0 + 4G_1) G_0 + r_1^{-3} 3(G_1 - G_0) K_0 \}}{D} \quad (10)$$

where

$$D = K_0 r_1^{-3} \{ 12r_1^{-3} (K_1 - K_0) (G_0 - G_1) + r_2 (3K_0 + 4G_1) (3K_1 + 4G_0) \} - 4G_0 r_0^{-3} \{ (K_1 - K_0) (3K_0 + 4G_1) (r_2^{-3} - r_1^{-3}) \} \quad (11)$$

The thermal expansion coefficients of the whole system and the shells of 0, 1 and 2 can be estimated from Eqs. (6), (7), (8), (9), (10), and (11) as derived in the following section.

2.2 Thermal Volume Expansion Coefficient of Blend System, α

From

$$1 + \alpha T = (1 + \beta_0 T)^3 \{ 1 + B_0 + A_0 r_0^{-3} (1 + \beta_0 T)^{-3} \}^3$$

we obtain

$$\alpha T = 3\beta_0 T + 3B_0 + 3A_0 r_0^{-3} (1 + \beta_0 T)^{-3} \quad (12)$$

Substituting Eqs. (6), (7) and (11) into Eq. (12) we obtain

$$\alpha = \alpha_0(1 - v) + \alpha_1 v - \frac{4(\alpha_0 - \alpha_1)(K_1 - K_0)v\{G_0(3K_0 + 4G_1)(1 - v) - 3K_0(G_0 - G_1)v_s\}}{K_0\{12(K_1 - K_0)(G_0 - G_1)v_s + (3K_0 + 4G_1)(3K_1 + 4G_0)\} + 4G_0(K_1 - K_0)(3K_0 + 4G_0)v} \quad (13)$$

where v is the volume fraction of component 1 to the total sphere having radius r_0 , and v_s is the volume ratio of the sphere with radius r_2 to the sphere with radius r_1 . Then, v and v_s are given by Eqs. (14) and (15), respectively.

$$v = (r_1^3 - r_2^3)/r_0^3 \quad (14)$$

$$v_s = r_2^3/r_1^3 \quad (15)$$

The specially simplified relation of $3\beta_i = \alpha_i$ ($i = 0$ and 1) is used for derivation of Eq. (13). v_s may be the parameter which represents the dispersed state of particles in the blend and from its definition, Eq. (16) is obtained.

$$0 \leq v_s \leq 1 - v \quad (16)$$

The change of the dispersed state according to the variation of v_s is schematically represented in Figure 2. The dispersed state of the model "4" is same in its mathematical expression as that of the model "2". That is, when the

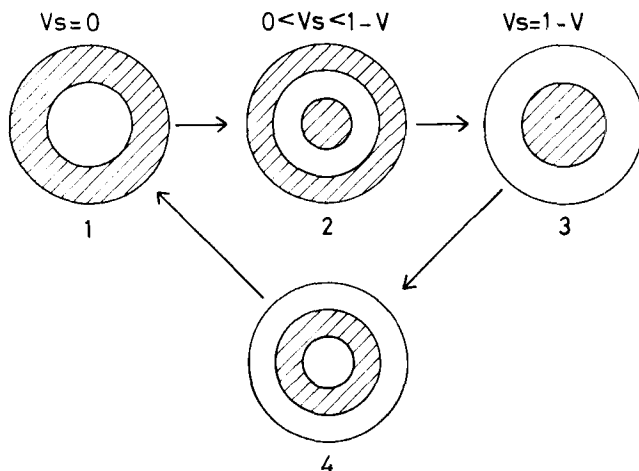


FIGURE 2 Change of the shell model depending on the change of the parameter v_s .

components of the shells of the model "2" are exchanged with each other, the dispersed state corresponding to the model "2" is changed into the one corresponding with the model "4" by replacing the shell numbers, 1 and 2 each other. Therefore, the equations given above are applicable to the state of the model "4". When $\alpha_0 > \alpha_1$ and $K_0 < K_1$, α increases with increasing v_s , and when $\alpha_0 < \alpha_1$ and $K_0 > K_1$, α decreases with increasing v_s . The maximum and minimum values of α are the values corresponding to $v_s = 1 - v$ and $v_s = 0$, respectively.

For the special case of $v_s = 0$ and $v_s = 1 - v$, Eqs. (17) and (18) are obtained, respectively. These equations are the same as derived by Kerner⁴ and the authors.⁷

$$\alpha = \alpha_0(1 - v) + \alpha_1 v - \frac{4G_0(K_1 - K_0)(\alpha_0 - \alpha_1)v(1 - v)}{4G_0(K_1 - K_0)v + K_0(3K_1 + 4G_0)} \quad \text{for } v_s = 0 \quad (17)$$

$$\alpha = \alpha_0(1 - v) + \alpha_1 v - \frac{4G_1(K_0 - K_1)(\alpha_1 - \alpha_0)v(1 - v)}{4G_1(K_0 - K_1)(1 - v) + K_1(3K_0 + 4G_1)} \quad \text{for } v_s = 1 - v \quad (18)$$

2.3 Expansion Coefficients of Shells

These coefficients can be obtained by following the same procedure as used for the calculation of α . The thermal expansion coefficient of the shell 0, $\alpha(0)$, is derived by the same procedure as in the case of calculation of α , based on the following relationship

$$1 + \alpha(0)T = \frac{r_0^3(1 + \beta_0 T)^3\{1 + A_0 r_0^{-3}(1 + \beta_0 T)^{-3} + B_0\}^3 - r_1^3(1 + \beta_1 T)^3\{1 + A_0 r_1^{-3}(1 + \alpha_1 T)^{-3} + B_0\}^3}{r_0^3 - r_1^3}$$

From this equation, Eq. (19) is obtained under the condition of $1 \gg \beta_0 T$, $1 \gg \{A_0 r_0^{-3}(1 + \beta_0 T)^{-3} + B_0\}$ and $\alpha = 3\beta$

$$\alpha(0) = \alpha_0 - \frac{4(\alpha_0 - \alpha_1)G_0 K_1(3K_0 + 4G_1)v}{K_0\{12(K_1 - K_0)(G_0 - G_1)v_s + (3K_0 + 4G_1)(3K_1 + 4G_0)\} + 4G_0(K_1 - K_0)(3K_0 + 4G_1)v} \quad (19)$$

In the special case of $v_s = 1 - v$ and $v_s = 0$, Eq. (19) becomes Eq. (20) and Eq. (21), respectively.

$$\alpha(0) = \alpha_0 - \frac{4(\alpha_0 - \alpha_1)G_0 K_1(3K_0 + 4G_1)v}{(3K_0 + 4G_0)\{4(K_1 - K_0)G_1v + K_0(4G_1 + 3K_1)\}} \quad \text{for } v_s = 1 - v \quad (20)$$

$$\alpha(0) = \alpha_0 - \frac{4(\alpha_0 - \alpha_1)G_0 K_1 v}{K_0(3K_1 + 4G_0) + 4G_0(K_1 - K_0)v} \quad \text{for } v_s = 0 \quad (21)$$

Eq. (20) gives the limiting value of the expansion coefficient of the shell 0. Eq. (20) gives the minimum and the maximum values of $\alpha(0)$ for $\alpha_0 > \alpha_1$ and $\alpha_0 < \alpha_1$, respectively. The value of $\alpha(0)$ is always between the values given by Eq. (20) and Eq. (21).

The expansion coefficient of the shell 1, $\alpha(1)$, is obtained by the same procedure as mentioned above. Thus,

$$\alpha(1) = \alpha_1 + \frac{4(\alpha_0 - \alpha_1)K_0\{G_0[3K_0(1 - v_s) - (3K_0 + 4G_1)v] + G_1(4G_0 + 3K_0 v_s)\}}{K_0\{12(K_1 - K_0)(G_0 - G_1)v_s + (3K_0 + 4G_1)(3K_1 + 4G_0)\} + 4G_0(K_1 - K_0)(3K_0 + 4G_1)v} \quad (22)$$

Eq. (22) is a monotonous increasing function when $\alpha_0 > \alpha_1$ and $G_1 > G_0$.

In the special case of $v_s = 1 - v$ and $v_s = 0$, Eqs. (23) and (24) can be derived, respectively, from Eq. (22).

$$\alpha(1) = \alpha_1 + \frac{4(\alpha_0 - \alpha_1)K_0 G_1(1 - v)}{K_1(3K_0 + 4G_1) + 4G_1(K_0 - K_1)(1 - v)} \quad \text{for } v_s = 1 - v \quad (23)$$

$$\alpha(1) = \alpha_1 - \frac{4(\alpha_0 - \alpha_1)K_0 G_0(1 - v)}{K_0(3K_1 + 4G_0) + 4G_0(K_1 - K_0)v} \quad \text{for } v_s = 0 \quad (24)$$

Eq. (23) coincides with Eq. (21) when suffixes 0 and 1, and v in Eq. (21), are replaced by suffixes 1 and 0, and $1 - v$, respectively. The value of $\alpha(1)$ is always between the values given by Eq. (23) and (24).

In the case of the shell (sphere 2), its expansion coefficient, $\alpha(2)$, is calculated by the same procedure as those of $\alpha(0)$ and $\alpha(1)$ and given by

$$\alpha(2) = \alpha_0 - \frac{4(\alpha_0 - \alpha_1)K_1\{(3K_0 + 4G_1)G_0 v + 3K_0(G_1 - G_0)(1 - v_s)\}}{K_0\{12(K_1 - K_0)(G_0 - G_1)v_s + (3K_0 + 4G_1)(3K_1 + 4G_0)\} + 4G_0(K_1 - K_0)(3K_0 + 4G_1)v} \quad (25)$$

In the special cases of $v_s = 1 - v$ and $v_s = 0$, Eq. (25) becomes Eq. (26) and Eq. (27), respectively

$$\alpha(2) = \alpha_0 - \frac{4(\alpha_0 - \alpha_1)K_1 G_1 v}{4(K_1 - K_0)G_1 v + (3K_1 + 4G_1)K_0} \quad \text{for } v_s = 1 - v \quad (26)$$

$$\alpha(2) = \alpha_0 - \frac{4(\alpha_0 - \alpha_1)K_1\{(3K_0 + 4G_1)G_0 v + 3K_0(G_1 - G_0)\}}{(3K_0 + 4G_1)(3K_1 K_0 + 4G_0 K_0 + 4G_0 K_1 v - 4G_0 K_0 v)} \quad \text{for } v_s = 0 \quad (27)$$

Eq. (27) gives the limiting value of $\alpha(2)$ when v_s tends to zero. $\alpha(2)$ of Eq. (27) gives the minimum value for $\alpha_0 > \alpha_1$ and the maximum value for $\alpha_0 < \alpha_1$ as a function of v . $\alpha(2)$ always takes the value between those given by Eqs. (26) and (27).

3 EXPERIMENTAL

3.1 Sample Preparation

The polymers studied are listed in Table I along with abbreviations and characterizations of materials. The blend of polymers A and B and the copolymer of comonomers A and B are denoted hereafter by A/B and A.B, respectively. The system of PS/PBD, ST.AN(AN content 25%)/PBD, and

TABLE I
Polymer samples

Polymers (Abbreviation)	Characterization of materials
Polystyrene (PS)	Prepared by usual technique of emulsion polymerization; $M_n = 8.9 \times 10^4$
Polyvinylchloride (PVC)	Manufactured by Japanese Geon Co. Ltd.; $M_n = 6.6 \times 10^4$
Polymethylmethacrylate (PMMA)	Product of Mitsubishi Rayon Co., Ltd.
Styrene-acrylonitrile	Prepared by usual technique of emulsion polymerization; AN content 25% and 50%
Polycarbonate (PC)	Product of Teijin Co., Ltd.
Vinylacetate-vinylchloride copolymer (VAc.VC)	Manufactured by Japanese Geon Co., Ltd.; VAc content 29%
Polyvinylacetate (PVAc)	Product of Nippon Synthetic Chemical Ind. Co., Ltd.
Acrylonitrile butadiene rubber (NBR)	Product of Japanese Geon Co., Ltd.; AN content 30%
Styrene-butadiene rubber (SBR)	Product of Japan Synthetic Rubber Co., Ltd.; ST content 24.5%
Polybutadiene (PBD)	Product of Firestone Co., Ltd., #2004; gel content 85%
<i>cis</i> -Polybutadiene (<i>cis</i> -PBD)	Product of Goodrich Gulf., Ltd.; <i>cis</i> content 97%

ST.AN(AN content 50%)/PBD were prepared by mixing the emulsions of PS, ST.AN(AN content 25%) and ST.AN(AN content 50%) with PBD latex, respectively. A 10% aqueous CaCl_2 solution was poured into the mixture of the resin emulsion and the PBD latex and the polymer blend was precipitated. For the blend systems of PS/SBR, PS/NBR, PS/PVAc, PS/VAc.VC, PS/PVC, PVC/SBR, PMMA/SBR, PMMA/PS, and PC/SBR, the component polymers were dissolved into the common solvent, and the resultant

solution was poured into the non-solvent to precipitate the blends. After drying the precipitates, the films of 0.2 to 0.4 mm thick were prepared by molding in a laboratory press.

3.2 Measurements

For the measurement of T_g , a dilatometer was used and T_g was defined as the temperature where two straight lines of a volume-temperature curve intersect. The average heating rate was $0.5^\circ\text{C}/\text{min}$. α_1 is the thermal expansion coefficient above the both T_g s of the blend system and α_g is the thermal expansion coefficient in a temperature range between the higher T_g and the lower T_g of both component polymers in the blend.

Dynamic viscoelasticity was measured using the Rheovibron, Model DDV-II, of Toyo Measuring Instruments Co., Ltd. The frequency adopted was 110 Hz and the average heating rate of the sample was $1^\circ\text{C}/\text{min}$. The temperatures of the absorption peak were used to determine the relative variation of T_g as a function of composition for a series of polystyrene/rubber blends.

4 RESULTS AND DISCUSSION

4.1 Thermal Expansion Coefficient

Figures 3, 4, 5 and 6 show the composition dependence of the thermal expansion coefficients α_1 and α_g for the systems of PS/PBD, PMMA/SBR, PVC/SBR and ST.AN/PBD, respectively. The full lines in these figures represent the linear relationship according to the law of volume additivity. The broken lines in these figures show the calculated values by Eq. (18). The model "3" in Figure 2 was adopted for calculation of α and the inner shell is composed of rubbery material. The calculation of α was made in a temperature range between both T_g s of the component polymers in the blend. The values of K and G employed for these calculations are tabulated in Table II. The behavior of the thermal expansion near T_g is very complicated because of the increased effect of the volume relaxation of the component polymers. This problem will be discussed in the later section, where the phenomena associated with an increase of T_g will be discussed as indicated in Section 1. The expansion coefficient calculated by Eq. (17) is nearly equal to the values calculated by assuming the volume additivity. The model "1" in Figure 2 was adopted for calculation of α given by Eq. (17). The outer shell is made of rubbery material. The observed thermal volume expansion coefficients shown in Figures 3, 4, 5 and 6 exist between the values calculated by Eqs. (17) and (18). In particular the values for the system of PS/PBD almost agree with those calculated by Eq. (18).

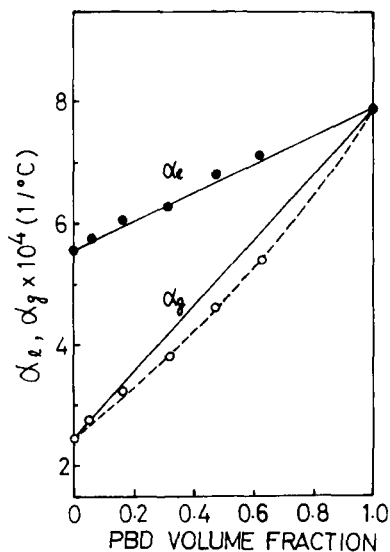


FIGURE 3 Thermal expansion coefficients α_1 and α_g vs. volume fraction of polybutadiene (PBD) for the system of PS/PBD. α_1 and α_g are the values at about 100°C and 20°C , respectively. Full lines and broken line indicate the values calculated by the additivity law and Eq. (18), respectively, and open circles are observed values.

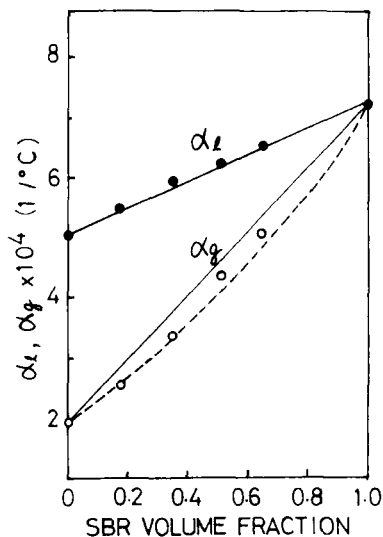


FIGURE 4 Thermal expansion coefficients α_1 and α_g vs. volume fraction of SBR for the system of SBR/PMMA. α_1 and α_g are the values at about 100°C and 20°C , respectively. Full lines and broken line indicate the values calculated by the additivity law and Eq. (18), respectively. Filled and open circles are observed values.

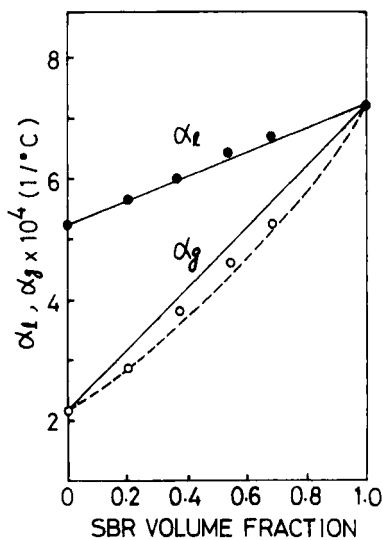


FIGURE 5 Thermal expansion coefficients α_1 and α_g vs. volume fraction of SBR for the system SBR/PVC. α_1 and α_g are the values at about 90°C and 20°C , respectively. Full lines and broken line indicate the values calculated by the additivity law and Eq. (18) respectively. Filled and open circles are observed values.

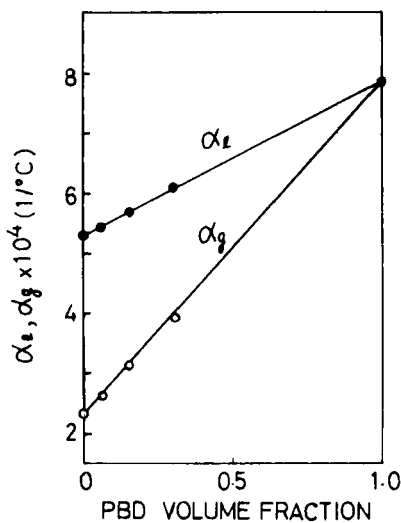


FIGURE 6 Thermal expansion coefficients α_1 and α_g vs. volume fraction of PBD for the system of ST.AN(AN 50%)/PBD. α_1 and α_g are the values at about 90°C and 20°C , respectively. Full lines indicate the values calculated by the additivity law. Filled and open circles are observed values.

TABLE II
K and *G* used for calculations

Polymers	<i>K</i> (dyn/cm ²)	<i>G</i> (dyn/cm ²)
PS	3.4×10^{10a}	1.2×10^{10a}
PVC	4.5×10^{10a}	1.2×10^{10a}
PMMA	5.0×10^{10a}	1.5×10^{10a}
SBR	1.8×10^{10b}	not used
PBD	1.8×10^{10b}	not used

^a Modulus in a glassy state

^b Modulus in a rubbery state

Both Eqs. (17) and (18) give almost the same values at sufficiently high temperatures above T_g s of both component polymers in the blend. The additivity law may be satisfied for the observed values of expansion coefficient above both T_g s. These facts may predict that the thermal stress caused by the difference of the expansion coefficients of two component polymers in the blend can be neglected above both T_g s. Such a negligibility of thermal stress effect is consistent with the results predicted by Eq. (13), (17), or (18).

The fact that the experimental values of α_g of PS/PBD as shown in Figure 3 were almost the same or a little greater than the values calculated by Eq. (18) means that the PBD components form the dispersed particles in the PS matrix in spite of the large content of PBD (30%). In this case, the dispersed state is probably like the model 2 of Figure 2, where the part of oblique lines (layer 1) corresponds to PBD.

On the other hand, α_g of ST.AN/PBD (Figure 6) can be expressed by Eq. (17), which is close to a value calculated on the base of the additivity law. This means that the thermal stress caused by the difference of expansion coefficients between two component polymers in the blend does not have much influence for the system of ST.AN/PBD. This may be due to one of the following conditions: (1) the mixed state is similar to the one represented schematically in Figure 2(2) that is, PS is dispersed in PBD, or (2) the mixed state is something like a lamellar or band structure, or (3) the relaxation effect of the matrix phase is so large that the thermal stress is relaxed independently of the dispersion state. The volume fraction of PBD in the blend actually investigated is smaller than 0.3. In such a case, case (1) is difficult to be realized. Case (2) is very rare according to the actual observations in such systems.¹¹ Thus, the third reason is most conceivable and seems to be reasonable to interpret the fact that the increase of T_g was not observed in the system of ST.AN/PBD.

As an example for the calculation of Eq. (13), the system of PS/PBD was adopted. The values cited in Tables II and III were used for this calculation and also the value of *G* of PBD 5.0×10^6 (dyn/cm²) was used. Figure 7 shows

TABLE III
 α_1 , α_2 and K_1 used for calculation

Sphere	Component Polymer	Composition	$\alpha_1(^{\circ}\text{C}^{-1})$	$\alpha_2(^{\circ}\text{C}^{-1})$	$K_1(\text{dyn/cm}^2)$
1	PS	0.8	5.55×10^{-4}	2.45×10^{-4}	not used
0	PBD	0.2	7.90×10^{-4}	not used	1.8×10^{10}

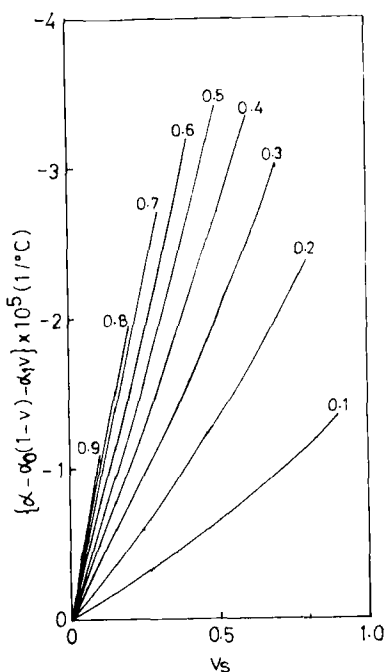


FIGURE 7 $\alpha - \alpha_0(1-v) - \alpha_1v$ vs. v_s for the system of PS/PBD. The figures in this figure indicate the value of v .

the variation of $\alpha - [\alpha_0(1-v) + \alpha_1v]$ with the value of v_s at various amounts of v . The value of $\alpha - \alpha_0(1-v) - \alpha_1v$ represents the amount of the deviation from the additivity law of thermal expansion coefficient. As seen in this figure the larger the value of v , that is, the smaller the volume fraction of PBD is, the greater the v_s dependence of this deviation is.

When the volume ratio of rubber components of the shells 0 to 2 is constant, the v dependence of the deviation from the additivity law of thermal expansion coefficient was shown in Figure 8 as a function of v_s . These values of this figure

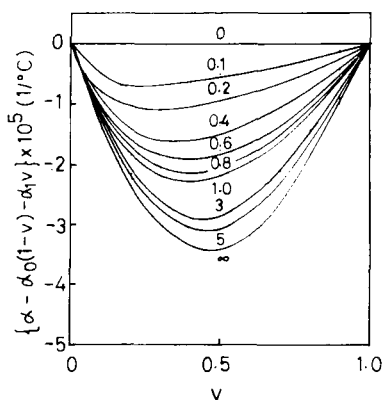


FIGURE 8 $\alpha - \alpha_0(1 - v) - \alpha_1v$ vs. v for the system of PS/PBD. The figures in this figure indicate the volume ratio of shell 0 and shell 2.

were transferred from Figure 7. For example, when the volume ratio of shells 0 and 2 equals 1 the volume fraction of shell 0 is $0.5(1 - v)$ and from the definition of v_s we obtain $v_s = 0.5(1 - v) / \{0.5(1 - v) + v\}$. From the lines of constant v in Figure 7, the value of $\alpha - \alpha_0(1 - v) - \alpha_1v$ at the point of v_s obtained above can be read. That is, when $v = 0.5$, v_s is 0.333 and from the line of $v = 0.5$ the value of 2.18×10^{-5} is obtained. With decreasing content of the rubber the deviation from the additivity law of thermal expansion coefficient is affected by the change of the volume ratio of the shells 0 and 2. On the other hand, when the rubber content is very large such as 0.8 or 0.9 the deviation mentioned above is large even if the volume ratio of shells 0 to 2 is small.

It will be recognized from these examples that most of the expansion coefficients of two separate phase system are described by Eq. (13). However, there is one special case in which Eq. (13) can not be applied in spite of two separate phase system. It is the system of PS/PMMA. Figure 9 shows that the observed expansion coefficients of this system above T_g deviate considerably from the estimated values (full line) given by Eq. (13). This deviation may be due to the molecular interaction between both components. By utilizing this relation, we will be able to estimate the degree of molecular interaction qualitatively by measuring the deviation of expansion coefficient from the calculated curve above T_g .

4.2 Abnormal Phenomena in T_g of Two Separate Phase System

As mentioned in Section 1, there are two T_g s for the blend system composed of two separate phase. The higher T_g of the two T_g s of the blend system is noted by T_{g1b} and the lower T_g by T_{g2b} . The T_g s located at a high and a low

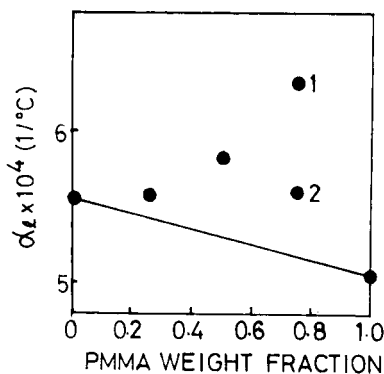


FIGURE 9 α_1 vs. weight fraction of PMMA for the system of PS/PMMA. Full line represents the relationship calculated by the additivity law above T_g . Filled circles are observed values. Numbers, 1 and 2, indicate the value above 115°C and the value between 100°C and 115°C , respectively.

temperature range for the mono-component polymers are denoted by T_{g1} and T_{g2} , respectively. The deviation of T_g caused by mixing from the original T_g is classified as follows.

- (1) $T_{g1b} = T_{g1}, T_{g2b} = T_{g2}$
- (2) $T_{g1b} = T_{g1}, T_{g2b} > T_{g2}$
- (3) $T_{g1b} = T_{g1}, T_{g2b} < T_{g2}$
- (4) $T_{g1b} < T_{g1}, T_{g2b} > T_{g2}$
- (5) $T_{g1b} < T_{g1}, T_{g2b} < T_{g2}$
- (6) $T_{g1b} < T_{g1}, T_{g2b} = T_{g2}$
- (7) $T_{g1b} > T_{g1}, T_{g2b} > T_{g2}$
- (8) $T_{g1b} > T_{g1}, T_{g2b} < T_{g2}$
- (9) $T_{g1b} > T_{g1}, T_{g2b} = T_{g2}$

Cases (1) and (2) in this classification are the typical ones of the two separate phase system. For example, the system of ST.AN(AN content 50%)/PBD belongs to case (2). One reason for $T_{g2b} > T_{g2}$ is due to the filler effect of component 1. In the cases of (4) and (9), their systems approach the partially miscible system because of the increase of their mutual solubilities (for example, ST.AN/NBR²). There are no examples for the cases of (3), (5) and (6). As mentioned already in Section 1, the cases of (7) and (8) were found using one series of special systems composed of some plastic and rubber components. In the later parts, we will frequently call the components having

higher and lower T_g the plastic and rubber components, respectively. The discussions of these cases are given in the following sections.

4.2.1 *Increase in T_g of plastic component* Figure 10 shows the composition dependence of T_g of PS in the blend systems which contain the polymer with lower T_g than PS as a function of weight fraction of the partner polymer.

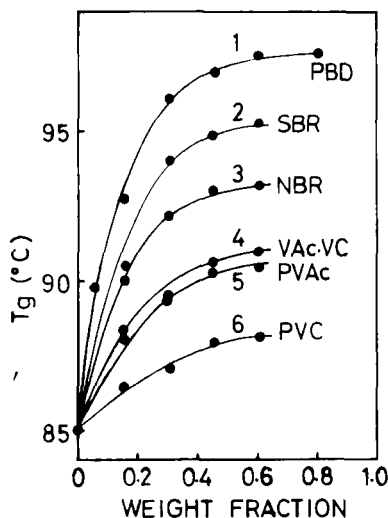


FIGURE 10 T_g of PS vs. composition of the blend. The polymers indicated are the partners of PS in the blend systems.

Although the T_g of PS increases with increase of the PS weight fraction, there can be clear differences among the systems with different partner polymers.

Figure 11 shows the relative change of T_g of the plastic component (with higher T_g), ΔT_g , as a function of weight fraction of the rubber component (lower T_g). ΔT_g is defined as the difference of T_g s of the plastic component between before and after mixing. From Figure 11 it is clear that ΔT_g increases with increase of the weight fraction of the rubber component and that there are distinct differences in ΔT_g among the systems with different plastic components when the comparison is made at the same composition of PBD or SBR. The following three reasons will be considered for the increase of T_g of the plastic component in the blend: (1) filler effect, (2) thermal stress effect caused by the difference of thermal expansion coefficients between the plastic and rubber components, and (3) molecular interaction between the component polymers.

Since the partner polymer to the plastic component is a rubber, the filler

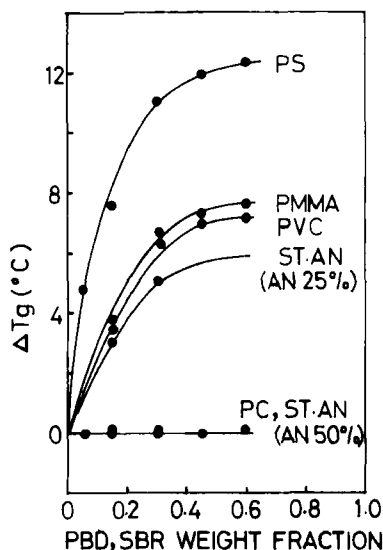


FIGURE 11 Change of T_g (or ΔT_g) of plastic component vs. weight fraction of rubber component (PBD or SBR) for the blend. The polymers denoted in this figure indicate the plastic components.

effect cannot be expected. The effect of thermal stress is most probable as the origin for the rise of T_g . As mentioned before the change of the thermal expansion coefficient generated by the thermal stress is described by Eq. (13) and Eqs. (17) and (18). Especially, Eq. (18) is applicable to the system of PS/PBD in which the rise of T_g is remarkable.

Although the expansion coefficient of the spherical shell 1 is given by Eq. (22), we try to evaluate it using the equation derived from Eq. (22) in the special case of $v_s = 1 - v$ (cf. Figure 2(3)). When $v_s = 1 - v$, the thermal expansion coefficients of the blend and the components 1 (plastic phase) and 0 (rubber phase) are given by Eqs. (18), (23) and (26), respectively. For the isotropic material, Eq. (28) is given.

$$E = 2G(1 + \nu) = 3K(1 - 2\nu) \quad (28)$$

where E is tensile modulus and ν is Poisson's ratio.

The calculation on the system of PS/PBD is made as follows. The relaxation effects are expected in E , G , and K , which cannot be neglected near T_g of PS. As the heating and cooling rate of dilatometric measurements was $0.5^\circ\text{C}/\text{min.}$, the values of E , G , and K at 120 sec. were used. The numerical values employed were summarized in Table III. The T_g of PS used was 75°C . Table IV shows the relaxation modulus and Poisson's ratio (ν) of PS at various temperatures. The relaxation moduli listed in Table IV are observed values.

TABLE IV
E and ν of PS

Temperature ($^{\circ}\text{C}$)	ν^a	$E(120)(\text{dyn/cm}^2)^b$
75	0.36	2×10^{10}
80	0.37	1.7×10^{10}
85	0.39	9.8×10^9
90	0.46	3×10^9
95	0.497	1×10^8
100	0.4997	1.5×10^7
105	0.49981	1.22×10^7
110	0.49985	9.45×10^6

^a Interpolated values

^b Relaxation modulus at 120 sec. Cf. A. V. Tobolsky, *Properties and Structures of Polymers* (Wiley, New York, 1960), p. 74.

The values of ν at room temperature and at sufficiently high temperature above T_g are evaluated as 0.35 and 0.5, respectively. The ν values between these temperatures were evaluated assuming a smooth bulk modulus-temperature curve.

Figure 12 shows the result of calculations. The values on the abscissa are $\{\alpha_0 - \alpha(0)\}/(\alpha_0 - \alpha_1)$, $\{\alpha_1 - \alpha(1)\}/(\alpha_0 - \alpha_1)$ and $\{\alpha_0(1 - \nu) + \alpha_1\nu - \alpha\}/(\alpha_0 - \alpha_1)$. It can be seen from Figure 12 that the values of PS deviate in the cooling process from the equilibrium values about 95°C . Above 95°C , the volume of PS is nearly the same before mixing, and below 95°C , the volume becomes smaller than before mixing. As the difference of the thermal expansion coefficients of both homopolymers, $(\alpha_0 - \alpha_1)$, is 2.35×10^{-4} at $T > T_g$, the volume contraction of PS between 95°C and 75°C caused by thermal stress, Δv , is approximately calculated by Eq. (29),

$$\frac{\Delta v}{v} = 2.35 \times 10^{-4} \int_{75}^{95} \kappa(T) dT \simeq 1.76 \times 10^{-4} \quad (29)$$

where $\kappa(T)$ is

$$4G_1K_0(1 - \nu)/\{K_1(3K_0 + 4G_1) + 4G_1(K_0 - K_1)(1 - \nu)\}.$$

If this volume contraction is spent for the decrease of free volume, the increase of T_g from the thermal stress is roughly given by the equation $\Delta v/v/\Delta\alpha_f = 5.69 \times 10^{-1}$ ($^{\circ}\text{C}$), where $\Delta\alpha_f$ is the expansion coefficient of free volume fraction which is expressed by the difference of thermal expansion coefficient between glassy and rubbery states. The change of T_g caused by the thermal stress gives rise to the change of temperature dependence of K , G and ν , which in turn makes the calculated T_g increase. Assuming 5°C

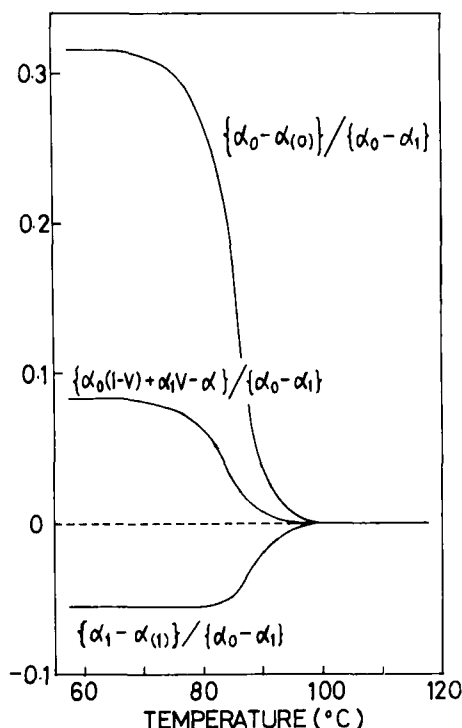


FIGURE 12 Calculated temperature dependence of the expansion coefficients of the component polymers in the blend system. Refer to the text for the denoted quantities.

increase of T_g of PS from the thermal stress, the values of K , G and ν shift to the higher temperature side by 5°C than those before mixing. The value of volume contraction at 75°C , $\Delta v/v$, was calculated through a similar procedure to Eq. (29) for this system and is about $3/2$ times of the value given by Eq. (29). Therefore, the degree of the increase of T_g from the thermal stress, ΔT_g , exists in the following range in the case mentioned above.

$$5.69 \times 10^{-1} (^\circ\text{C}) < \Delta T_g < 1.98 (^\circ\text{C}) \quad (30)$$

Eq. (24) gives the maximum increase of T_g of PS and its value is about 2°C . It should be noted that the observed volume is the whole volume of the blend and not of PS itself in the blend. Therefore, when the T_g of PS in the blend is decided as the temperature of the break point in the volume-temperature curve, the change of T_g from the thermal stress should be estimated from Eq. (13), which expresses the temperature dependence of the whole volume of the blend.

It is obvious from Figure 12 that the deviation of the specific volume of the blend system appears below 89°C in the cooling process if the T_g of PS is assumed as 75°C. The calculated specific volume of the blend is larger than the value estimated from the volume additivity law. The value of T_g obtained from the volume temperature curve is, therefore, 82 to 85°C. The former is taken as the average value of 89 and 75°C, and the latter is the temperature at which the d^2v/dT^2 is maximum. As the T_g of PS changes to 76 ~ 77°C from the thermal stress discussed above, the observed T_g is conclusively estimated as 83 ~ 84°C or 85 ~ 86°C. That is, the estimated increase of T_g from the thermal stress for this system, where $v = 0.8$, is 8 ~ 12°C and the observed value was 9.7°C. The agreement between the calculated and the observed value is satisfactorily good. According to Eq. (24), the T_g of PS in the blend increases with increasing composition of PBD. On the other hand, the T_g estimated from the volume-temperature curve of the blend exhibits the maximum at $v = 0.5$ as proved by Eq. (18). Actually, since v_s decreases with increase of the fraction of PBD, the T_g of PS must be lower than those given by Eqs. (24) and (18).

From Eqs. (24) and (18), we may obtain some predictions on the increase of T_g of PS caused by the thermal stress. ΔT_g estimated from the temperature dependence of the volume of plastic component itself is given by the following equation, which is derived with the same procedure as in Eq. (29).

$$\begin{aligned} \Delta T_g &\simeq \frac{(\alpha_0 - \alpha_1)}{\Delta\alpha_f} \int_{T_{g1b}}^{\infty} \kappa(T) dT \\ &= \frac{4(\alpha_0 - \alpha_1)(1 - v)}{\Delta\alpha_f} \int_{T_{g1b}}^{\infty} \frac{G_1 K_0}{K_1(3K_0 + 4G_1) + 4G_1(K_0 - K_1)(1 - v)} dT \quad (31) \end{aligned}$$

The predictions are that (1) there is a mutual relationship between the increase of T_g and the negative deviation of the thermal expansion coefficient of the blend from the additivity law as found in Figure 3, since the increase of v_s makes the T_g of PS increased and the thermal expansion coefficient decreased (cf. Figure 7); (2) the greater the difference of the thermal expansion coefficients above T_g between the rubber and the plastic components, $(\alpha_0 - \alpha_1)$, the larger the degree of increase of T_g of the plastic component is; and (3) the increase of T_g is proportional to $(1 - v)$ when $(1 - v)$ is very small (see Eq. 24). On the other hand, the T_g estimated from the temperature dependence of the whole volume of the blend, not of PS itself, will exhibit the maximum because of the existence of the maximum deviation of α at $v = 0.5$ (see Eq. (18) and Figure 8).

The predictions of (1) and (3) are consistent with the results of Figures 10 and 11 qualitatively. Figure 13 shows the relationship between ΔT_g and $(\alpha_0 - \alpha_1)$. There is some trend toward consistency with the prediction (2)

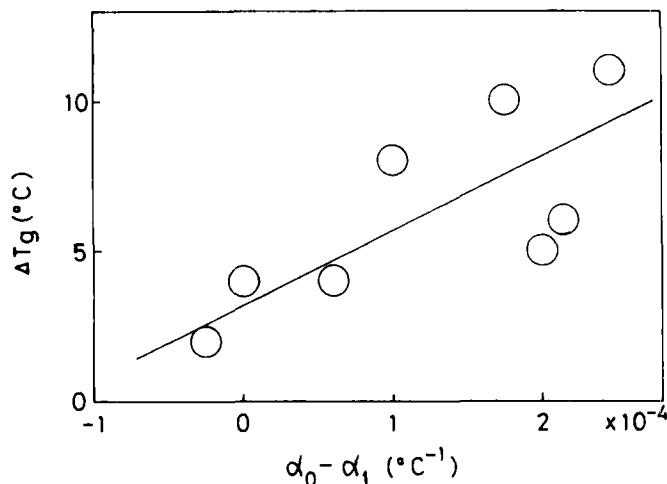


FIGURE 13 Relationship between ΔT_g and $(\alpha_1 - \alpha_0)$. $(\alpha_1 - \alpha_0)$ is the difference of the thermal expansion coefficient between component 1 and 0 above both $T_{g,s}$.

even though experimental points are scattered. It should be noted that, even in the case of $\alpha_0 - \alpha_1 = 0$, ΔT_g in Figure 13 equals to 3°C . This result means that the origin of the increase of T_g is not always from the thermal stress.

The increase in $T_{E^*_{\max}}$ of the system PS/PBD, which is taken as the measure of T_g but is higher by about 20°C than T_g was observed. This phenomena of increase of T_g may occur due to the thermal stress or the decrease of the activation energy (ΔH_a^*) generated by the increase of the thermal expansion coefficient from the thermal stress. The activation energy is given by Eq. (32).

$$\Delta H_a^* = RT^2 \Delta\alpha_f / f(T)^2 \quad (32)$$

where R is gas constant and $f(T)$ is the free volume fraction at temperature T . Equation (33) is obtained by differentiating Eq. (32) with $f(T)$.

$$\{d\Delta H_a^*/df(T)\}_T = \{RT^2/f(T)^3\}(-2\Delta\alpha_f) < 0 \quad (33)$$

ΔH_a^* decreases with increasing $f(T)$. $f(T)$ of PS above 90°C is slightly increased by mixing because of the increase of $\Delta\alpha_f$. As mentioned in Eqs. (22), (23) and (24), $\Delta\alpha_f$ of PS increases by mixing and ΔH_a^* of PS decreases by mixing. This decrease of ΔH_a^* gives rise to the shift of $T_{E^*_{\max}}$ to higher temperature at the measuring frequency.

4.2.2 T_g of rubber phase The thermal expansion coefficient of rubber is given by Eqs. (19) and (25). In a special case, where the thermal expansion coefficient of the dispersed rubber is most affected by the thermal stress, Eq. (27) is effective. The model "2" of Figure 2 was adopted as a schematic

model. The plastic phase is frozen in a glassy state near T_g of rubber, and its expansion coefficient in accordance with the value in a glassy state. Therefore, the $(\alpha_0 - \alpha_1)$ is always positive near T_g of rubber and the expansion coefficient of the rubber becomes smaller than one before mixing as expected from the decrease of T_g of rubber phase. The degree of decrease of T_g of the rubber phase can be calculated by Eq. (27) following the same procedure as Eq. (31). That is, the volume expansion of the rubber component may make free volume increased due to the thermal stress. The equation of ΔT_g is then

$$\Delta T_g \geq \frac{1}{\Delta\alpha_f} \int_{T_{g2b}}^{\infty} \{\alpha(2) - \alpha_0\} dT$$

or

$$\Delta T_g \geq$$

$$\frac{4(\alpha_1 - \alpha_0)}{\Delta\alpha_f} \int_{T_{g2b}}^{\infty} \frac{K_1\{(3K_0 + 4G_1)G_0v + 3K_0(G_1 - G_0)\}}{(3K_0 + 4G_1)(3K_1K_0 + 4G_0K_0 + 4G_0K_1v - 4G_0K_0v)} dT$$

or

$$\Delta T_g \geq \frac{4(\alpha_1 - \alpha_0)K_1\{(3K_0 + 4G_1)G_0v + 3K_0(G_1 - G_0)\}(T_{g1} - T_{g2})}{(3K_0 + 4G_1)(3K_1K_0 + 4G_0K_0 + 4G_0K_1v - 4G_0K_1v - 4G_0K_0v) \Delta\alpha_f} \quad (34)$$

The phenomena that the T_g of the rubber phase in the blend, block and graft copolymers decreases with respect to the T_g of the homo-material have been often observed, but the theoretical investigations have not been made as yet.^{2,3} Eq. (34) predicts that the decrease of T_g from the thermal stress is proportional to the difference of T_g between two components, $T_{g1} - T_{g2}$, to the difference between α_1 of the plastic and α_0 of the rubber, $\alpha_1 - \alpha_0$, and approximately to the volume fraction of the plastic, v . As the actual expansion coefficient exists between the values given by Eq. (26) and Eq. (21), ΔT_g also exists between the values calculated from the same equations. Thus, the following equation is obtained

$$\frac{4(T_{g1} - T_{g2})(\alpha_1 - \alpha_0)K_1G_0v}{\{(K_1 - K_0)4G_0v + K_0(3K_1 + 4G_0)\} \Delta\alpha_f} > \Delta T_g > \frac{4(T_{g1} - T_{g2})(\alpha_1 - \alpha_0)K_1G_1v}{\{(K_1 - K_0)4G_1v + K_0(3K_1 + 4G_1)\} \Delta\alpha_f} \quad (35)$$

In this derivation, the relaxation effect of plastic phase and the change of $(T_{g1} - T_{g2})$ by mixing are neglected.

Only the thermal stress was taken into consideration concerning the change of T_g of rubber phase. Other effects, such as crosslinking and the filler effect

originating in mixing, will increase the T_g of the rubber phase. In such a case, the change of T_g due to thermal stress is difficult to detect separately. It may be possible to say that when the decrease of T_g of the rubber phase in the two separate phase system is observed, the origins of this decrease may be the thermal stress and/or the molecular interaction between the component polymers. PMMA/*cis*-PBD and PVC/*cis*-PBD systems^{2, 3} are the examples in which the T_g of the rubber phase shifts to the lower temperature side when blended with plastics.

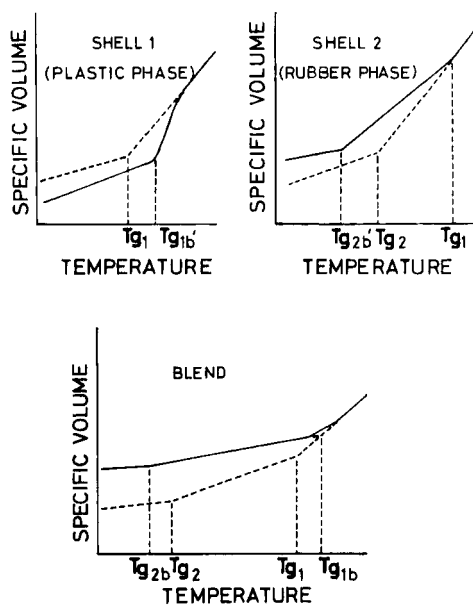


FIGURE 14. Schematic representation of the specific volume-temperature curves of the shells 1 and 2 and the blend (full lines). T_{g1} and $T_{g1b'}$ are the T_g s of the pure component 1 and the one after mixing, respectively. T_{g2} and $T_{g2b'}$ are the T_g s of the pure component 2 and the one after mixing, respectively. T_{g1b} and T_{g2b} are the T_g s of component 1 and 2 estimated from the whole specific volume of the blend. In general, the relation of $T_{g1b} > T_{g1b'}$ and $T_{g2b} > T_{g2b'}$ hold (refer to the text). Broken lines indicate the values free from thermal stress.

Figure 14 shows the schematic representation of the specific volume-temperature curves for the shells 1 and 2 and the blend system in Figure 1(3). Eqs. (18), (23), and (26) were used in order to calculate the values of α , $\alpha(1)$ and $\alpha(2)$, respectively. It is apparent from this figure that the specific volume of shell 1 (plastic phase) becomes smaller than before mixing (broken line) and the specific volume of shell 2 (rubber phase) becomes larger than before mixing, and the specific volume of the whole blend system becomes larger than the one estimated from the volume additivity law. The difference between

the values calculated by eq. (18) and the additivity law is about $1 \times 10^{-3} \sim 1 \times 10^{-4}$ (cm^3/g) in a temperature range from room temperature to T_{g1} .

4.2.3 Abnormal behavior of PS/PMMA system The blend system composed of the polymers with the same chemical structure but the different molecular weight is one of the examples, in which the components have similar T_g s. Although the T_g of the higher molecular weight fraction shifts to the lower temperature side by mixing, and that of the lower molecular weight fraction shifts to the higher temperature side, in the case of the insufficiently mixed state, the T_g of the system¹⁰ is somewhat higher than the one calculated by the method proposed for the perfectly miscible system.² This discrepancy may be considered to be caused by the effect of the thermal stress.

It should be noted that the effect of thermal stress for the system composed of the components with similar T_g s is usually so small that the molecular interaction between the component polymers is rather distinctly detected. For example, the T_g s of the two polymers in the blend system of PS/PMMA are 90°C and 75°C , respectively, and the difference of T_g is only 15°C . The specific volume-temperature curve is calculated by the same method mentioned in Sections 4.1, 4.2.1 and 4.2.2. In this case, the values of K and ν of PMMA used were evaluated by shifting the values of K and ν of PS to the high temperature side by an amount of 15°C . PS and PMMA correspond to the component 0 and the component 1 in the equation and in this case $\nu = 0.8$ was used.

Figure 15 shows the result of the calculation. The expansion coefficients were calculated by Eqs. (18), (23) and (26), and the degree of the shift of T_g was estimated from Eq. (29). The T_g of component 1 increased by ca. 1°C

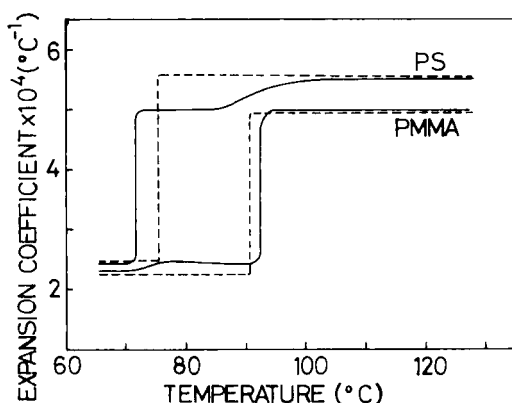


FIGURE 15 Calculated temperature dependence of the expansion coefficient of the system of PS/PMMA. Full lines indicate the values calculated by Eqs. (18), (23) and (26). Broken lines indicate the values of the component before mixing.

and the T_g of the component 0 decreases by ca. 4°C. The respective shifts of T_g s of PMMA and PS to a high temperature side and to a low temperature side are too small and too large in comparison with the observed ones. According to this calculation, the stepwise change of the thermal expansion coefficient of the blend system at T_{g1} is about 2% larger than the change expected by the additivity law and the stepwise change at T_{g2} is about 2% smaller than the one expected by the additivity law. Although these tendencies predicted by the calculation were actually observed, the quantitative agreement between the calculated and the observed values could not be obtained. For the same type of systems with other compositions, qualitative but not quantitative agreement between the calculated and the observed values can be found: the observed values of the increase of T_g are always larger than the calculated ones and also the thermal expansion coefficients observed are always greater than the calculated ones. According to the calculation cited in Section 2, the thermal expansion coefficient above T_g is calculated by the additivity law. On the other hand, the observed values are larger than that from the additivity law.² These discrepancies between the calculated and the observed values may be caused by the molecular interaction which is neglected in the calculation.

The fact that the thermal expansion coefficient above T_g is larger than the one expected from the additivity law may suggest the existence of strong molecular interaction between the component polymers. These discrepancies may be explained as follows. In some blend systems composed of two separate phases in equilibrium, the cohesive force exerted among the same component polymers and the repulsion force interacted among the different component polymers should be taken into account. The expansion coefficient of this system becomes larger than that of the additivity law when the repulsion force is generated more strongly by mixing. We have already reported on the treatment of the molecular interaction in such a case.² As discussed above, at sufficiently high temperatures above T_g , the thermal expansion coefficient of the blend is increased by the repulsive force and around T_g the increase of T_g is caused by the thermal stress and the molecular interaction.

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