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EFFECTS OF MOLECULAR WEIGHT AND INTERACTION PARAMETER ON THE GLASS TRANSITION TEMPERATURE OF POLYSTYRENE MIXTURES AND ITS BLENDS WITH POLYSTYRENE/POLY (2,6-DIMETHYL-*p*-PHENYLENE OXIDE)

LIJIA AN,* DAYONG HE, JIAOKAI JING, ZHIGANG WANG, DONGHONG YU and BINGZHENG JIANG

Polymer Physics Laboratory, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun 130022, People's Republic of China

ZHENHUA JIANG and RONGTANG MA

Department of Chemistry, Jilin University, Changchun, 130023, People's Republic of China

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Abstract—The glass transition temperature (T_g) of mixtures of polystyrene (PS) with different molecular weight and of blends of poly(2,6-dimethyl-*p*-phenylene oxide) (PPO) and polystyrene with different molecular weight (DMWPS) was studied by a DSC method. For the whole range of composition, the curves of T_g vs composition obtained by experiment were compared with predictions from the Fox, Gordon–Taylor, Couchman and Lu–Weiss, equations. It was found that the experimental results were not in agreement with those from the Fox, Gordon–Taylor and Couchman equations for the binary mixtures of DMWPS, where the interaction parameter χ was approximately zero. However, for the blends PPO/DMWPS ($\chi < 0$), with an increase of molecular weight of PS, it was shown that the experimental results fitted well with those obtained from the Couchman, Gordon–Taylor and Fox equations, respectively. Furthermore, the Gordon–Taylor equation was nearly identical to the Lu–Weiss equation when $|\chi|$ was not very large. Further, the dependence of the change of heat capacity associated with the glass transition (ΔC_p) on the molecular weight of PS was investigated and an empirical equation was presented. © 1997 Elsevier Science Ltd

INTRODUCTION

The glass transition temperature of polymer mixtures can be calculated from values of the pure components. Many empirical formulae suggested by Gordon–Taylor [1], Fox [2], Jenckel–Heusch [3] and Simha–Boyer [4] *et al.* were successively presented and extensively used in practice. Couchman [5] suggested a theoretical equation from classical thermodynamics, which could be reduced approximately to the Gordon–Taylor or Fox equations [5]. However, some of the problems of the thermodynamics in Couchman's derivation were discussed by Goldstein [6]. According to the Gibbs–DiMarzio molecular theory of the glass transition [7], Gordon [8] *et al.* obtained a formula, whose form was identical to that of the Gordon–Taylor equation. By using statistical thermodynamics, they provided a physical meaning of the adjustable parameter in the Gordon–Taylor equation. These formed the theoretical foundation of the Gordon–Taylor equation. Taking the specific interaction between polymer components into account, Kwei [9] introduced an interaction term into the Gordon–Taylor equation and obtained a generalized Kwei equation. By adjusting two parameters of this equation, this generalized equation [10] can fit well with all curves of the glass transition temperature (T_g) vs composition, absent of a cusp, for polymer blends [11]. Somewhat later, Lu and Weiss [12, 13] presented a specific formula by combining the Flory–Huggins interaction parameter (χ) [14] with the Kwei equation. Painter *et al.* [15] and Braun *et al.* [16] also

Table 1. List of the monodisperse polystyrene studied

PS samples	M_w ($\times 10^{-4}$)	η	T_g (K)	ΔC_p (J/g K)
PS-1	0.0859	1.15	282	0.466
PS-2	0.29	1.05	335	0.406
PS-3	0.36	1.06	345	0.396
PS-4	0.40	1.04	343	0.396
PS-5	0.51	1.04	358	0.389
PS-6	0.56	1.03	357	0.387
PS-7	0.71	1.03	360	0.385
PS-8	1.00	1.03	358	0.381
PS-9	2.09	1.03	366	0.370
PS-10	2.24	1.03	374	0.367
PS-11	12.9	1.06	379	0.359
PS-12	16.8	1.02	380	0.355
PS-13	34.1	1.07	380.5	0.352
PS-14	58.2	1.11	381	0.352

T_g and ΔC_p are the average values of three experimental results. η is the polydispersity index.

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*To whom all correspondence should be addressed.

Table 2. Glass transition data of the binary mixtures of PS of different molecular weights

	0/100	20/80	40/60	50/50	60/40	80/20	100/0	ΔC_{p1} (J/g K)	ΔC_{p2} (J/g K)	$k = \frac{\Delta C_{p1}}{\Delta C_{p2}}$
PS-1/PS-11	379	350	325	311.5	301.5	289	282	0.359	0.466	1.30
PS-2/PS-11	379	365	356	349	345	341	335	0.359	0.406	1.13

ΔC_{p1} is the change in heat capacity associated with glass transition for PS-11.
ΔC_{p2} is the change in heat capacity associated with glass transition for PS-1 or PS-2.

Table 3. Glass transition data of the blends of PPO with different molecular weight PS

	0/100	20/80	40/60	50/50	60/40	80/20	100/0	ΔC_{p1} (J/g K)	ΔC_{p2} (J/g K)	$k = \frac{\Delta C_{p1}}{\Delta C_{p2}}$
PS-1/PPO	459	417	369	349	330	302	284	0.247	0.456	1.85
PS-5/PPO	489	451	425	411	396	375	361	0.247	0.392	1.59
PS-10/PPO	489	457	432	420	410	391	376	0.247	0.364	1.47
PS-11/PPO	489	461	434	425	413	396	379	0.247	0.359	1.45
PS-14/PPO	489	466	438	425	417	399	382	0.247	0.352	1.43

ΔC_{p1} is the change in heat capacity associated with glass transition for PPO.
ΔC_{p2} is the change in heat capacity associated with glass transition for the different molecular weight PS.

performed much significant work in this respect. However, the dependence of these equations (for example, the Gordon–Taylor, Fox and Couchman equations *et al.*) on the interaction parameter and molecular weight is seldom studied. In this paper, the effects of the interaction parameter and molecular weight on the relationship of T_g and composition are presented, and the adaptability of the empirical and theoretical equations are also discussed.

EXPERIMENTAL

The molecular parameters of monodisperse PS used in this work are listed in Table 1. Each PS sample was dissolved in benzene to form a solution with a concentration of 5 mg/mL. Blends PS-1/PS-11 and PS-2/PS-11 with the weight ratio of 0/100, 20/80, 40/60, 50/50, 60/40, 80/20 and 100/0 were prepared from benzene solution (5 mg/mL). A similar method was used to prepare blends of poly(2,6-dimethyl-*p*-phenylene oxide) ($M_w = 4.83 \times 10^4$, $M_w/M_n = 1.723$) and PS with different molecular weights (PS-1, PS-5, PS-10, PS-11 and PS-14) from chloroform solution (5 mg/mL). The solvent was removed in air by evaporation. The cast films were dried in a vacuum oven at 85 ± 2°C for 3 days and then at a temperature 20–30°C higher than T_g of the respective sample for 36 hr.

Thermal analysis of the samples was performed with a Perkin–Elmer DSC-2C calorimeter with a heating rate of 20°C/min by twice scanning, and the sample weight was 10 mg. The samples were first scanned until the temperature was 30°C higher than the T_g, then quickly quenched to −40°C and scanned for the second time. T_g was defined as

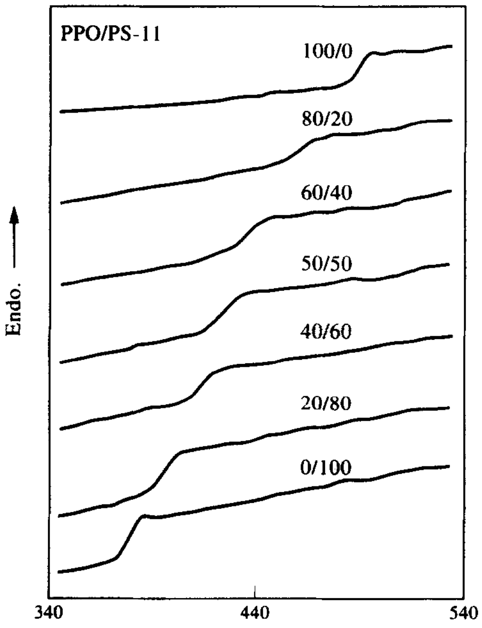

Fig. 1. DSC scans for PPO/PS-11 blends.

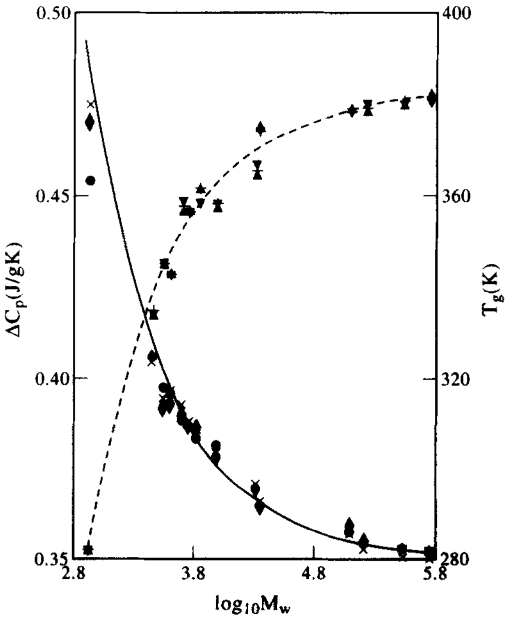

Fig. 2. ΔC_p and T_g vs $\log_{10} M_w$ for DMWPS: ▲, ▼ and + represent the first, second and third experimental values of T_g, respectively. ●, ◆ and x represent the first, second and third experimental values of ΔC_p, respectively. – – – the fitted curve of the average T_g vs $\log_{10} M_w$. — the calculated curve from equation (1).

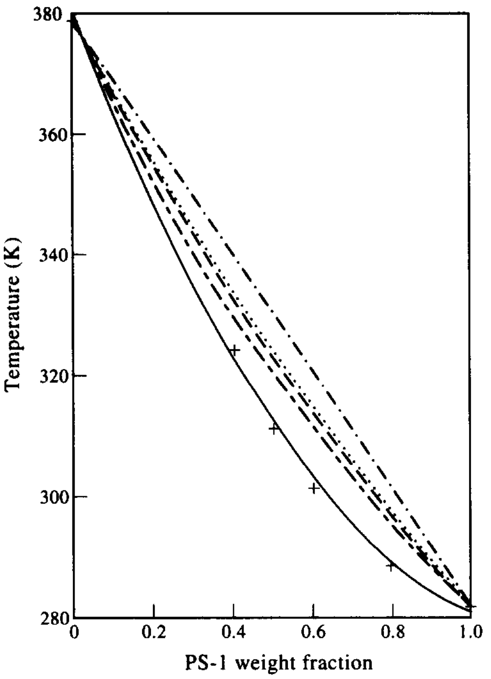

Fig. 3. Dependence of T_g on composition in PS-1/PS-11 mixtures: + experimental values; -·- additive curve; — experimental curve; ··· Fox equation curve; --- Gordon–Taylor equation curve for $k = 1.30$; —-— Couchman equation curve for $k = 1.30$.

the midpoint of the change in specific heat for the second scanning and ΔC_p was the change in heat capacity associated with the glass transition with values given in Tables 1, 2 and 3. The DSC thermograms are shown in Fig. 1 (with only the DSC diagram of blends PPO/PS-11 cited as an example).

RESULTS AND DISCUSSION

Dependence of ΔC_p on molecular weight

The experimental values of ΔC_p for different molecular weights are shown in Fig. 2. ΔC_p decreases with an increase of molecular weight and finally approaches to an asymptotic constant (for PS, the value, $\Delta C_{p\infty}$ is 0.35 J/g K). The relationship between ΔC_p and molecular weight of PS can be fitted by the following equation

$$\Delta C_p = [1 + (D_e/D_w)^{2/3}]\Delta C_{p\infty}, \tag{1}$$

where D_e is the number of the end-groups in a polymer molecule and D_w is the weight-average degree of polymerization. For linear polymer, $D_e = 2$, $D_w = M_w/M$, where M is the molecular weight of a repeat unit and M_w is the weight-average molecular weight. In equation (1), it is obvious that ΔC_p is related to the ratio of D_e and D_w, i.e. the larger the ratio, the larger the ΔC_p. Therefore, ΔC_p strongly depends on the concentration of the free end-groups in bulk polymer.

Binary mixtures of DMWPS

For binary miscible mixtures of polymers, the dependence of T_g on composition can be presented by three well-known equations [1, 2, 5]:

Fox equation $$\frac{1}{T_g} = \frac{w_1}{T_{g1}} + \frac{w_2}{T_{g2}} \tag{2}$$

Couchman equation

$$\ln T_g = \frac{w_1 \ln T_{g1} + k w_2 \ln T_{g2}}{w_1 + k w_2} \tag{3}$$

Gordon–Taylor equation

$$T_g = \frac{w_1 T_{g1} + k w_2 T_{g2}}{w_1 + k w_2}, \tag{4}$$

where w_i $(i = 1, 2)$ is the weight fraction of component i; T_{gi} $(i = 1, 2)$ is the glass transition temperature of component i; T_g is the glass transition temperature of a mixture; k is equal to $\Delta C_{p2}/\Delta C_{p1}$. In these equations the interaction between components is not considered ($\chi = 0$). Therefore, it is expected that these equations would give a good fit to results for mixtures having $\chi = 0$. However, this is far away from our expectation by comparing predictions with the experimental results. It is evident that the experimental curves in Figs 3 and 4 show a clear negative deviation from the calculated values using the above equations. Further investigation is in progress at our laboratory.

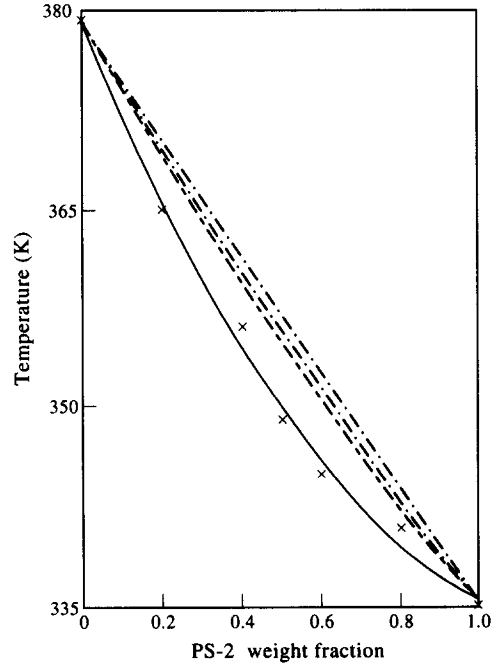

Fig. 4. Dependence of T_g on composition in PS-2/PS-11 mixtures: x experimental values; -·- additive curve; — experimental curve; ··· Fox equation curve; --- Gordon–Taylor equation curve for $k = 1.13$; —-— Couchman equation curve for $k = 1.13$.

Binary blends of PPO and DMWPS

The blends PPO/PS are compatible at a segmental level [17]. The curves of T_g vs composition of the PPO/DMWPS blends are shown in Figs 5(a)–(e). According to observations, it can be known that the experimental values measured by DSC fit quite well with those calculated from the Couchman, Gordon–Taylor and Fox equations with the increase of molecular weight of PS. When the molecular weight of PS is very low, the measured values are basically identical with the results of the Couchman equation. With an increase of molecular weight of PS, the experimental results gradually drift away from the values of the Couchman equation and fit those of the Gordon–Taylor equation. As the molecular weight of

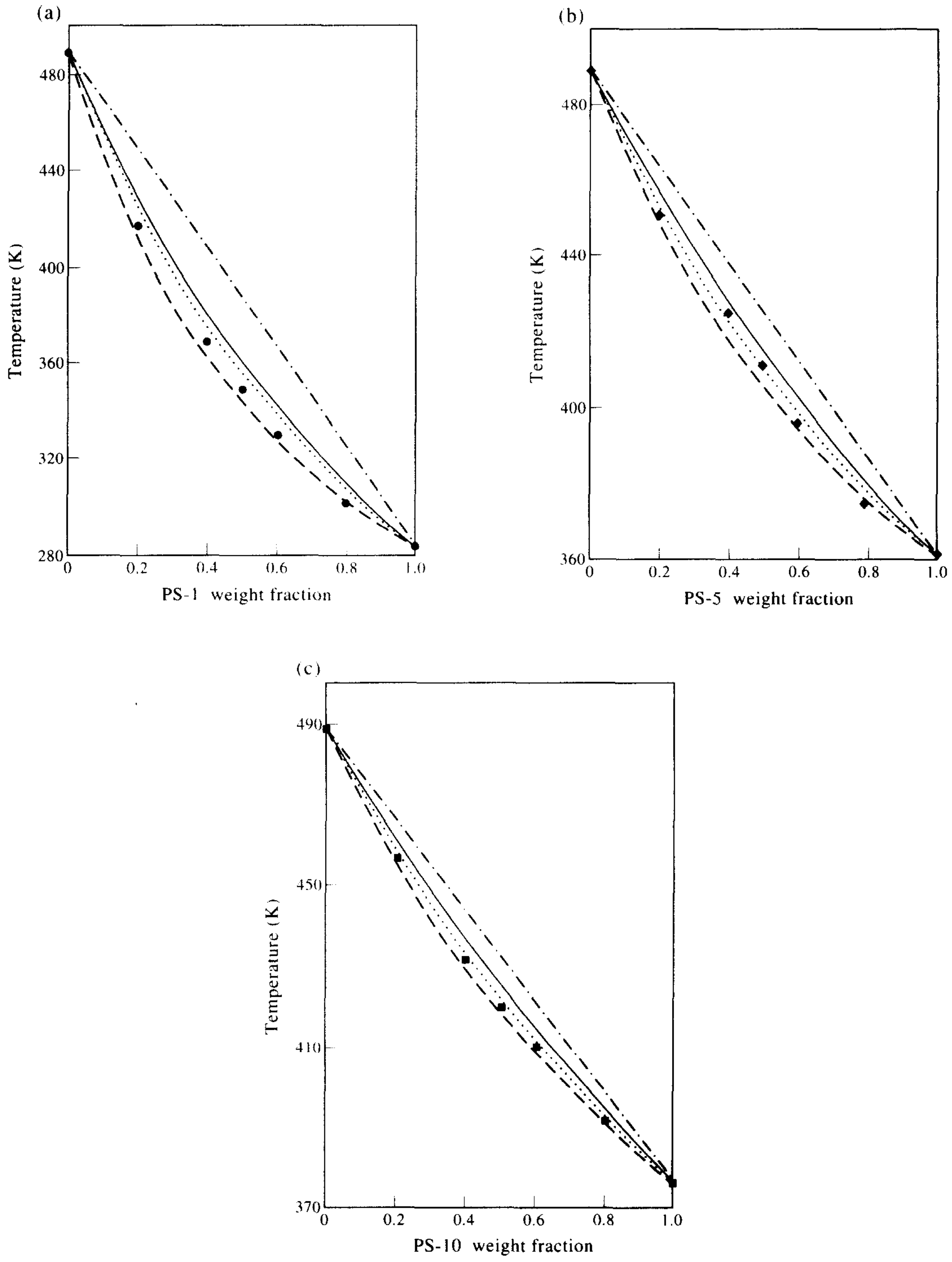

Fig. 5 (a–c) Caption on next page.

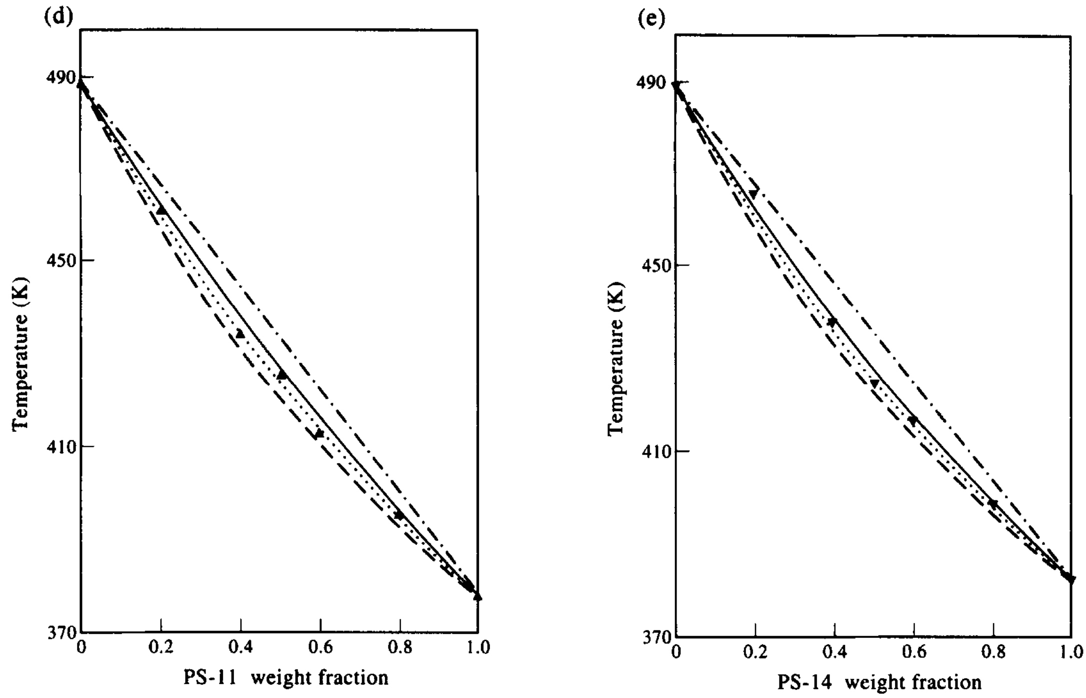

Fig. 5. Dependence of T_g on composition in PPO/DMWPS blends: (a) PPO/PS-1; (b) PPO/PS-5; (c) PPO/PS-10; (d) PPO/PS-11; (e) PPO/PS-14. ●, ◆, ■, ▲ and ▼ represent the experimental values of T_g in PPO/PS-1, PPO/PS-5, PPO/PS-10, PPO/PS-11 and PPO/PS-14, respectively. – · – additive curve; — Fox equation curve; · · · Gordon–Taylor equation curve; – – Couchman equation curve. k is shown in Table 3.

PS is very high ($M_w > 5.8 \times 10^5$), the Gordon–Taylor and Fox equations can give good fit to the experimental values. We think that the trend of T_g composition and the molecular weight of PS is related to the ΔC_p of PS, because the parameter, k, is dependent on ΔC_p of PS and PPO, where ΔC_p is a constant. The Gordon–Taylor equation could cover a broader range. Although the blends PPO/PS have a negative interaction parameter and are different from the mixtures of PS ($\chi = 0$), the calculated curves from equation (1), (2) and (3) are coincident with the experimental curves. Therefore, it is expected that the above equations are useful for polymer blends with a negative value of χ (for PPO/PS blends, $\chi = -0.06$ [18, 19]).

Effects of χ on T_g of blends

Lu and Weiss [12] found that the Fox and Couchman equations, including the Gordon–Taylor equation, was not suitable to predict T_g for miscible systems with strong-specific interactions (for example, blends of polyamide-6 and manganese sulfonated polystyrene). They presented a modified equation for this system, i.e.

$$T_g = \frac{w_1 T_{g1} + w_2 T_{g2}}{w_1 + k w_2} - \frac{\chi R (T_{g2} - T_{g1}) b w_1 w_2}{\Delta C_{p1}(w_1 + k w_2)(w_1 + b w_2)^2}, \quad (5)$$

where b is the ratio of amorphous densities of polymer **2** and polymer **1**; R is the gas constant. In equation (5), $T_{g2} > T_{g1}$. If $T_{g2} < T_{g1}$, $(T_{g2} - T_{g1})$ in equation (5) is replaced by $(T_{g1} - T_{g2})$, for PPO/PS blends, the specific interaction was found to be

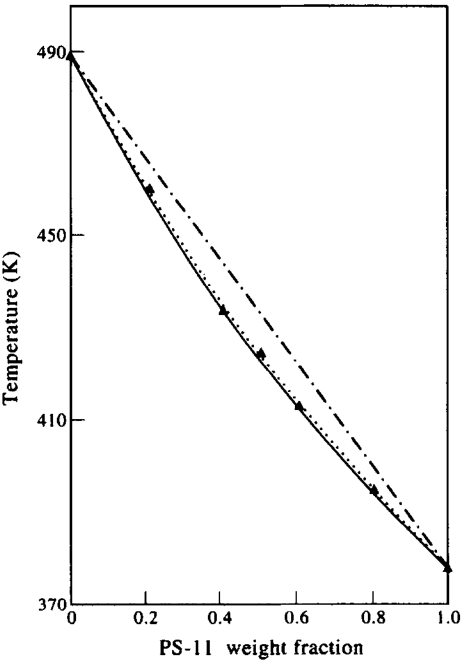

Fig. 6. Dependence of T_g on composition in PPO/PS-11 blends: ▲ experimental values; – · – additive curve; — Gordon–Taylor equation curve; · · · Lu–Weiss equation curve.

$\chi = -0.06$ [18, 19]. Figure 6 gives the curves of the Gordon–Taylor and Lu–Weiss equations and the experimental values. It is shown that the calculated results of the Gordon–Taylor equation is basically identical to those of the Lu–Weiss equation. It results because the interaction between components is not so strong and so the increase of T_g is not evident. As seen from equation (5) itself, the maximum of values of χ's coefficient in the second term (including negative sign) is only about -7.4 K. Since χ is too small ($= -0.06$), the maximum of T_g's increment is only 0.45 K. Therefore, it is suggested that the Gordon–Taylor equation should be accurate enough to calculate T_g of blends with not very strong specific interactions and that the Lu–Weiss equation should be used for polymer blends with strong-specific interactions.

CONCLUSIONS

Our results suggest that the Fox, Couchman and Gordon–Taylor equations could be applied to polymer blends if the interaction between their molecules in not too strong. For a system with strong-specific interactions, the Lu–Weiss equation is a better formula. However, it is also proposed that the above equations could not be applied to mixtures when the interaction between components was very weak ($\chi = 0$). It is also found that the Fox, Couchman and Gordon–Taylor equations are only suitable for describing the experimental results for a different molecular weight range of components.

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REFERENCES

1. Gordon, M. and Taylor, J. S., *J. Applied Chem.*, 1952, **2**, 493.
2. Fox, T. G., *Bull. Am. Phys. Soc.*, 1956, **1**, 123.
3. Jenckel, E. and Heusch, R., *Kolloida Zh.*, 1953, **130**, 89.
4. Simha, R. and Boyer, R. F., *J. Chem. Phys.*, 1962, **37**, 1003.
5. Couchman, P. R., *Macromolecules*, 1978, **11**, 1156.
6. Goldstein, M., *Macromolecules*, 1985, **18**, 277.
7. Gibbs, J. H. and DiMarzio, E. A., *J. Chem. Phys.*, 1958, **28**, 373; DiMarzio, E. A. and Gibbs, J. H., *J. Chem. Phys.*, 1958, **28**, 807.
8. Gordon, J. M., Rouse, G. B., Gibbs, J. H. and Risen, W. M., *J. Chem. Phys.*, 1977, **66**, 4971.
9. Kwei, T. K., *J. Polym. Sci., Polym. Lett. Edn*, 1984, **22**, 307.
10. Lin, A. A., Kwei, T. K. and Reiser, A., *Macromolecules*, 1989, **22**, 4112.
11. Pedrosa, P., Pomposa, J. A., Calahorra, E. and Cortazar, M., *Macromolecules*, 1994, **27**, 102.
12. Lu, X. Y. and Weiss, R. A., *Macromolecules*, 1991, **24**, 4381.
13. Lu, X. Y. and Weiss, R. A., *Macromolecules*, 1992, **25**, 3242.
14. Flory, P. J., *Principles of Polymer Chemistry*. Cornell University Press, Ithaca, New York, 1953.
15. Painter, P. C., Graf, J. F. and Coleman, M. M., *Macromolecules*, 1991, **24**, 5630.
16. Braun, G. and Kovacs, A. J., in *Physics of Non-crystalline Solids*. North-Holland Publishing Co., Amsterdam, 1965, p. 303.
17. Wignall, G. D., Child, H. R. and Li-Aravena, F., *Polym. Commun.*, 1980, **21**, 131.
18. Wu, S., *J. Polym. Sci., Part B: Polym. Phys.*, 1987, **25**, 2511.
19. Maconnachie, A., Kambour, R. P., White, D. M., Rostami, S. and Walsh, D. J., *Macromolecules*, 1984, **17**, 2645.