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The glass transition temperatures of PS/PPO blends: Couchman volume-based equation and its verification

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Abstract

The glass transition temperatures (T_g) of PS/PPO blends with different compositions were studied under various pressures by means of a PVT-100 analyzer. A general relation of T_g and pressure of the PS/PPO system was deduced by fitting the experimental T_g's. Couchman volume-based equation was testified with the aid of those data. It was found that the experimental T_g's do not obey the Couchman equation of glass transition temperature based on thermodynamic theory. According to our studies, the major reason of the deviation is caused by the neglect of ΔV_{mix}. © 2001 Published by Elsevier Science Ltd.

Keywords: Glass transition temperature; Couchman equation; PVT data

1. Introduction

It is well known that the polystyrene (PS)/poly (2,6-dimethyl-1,4-phenylene oxide) (PPO) blend is a completely compatible system and has been widely studied by different methods in the past 30 years [1–4]. Two different polymers will be mixed at the segmental level if there is an especially favorable interaction between them. As far as we know, all of the evidences indicate that the PS/PPO blend is miscible in all proportions and over a considerable range of molecular weights [3,5–7]. So there is a single glass transition temperature (T_g) for the PS/PPO blend.

Many empirical formulae have been used to elucidate the glass transition temperature of compatible polymer blends [8–13]. Among them, the Couchman formulae deduced on the basis of enthalpy, entropy and free volume theory [14–18] are more clear and reliable. But it is criticized by Goldstain [19], saying that Couchman 'bypassed any consideration of molecular theories of the transition (such as the Gibbs–DiMarzio entropy [20] or free volume theories [21–23]) although molecular considerations are used to estimate the values of certain thermodynamic quantities'. However, Goldstain did not solve the problem either although he advanced a new hypothesis to replace the old one. His hypothesis was also pointed out to be incomplete by Couchman [24]. The definition of ΔV_{mix} in Couchman theory is different from the common one presented by Goldstain [19] and other authors. Generally, it is difficult to obtain the difference of ΔV_{mix} from experiments. The focus they have been disputing is whether the thermodynamic quantities (H, S and V) of mixing of polymers are continuous or not at the glass transition temperature. Couchman pointed out that the curves of T_g vs. composition deduced from the enthalpy and entropy theories are concave, while the ones deduced from the free volume theory are convex [24]. Couchman equations have been proved in the system of PS/PPO [25,26]. The formulae obtained from the enthalpy and entropy theories are considered as reliable ones because they are in accordance with the experimental data. Moreover, Maeda et al. [27] studied the glass transition temperature of the PPO/poly(styrene-*co*-*p*-fluorostyrene) system at different compositions and pressures by using high pressure differential thermal analysis. But all the experimental results were obtained by means of the thermal method. This method should not be applied to the volume-based relation because of the different measuring process. The present paper covers the studies of T_g's of the PS/PPO blends with different compositions under pressure by using a PVT-100 analyzer. This study is aimed to calculate the ΔV_{mix} defined by Couchman and then to testify the validity of Couchman volume-based equation.

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2. Theoretical background

Couchman [14] advanced the T_g equation based on free volume theory,

$$v_{\mathrm{tot}}^{\mathrm{s}} = x_1 v_1^{\mathrm{s}} + x_2 v_2^{\mathrm{s}} + \Delta v_{\mathrm{mix}}^{\mathrm{s}} \tag{1}$$

where s represents glassy state or liquid state, v_1^{s}, v_2^{s} and $v_{\mathrm{tot}}^{\mathrm{s}}$ the mole volumes of pure components 1, 2 and their blend, respectively, x_1 and x_2 the mole fractions of the two components in the blend, $\Delta v_{\mathrm{mix}}^{\mathrm{s}}$ includes all excess volume changes associated with the mixing of the two components in glassy or liquid state. Eq. (1) can be re-written by using the specific volume (V_{sp}) and weight fraction (w_{t}), as follows:

$$V_{\mathrm{sp}}^{\mathrm{s}} = w_{\mathrm{t1}} V_{\mathrm{sp1}}^{\mathrm{s}} + w_{\mathrm{t2}} V_{\mathrm{sp2}}^{\mathrm{s}} + \Delta V_{\mathrm{spmix}}^{\mathrm{s}} \tag{2}$$

where $\Delta V_{\mathrm{spmix}}^{\mathrm{s}}$ refers to all the deviations from the additivity of $V_{\mathrm{sp1}}^{\mathrm{s}}$ and $V_{\mathrm{sp2}}^{\mathrm{s}}$. The specific volume of the mixture at its glass transition temperature can be obtained from Eq. (2) either in glassy state or in liquid state, which leads

$$\begin{aligned} V_{\mathrm{sp}}^{\mathrm{g}} &= w_{\mathrm{t1}} V_{\mathrm{sp1}}^{\mathrm{g}}(T = T_{\mathrm{g}}) + w_{\mathrm{t2}} V_{\mathrm{sp2}}^{\mathrm{g}}(T = T_{\mathrm{g}}) \\ &\quad + \Delta V_{\mathrm{mix}}^{\mathrm{g}}(T = T_{\mathrm{g}}) = w_{\mathrm{t1}} V_{\mathrm{sp1}}^{0}\left(1 + \int_{T_{\mathrm{g1}}}^{T_{\mathrm{g}}} \alpha_1^{\mathrm{g}}\,\mathrm{d}T\right) \\ &\quad + w_{\mathrm{t2}} V_{\mathrm{sp2}}^{0}\left(1 + \int_{T_{\mathrm{g2}}}^{T_{\mathrm{g}}} \alpha_2^{\mathrm{g}}\,\mathrm{d}T\right) + \Delta V_{\mathrm{spmix}}^{\mathrm{g}}(T = T_{\mathrm{g}}) \end{aligned} \tag{3}$$

or

$$\begin{aligned} V_{\mathrm{sp}}^{\mathrm{l}} &= w_{\mathrm{t1}} V_{\mathrm{sp1}}^{\mathrm{l}}(T = T_{\mathrm{g}}) + w_{\mathrm{t2}} V_{\mathrm{sp2}}^{\mathrm{l}}(T = T_{\mathrm{g}}) \\ &\quad + \Delta V_{\mathrm{mix}}^{\mathrm{l}}(T = T_{\mathrm{g}}) = w_{\mathrm{t1}} V_{\mathrm{sp1}}^{0}\left(1 + \int_{T_{\mathrm{g1}}}^{T_{\mathrm{g}}} \alpha_1^{\mathrm{l}}\,\mathrm{d}T\right) \\ &\quad + w_{\mathrm{t2}} V_{\mathrm{sp2}}^{0}\left(1 + \int_{T_{\mathrm{g2}}}^{T_{\mathrm{g}}} \alpha_2^{\mathrm{l}}\,\mathrm{d}T\right) + \Delta V_{\mathrm{spmix}}^{\mathrm{l}}(T = T_{\mathrm{g}}) \end{aligned} \tag{4}$$

where superscripts g and l refer to glassy and liquid states, respectively, V_{sp1}^{0} and V_{sp2}^{0} represent the specific volumes of the two pure components at their corresponding T_{g}s, respectively, α the thermal expansion coefficient and its definition is $\alpha = (1/V_{\mathrm{sp}}^{0})(\partial V_{\mathrm{sp}}/\partial T)_P$.

Since $V_{\mathrm{sp}}^{\mathrm{l}} = V_{\mathrm{sp}}^{\mathrm{g}}$ at T_{g}, we have

$$\begin{aligned} & w_{\mathrm{t1}} V_{\mathrm{sp1}}^{0} \int_{T_{\mathrm{g1}}}^{T_{\mathrm{g}}} (\alpha_1^{\mathrm{l}} - \alpha_1^{\mathrm{g}})\,\mathrm{d}T + w_{\mathrm{t2}} V_{\mathrm{sp2}}^{0} \int_{T_{\mathrm{g2}}}^{T_{\mathrm{g}}} (\alpha_2^{\mathrm{l}} - \alpha_2^{\mathrm{g}})\,\mathrm{d}T \\ &\quad + (\Delta V_{\mathrm{spmix}}^{\mathrm{l}} - \Delta V_{\mathrm{spmix}}^{\mathrm{g}}) = 0 \end{aligned} \tag{5}$$

If the thermal expansion coefficient is redefined as

$$E = V_{\mathrm{sp}}^{0}\alpha = \left(\frac{\partial V_{\mathrm{sp}}}{\partial T}\right)_P \tag{6}$$

then Eq. (5) can be rewritten as follows:

$$\begin{aligned} & w_{\mathrm{t1}} \int_{T_{\mathrm{g1}}}^{T_{\mathrm{g}}} (E_1^{\mathrm{l}} - E_1^{\mathrm{g}})\,\mathrm{d}T + w_{\mathrm{t2}} \int_{T_{\mathrm{g2}}}^{T_{\mathrm{g}}} (E_2^{\mathrm{l}} - E_2^{\mathrm{g}})\,\mathrm{d}T \\ &\quad + (\Delta V_{\mathrm{spmix}}^{\mathrm{l}} - \Delta V_{\mathrm{spmix}}^{\mathrm{g}}) = 0 \end{aligned} \tag{7}$$

where E can be easily calculated from PVT data. It has been pointed out by Shiomi et al. [28] and Yang et al. [29] that the thermal expansion coefficient is a function of temperature. However, according to their results, this temperature dependence of the thermal expansion coefficient is not obvious. For simplification, we have proposed that E is independent of temperature. Thus, Eq. (7) can be simplified as

$$\begin{aligned} & w_{\mathrm{t1}}(E_1^{\mathrm{l}} - E_1^{\mathrm{g}})(T_{\mathrm{g}} - T_{\mathrm{g1}}) + w_{\mathrm{t2}}(E_2^{\mathrm{l}} - E_2^{\mathrm{g}})(T_{\mathrm{g}} - T_{\mathrm{g2}}) \\ &\quad + (\Delta V_{\mathrm{spmix}}^{\mathrm{l}} - \Delta V_{\mathrm{spmix}}^{\mathrm{g}}) = 0 \end{aligned} \tag{8}$$

that is,

$$T_{\mathrm{g}} = \frac{w_{\mathrm{t1}} T_{\mathrm{g1}} + w_{\mathrm{t2}} K T_{\mathrm{g2}}}{w_{\mathrm{t1}} + w_{\mathrm{t2}} K} - \frac{(\Delta V_{\mathrm{spmix}}^{\mathrm{l}} - \Delta V_{\mathrm{spmix}}^{\mathrm{g}})/\Delta E_1}{w_{\mathrm{t1}} + w_{\mathrm{t2}} K} \tag{9}$$

where $K = \Delta E_2/\Delta E_1$, $\Delta E = E^{\mathrm{l}} - E^{\mathrm{g}}$. Eq. (9) coincides with Gordon–Taylor equation when the second term is omitted. The parameter K in Eq. (9) is clearly defined and can be easily derived from PVT data. Couchman did not estimate the value of ΔV_{mix} and assumed that $\Delta V_{\mathrm{mix}}^{\mathrm{l}} = \Delta V_{\mathrm{mix}}^{\mathrm{g}}$ although he also thought it is not plausible sometimes [15,24]. Anyway, he has cut off the second term of Eq. (9) in his final expression:

$$T_{\mathrm{g}} = \frac{w_{\mathrm{t1}} T_{\mathrm{g1}} + w_{\mathrm{t2}} K T_{\mathrm{g2}}}{w_{\mathrm{t1}} + w_{\mathrm{t2}} K} \tag{10}$$

3. Experimental

3.1. Materials

PS was obtained from Shanghai GaoQiao Petrochemical, China (type: TY-324, common grade) and was used as received. PPO was purchased from Polysciences, Warrington, PA. The molecular parameters of PS and PPO are listed in Table 1.

3.2. Sample preparation

PS and PPO were dried in vacuum at 70°C for 18 h and then dissolved in benzene to form the solutions of PS and

Table 1
Characterization of PS and PPO

Polymers	$\bar{M}_{\mathrm{n}}$ (kg/mol)	$\bar{M}_{\mathrm{w}}$ (kg/mol)	$\eta(\bar{M}_{\mathrm{w}}/\bar{M}_{\mathrm{n}})$
PS	45.8	155	3.384
PPO	19.2	55.9	2.911

PPO with a concentration of 3 g/100 ml, respectively. The PS/PPO mixtures (the weight ratios are 0/100, 20/80, 40/60, 60/40, 80/20 and 100/0) were made by mixing the PS/benzene and PPO/benzene solutions with a certain volume ratio. Then the solvent was removed in air by evaporation. Finally, the cast films were dried in a vacuum oven at 90 ± 2°C for four weeks in order to evaporate the residual solvent.

3.3. P–V–T measurement

The PVT data of the pure components and the mixture of PS/PPO were measured by means of a PVT 100 analyzer (SWO Polytechnic GmbH, Germany), by which the measurement accuracy of specific volume is smaller than 0.001 cm^3/g and the temperature can be controlled within ±0.3°C. The operation was performed under the following conditions:

1. measurement type: isobaric cooling;
2. cooling rate: 1°C/min;
3. rest-period time at the maximal temperature: 7 min at every measuring pressure;
4. pressure range: 1–1200 bar (the interval is 200 bar);
5. temperature range: 70–310°C, T_g's of the PS/PPO blends at various pressure are in this range.

4. Results and discussion

4.1. Pressure dependence of T_g

The experimental PVT data of pure PS, as an example, are shown in Fig. 1. It can be seen that the specific volume decreases with the increase of pressure at a certain temperature. The variation of specific volume with temperature is typically changed at glass transition temperature. It can be used to get the T_g from the PVT data. Glass transition temperature T_g is defined as the temperature of intersection of the two extrapolation curves, as shown in Fig. 2. Fig. 3 shows the glass transition temperatures of the PS/PPO blends with different compositions plotted as a function of pressures.

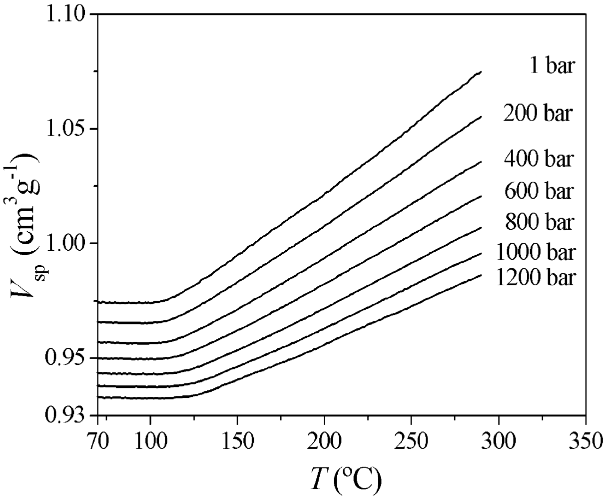

Fig. 1. The PVT data of pure PS measured with a PVT-100 analyzer.

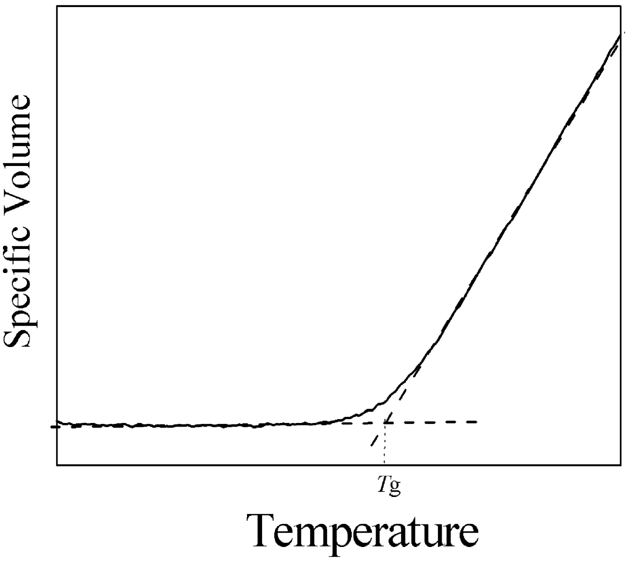

Fig. 2. The schematic diagram of the definition of glass transition temperature. Solid line stands for the volume–temperature curve. Dashed lines represent the extrapolation lines.

It can be seen that the glass transition temperature increases with increase of both the pressure and the composition of PPO. Quach [30] considered that the glass transition temperature is linearly changing with the pressure. Here, we also use this relation and assume that dT_g/dP is composition dependent, which can be expressed as

$$\frac{dT_g}{dP} = f(w_t) \tag{11}$$

where w_t is the weight fraction of PPO.

Based on our experimental data and Eq. (11), the relationship between T_g and pressure can be calculated by using the least-squares method. The fitting results are shown in Fig. 3 and the following expression is obtained.

$$T_g = T_g(P = 1\text{ bar}) + f(w_t)P \tag{12}$$

where

$$f(w_t) = 0.0186 - 0.00653w_t + 0.03571w_t^2 \tag{13}$$

Eq. (12) is a general expression about the relationship between T_g and pressure for the PS/PPO blends.

4.2. Verification of Couchman volume-based relation about glass transition temperature

4.2.1. The definition of ΔV_{mix} in Couchman equation

Fig. 4 gives the schematic representation of the behavior of the specific volume–temperature relationship for the two pure components and a fixed-fraction mixture. For

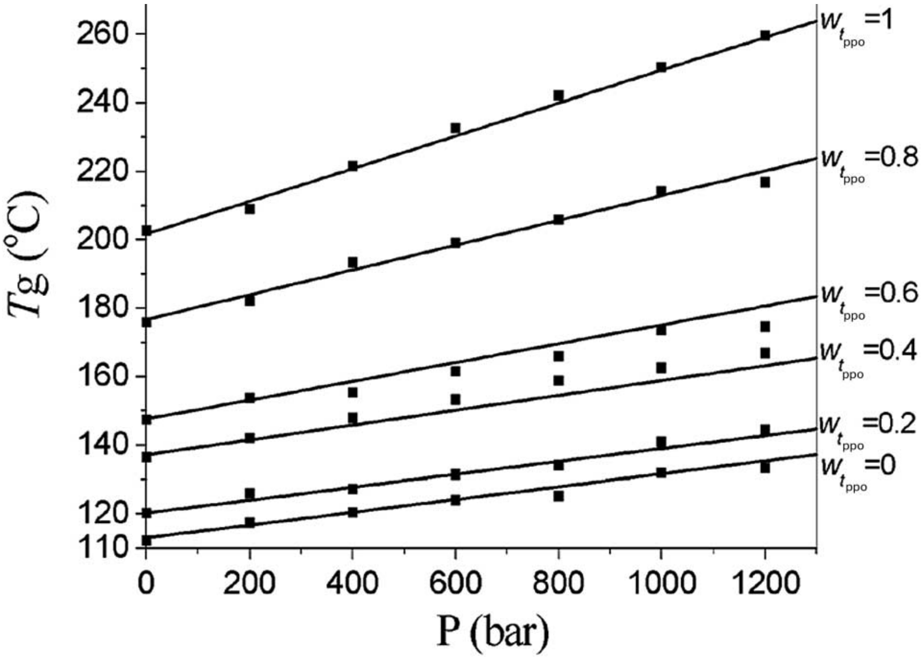

Fig. 3. The relationship between T_g and pressure of the PS/PPO blends at different compositions. The scatter points represent the T_g's obtained from experiment and the solid lines stand for those calculated from formula $T_g = T_g(P = 1\text{ bar}) + f(w_t)P$, where $f(w_t) = 0.0186 - 0.00653 w_{tPPO} + 0.03571 w_{tPPO}^2$.

simplification, the linear dependence of specific volume on temperature for liquid and glassy states is used. The lines 1L–1G and 2L–2G represent the volume–temperature relationships of the two pure polymers with their extrapolations to the T_g of the mixture (the extrapolation of polymer 1 is in glassy state while that of polymer 2 is in liquid state). The solid lines G_M and L_M describe the volume–temperature relationship of the mixture. The dashed lines G'_M and L'_M represent the specific volume in linear additivity of 1G (extrapolation to T_g) and 2G and that of 1L and 2L (extrapolation to T_g), respectively. From Eq. (2), it can easily be seen that the ΔV_{mix}^{l} at T_g should be the difference between the volumes at A and C, while ΔV_{mix}^{g} at T_g should be that of B and C. In Couchman's definition, ΔV_{mix} is divided into two parts, i.e. in glassy state and in liquid state, and there is no connection between those two parts. T_g is the critical temperature of ΔV_{mix} in liquid and glassy states. So the $\Delta V_{mix}^{l} - \Delta V_{mix}^{g}$ may not be equal to zero and the continuities of ΔV_{mix}'s at T_g have nothing to do with that difference. The most important thing is whether the difference between ΔV_{mix}^{l} and ΔV_{mix}^{g} can be neglected or not since ΔV_{mix}^{l} may not be equal to ΔV_{mix}^{g} at T_g.

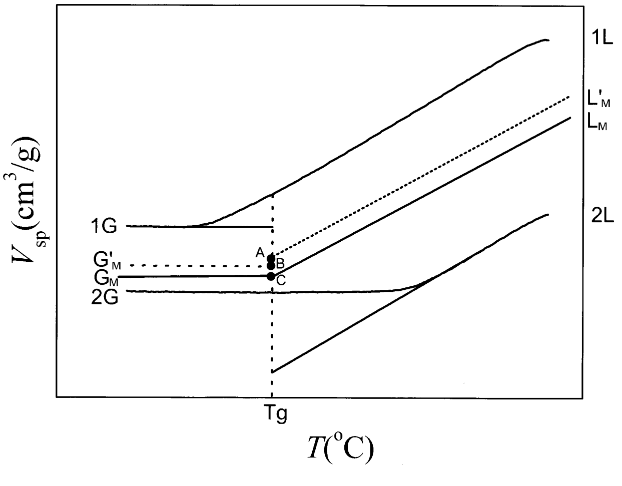

Fig. 4. The definition of ΔV_{mix} in Couchman volume-based relation. All of the lines are described in Section 4.2.1.

4.2.2. Verification of Couchman volume-based equation

With the aid of above discussions, the differences between ΔV_{spmix}^{l} and ΔV_{spmix}^{g} at different pressures can be calculated from the PVT data of the PS/PPO blends. Fig. 5 shows the plots of $\Delta V_{spmix}^{l} - \Delta V_{spmix}^{g}$ at different pressures. It can be seen that the difference is dependent on composition. As there has been no expression about the relationship between $\Delta V_{spmix}^{l} - \Delta V_{spmix}^{g}$ and composition before, we consider the additional term, $q w_{t1} w_{t2}$, of the Kwei's equation [31] about T_g, it is hence obtained,

$$\Delta V_{spmix}^{l} - \Delta V_{spmix}^{g} = q w_{t1} w_{t2} (w_{t1} + w_{t2} K) \Delta E_1 \tag{14}$$

where q is the parameter in Kwei's equation, which is determined by our calculated results of $\Delta V_{spmix}^{l} - \Delta V_{spmix}^{g}$ w_{t1} and

Table 2
Values of q in Kwei's equation for the PS/PPO system at different pressure

P (bar)	1	200	400	600	800
q (K)	76.956	56.457	60.068	51.132	50.721

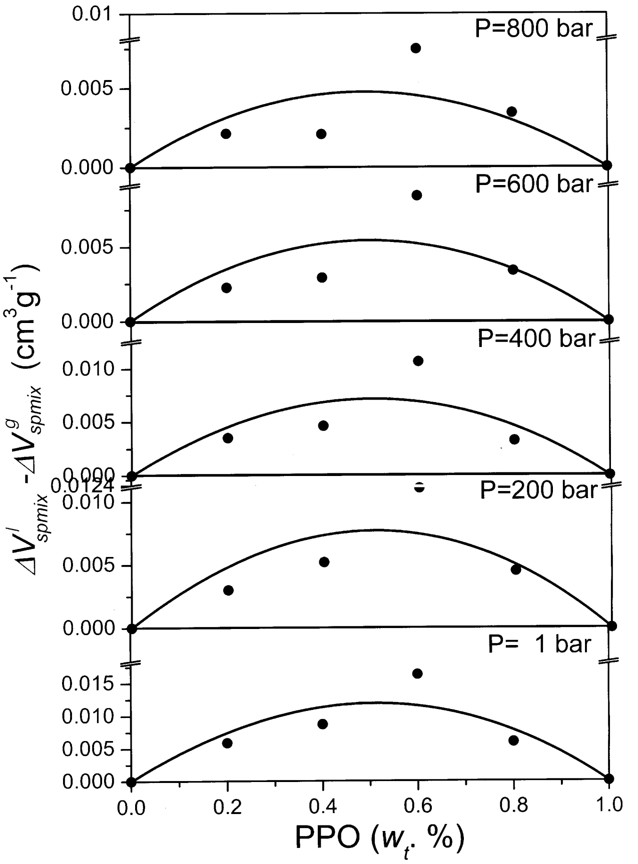

Fig. 5. The relationship between $\Delta V^{\mathrm{l}}_{\mathrm{mix}} - \Delta V^{\mathrm{g}}_{\mathrm{mix}}$ and composition of PPO at different pressures. The solid points and lines represent the calculated results via Eq. (2) and the fitting ones from Eq. (14), respectively.

w_{t2} are the weight fractions of PS and PPO in the PS/PPO blends. This expression guarantees the boundary condition ($\Delta V^{\mathrm{l}}_{\mathrm{spmix}} - \Delta V^{\mathrm{g}}_{\mathrm{spmix}} = 0$ at $w_{\mathrm{t}} = 0$ and 1) and the asymmetric relationship between $\Delta V^{\mathrm{l}}_{\mathrm{spmix}} - \Delta V^{\mathrm{g}}_{\mathrm{spmix}}$ and composition. The fitting results are also shown in Fig. 5. Table 2 shows the values of q at different pressures.

The other parameters in Eq. (9) can be obtained from the experimental PVT data with the aid of corresponding equations mentioned above and are listed in Table 3. Couchman volume-based equation can be estimated from those parameters. Fig. 6 shows the results at different pressures. The curves calculated from the original Couchman volume-based equation (Eq. (10)) are not convex at all of the measuring pressures. When the pressure increases, the parameter K decreases and thus the concave curve occurs. But it still deviates far from the experimental data. The good agreement between Couchman completed equation (Eq. (9)) and the experimental data demonstrates that the complete one is plausible. The relationship between the second term

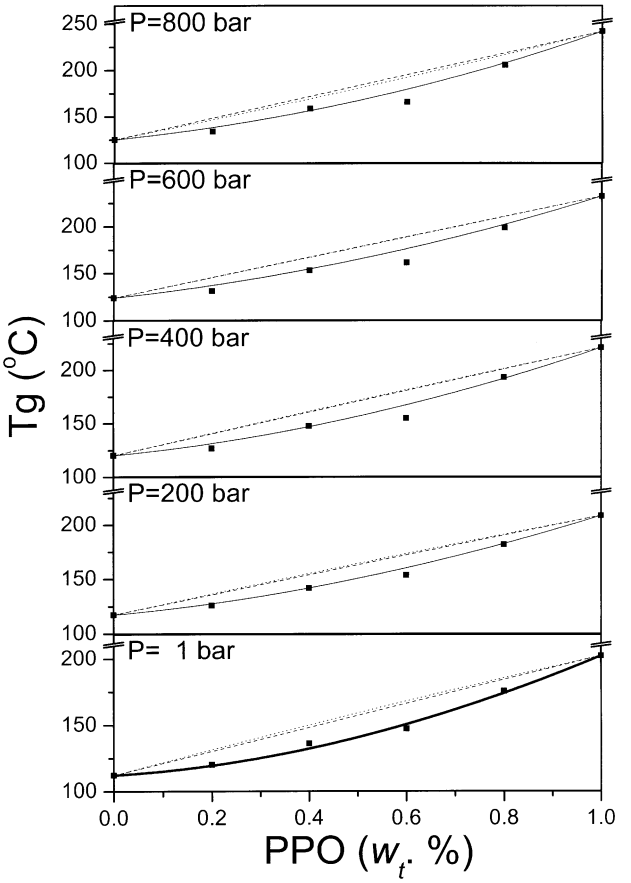

Fig. 6. The relationship between T_{g} and the composition of PPO at different pressures. The solid, dashed and dotted lines represent the curves calculated from the complete Couchman volume-based equation (Eq. (9)), the original equation (Eq. (10)) and the additivity of the glass transition temperature of pure PS and pure PPO. The scatter points represent the T_{g}'s obtained from PVT data.

Table 3
Values of ΔE and K mentioned in Eq. (9) ($\Delta E_1 = E_{1l} - E_{1g}$, $\Delta E_2 = E_{2l} - E_{2g}$, $K = \Delta E_2/\Delta E_1$. Subscripts 1 and 2 represent component PS and PPO, respectively)

P (bar)	1	200	400	600	800
E_{1l} (cm^3/g °C)	5.945×10^{-4}	5.318×10^{-4}	4.688×10^{-4}	4.281×10^{-4}	3.932×10^{-4}
E_{1g} (cm^3/g °C)	1.792×10^{-6}	1.520×10^{-6}	1.204×10^{-6}	1.066×10^{-6}	0.745×10^{-6}
E_{2l} (cm^3/g °C)	6.468×10^{-4}	5.607×10^{-4}	4.819×10^{-4}	4.211×10^{-4}	3.561×10^{-4}
E_{2g} (cm^3/g °C)	9.686×10^{-6}	4.767×10^{-6}	4.272×10^{-6}	4.031×10^{-6}	3.802×10^{-6}
ΔE_1 (cm^3/g °C)	5.927×10^{-4}	5.303×10^{-4}	4.676×10^{-4}	4.270×10^{-4}	3.925×10^{-4}
ΔE_2 (cm^3/g °C)	6.458×10^{-4}	5.602×10^{-4}	4.815×10^{-4}	4.206×10^{-4}	3.557×10^{-4}
K	1.090	1.056	1.030	0.985	0.906

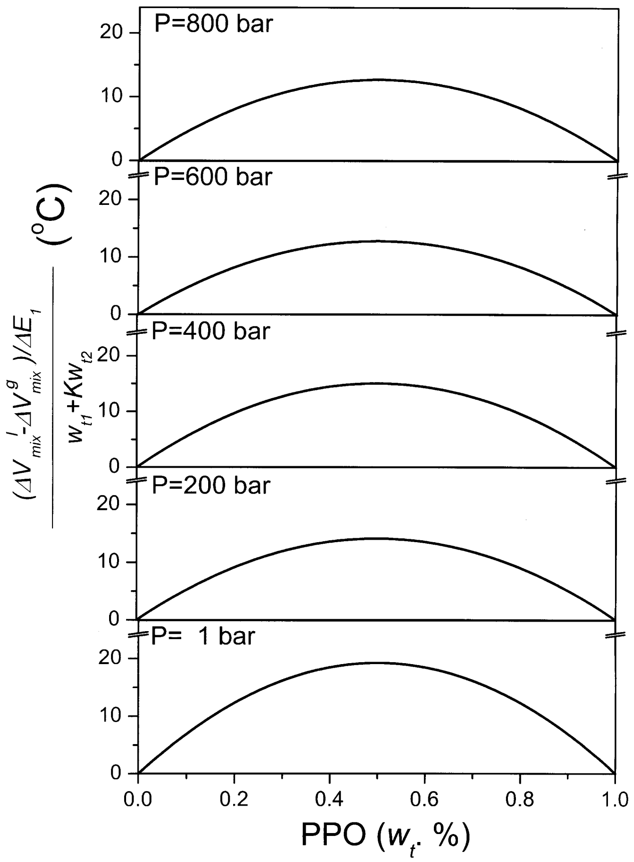

Fig. 7. The relationship between the second term in Eq. (9) and the composition of PPO at different pressures.

in Eq. (9) and the composition of PPO at different pressures is shown in Fig. 7. It can be seen that the maximum value of the term is reached about 10–20°C at different pressures. Such big values cannot be omitted otherwise a bigger deviation will occur.

5. Conclusion

In this paper, the plausibility of Couchman volume-based equation about glass transition temperature is discussed by virtue of volume method. Based on our results, the following conclusions are made:

1. The second term of Couchman volume-based equation was calculated. It is clear that the term cannot be omitted in the calculation. It is the major reason of the disparity between the equation and experimental T_gs.
2. The $\Delta V^{l}_{spmix} - \Delta V^{g}_{spmix}$ is dependent on the composition of the blends.
3. It is demonstrated that the continuity of ΔV_{mix} at T_g is not important in the estimation of T_g for polymer blends, while whether the value of $\Delta V^{l}_{spmix} - \Delta V^{g}_{spmix}$ can be omitted or not important indeed.
4. The general expression of the T_g of the PS/PPO system is derived by fitting the experimental data.

Couchman's volume-based equation about glass transition temperature is very practical since more clearly physical meanings of the terms in the expression are given and the expression can be simplified to different forms such as Gordon–Taylor equation, etc. But the neglect of $\Delta V^{l}_{spmix} - \Delta V^{g}_{spmix}$ is problematic because of its considerable value.

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