

Pressure-Dependent Glass-Transition Temperatures of Poly(methyl methacrylate)/Poly(styrene-co-acrylonitrile) Blends

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ABSTRACT: The pressure-dependent glass-transition temperatures (T_g 's) of poly(methyl methacrylate) (PMMA)/poly(styrene-co-acrylonitrile) (SAN) blends were determined by pressure–volume–temperature (PVT) dilatometry via an isobaric cooling procedure. The Gordon–Taylor and Fox equations were used to evaluate the relationships between the T_g 's and compositions of the PMMA/SAN system at different pressures. The relationships were well fitted by

the Gordon–Taylor equation, and the experimental data for T_g positively deviated from the values calculated with the Fox equation. Also, the influence of the cooling rate (during the PVT measurements) on T_g was examined. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 90: 959–962, 2003

Key words: glass transition; plastics; blends

INTRODUCTION

The glass-transition temperature (T_g) is an important property of polymers and their blends. There are many methods (e.g., differential scanning calorimetry,^{1,2} dynamic mechanical analysis,^{3,4} and dielectric analysis,^{5,6}) used to measure T_g , and we can usually determine T_g at the ambient pressure. However, the pressure dependence of T_g is very important to polymer processing and applications. Moreover, pressure–volume–temperature (PVT) dilatometry is a very con-

venient method for obtaining T_g values at different pressures.^{7–9}

Many empirical formulas, such as the Gordon–Taylor,¹⁰ Fox,¹¹ Jenckel–Heusch,¹² and Simha–Boyer¹³ equations, can be used to calculate the relationship between the T_g 's of polymer blends and their compositions. The Gordon–Taylor and Fox equations are widely used and can respectively be written as follows:

$$T_g = (w_1T_{g1} + kw_2T_{g2}) / (w_1 + kw_2) \quad (1)$$

$$1/T_g = w_1/T_{g1} + w_2/T_{g2} \quad (2)$$

where T_g , T_{g1} , and T_{g2} are the glass-transition temperatures of the blend, component 1, and component 2, respectively; w_1 and w_2 represent the weight fractions of components 1 and 2, respectively; and constant k can be given as the ratios of the changes in the thermal expansivity ($\Delta\alpha_2/\Delta\alpha_1$) or the changes in the heat capacity ($\Delta c_{p2}/\Delta c_{p1}$).¹⁴ Of course, k can also be regarded as an adjustable parameter for the best fitting of the experimental data.¹⁵ According to the Gibbs–Dimarzio molecular theory of T_g ,^{16,17} Gordon et al.¹⁸ presented a physical meaning of the adjustable parameter k in the Gordon–Taylor equation.

Considering the specific interactions between polymer components, Kwei¹⁹ introduced an interaction term into the Gordon–Taylor equation and obtained the following generalized Kwei equation:

$$T_g = (w_1T_{g1} + kw_2T_{g2}) / (w_1 + kw_2) + qw_1w_2 \quad (3)$$

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where k and q are both adjustable parameters. This makes it possible for the equation to fit the relationships between the T_g and composition for many blend systems.²⁰ Afterward, Lu and Weiss²¹ presented a specific formula by combining the Flory–Huggins interaction parameter with the Kwei equation. However, there are some different views concerning the Lu–Weiss derivation.²²

In this work, the Gordon–Taylor and Fox equations were applied to an evaluation of the relationships between the T_g and composition of the miscible poly(methyl methacrylate) (PMMA)/poly(styrene-co-acrylonitrile) (SAN) system at different pressures. Also, the influence of the cooling rate on T_g was examined.

EXPERIMENTAL

Materials

PMMA [weight-average molecular weight (M_w) = 3.87×10^5 , number-average molecular weight (M_n) = 1.04×10^5 ; Acros, New Jersey; Acros, Geel, Belgium] and SAN ($M_w = 1.49 \times 10^5$, $M_n = 5.6 \times 10^4$; Aldrich, Milwaukee, WI) with an acrylonitrile content of about 30 wt % were used as received without further purification.

Sample preparation

Films of PMMA100 (100 represents the pure component), SAN100, and their various blends were prepared via casting from 5% (g/cm³) 1,2-dichloroethane solutions. The films were dried *in vacuo* at 80°C for 3 days and at 120°C for 2 days so that the complete removal of the solvent was ensured.²³

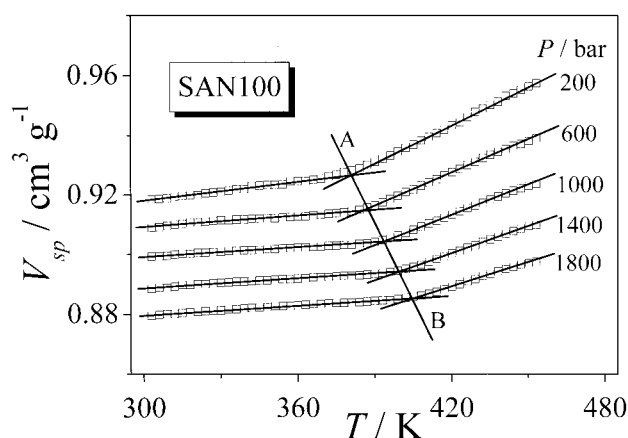


Figure 1 Specific volume (V_{sp}) of SAN100 as a function of the temperature and pressure at a cooling rate of 2°C min^{-1} . The open squares represent the experimental PVT data, and the line AB represents the pressure-dependent T_g 's.

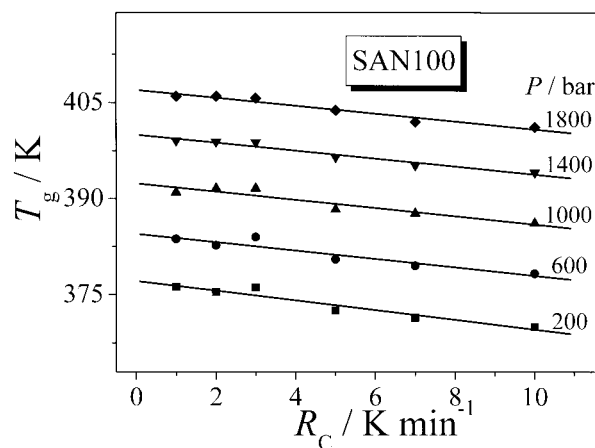


Figure 2 T_g of SAN100 as a function of the cooling rate (R_c) and pressure. The solid symbols represent the T_g values obtained from the PVT diagrams, and the solid lines are the fitted lines at different pressures.

PVT measurements

The PVT properties of all the samples were determined with a PVT-100 dilatometer (SWO Polymertechnik GmbH, Krefeld, Germany) via an isobaric cooling procedure in temperature and pressure ranges of 30–180°C and 200–1800 bar at intervals of 3°C and 200 bar, respectively. The cooling rate was 2°C min^{-1} (except for the study of the influence of the cooling rate on T_g). The samples were kept at the maximum temperature (180°C) for 7 min before every isobaric cooling measurement. The PVT data at 1 bar could be extrapolated from those at high pressures by means of the Tait equation of state.²⁴

RESULTS AND DISCUSSION

PVT diagram

The PVT properties of PMMA100, SAN100, and their blends, similar to those shown in Figure 1, were determined with the PVT-100 dilatometer. Figure 1 shows the specific volume of SAN100 as a function of the temperature and pressure (selected isobars with a pressure interval of 600 bar at a rate of cooling of $-2^\circ\text{C min}^{-1}$). The open squares represent the experimental PVT data. The specific volume of the sample decreased with an increase in the pressure at a fixed temperature, and this was due to the decrease in the free volume with the increase in pressure. Moreover, the specific volume decreased more clearly in the melt state than in the glass state. The cross points of the extrapolation lines of the PVT data in the melt and glass states could be considered T_g 's at the corresponding pressures, and the line AB shows the pressure-dependent T_g 's. It is obvious that the higher the pressure was, the higher T_g was, as expected.

TABLE I
Pressure-Dependent T_g 's of SAN100 Close to the Equilibrium States (When the Cooling Rate Was Zero)

T_g (°C)	Pressure (bar)			
	1	600	1200	1800
	98.7	111.4	122.5	133.8

Influence of the cooling rate on T_g

For the study of the influence of the cooling rate on T_g at different pressures, the PVT properties of SAN100 were measured by means of the isobaric cooling procedure at different cooling rates. Figure 2 shows T_g of SAN100 as a function of the cooling rate and pressure. The solid symbols represent the values of T_g obtained from the PVT diagrams, and the solid lines are the fitted ones at different pressures. From Figure 2, we can find that T_g decreased linearly with an increase in the cooling rate at a fixed pressure. These results seem just the opposite of what exists in the literature for another polymer.²⁵ We presume that the difference was due to the larger cooling rates (1–10°C/min) and the large size of the samples (ca. 15 mm high and 7 mm in diameter). The T_g 's were controlled by a dynamic factor at the larger cooling rate, and the temperature of the piston cylinder (the measured temperature) was usually lower than that of the bulk during cooling for a poor heat conductor of a large size. Moreover, the pressure-dependent T_g 's of SAN100 close to the equilibrium states (when the cooling rate was 0) could be extrapolated from those at different rates (see Table I).

Figure 3 shows T_g of SAN100 as a function of pressure at two different cooling rates. The solid squares

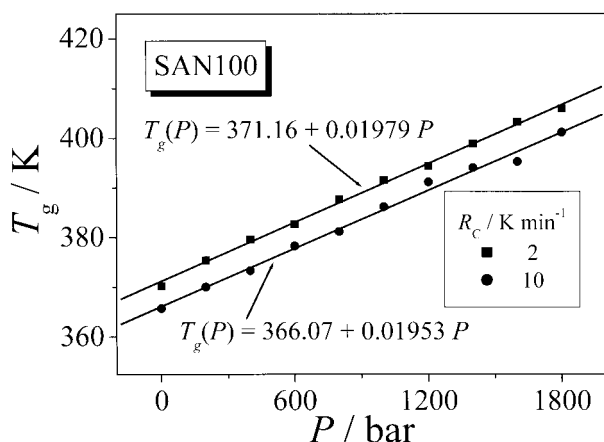


Figure 3 T_g of SAN100 as a function of pressure at two different cooling rates (R_c). The solid squares and circles represent the experimental data for T_g at $R_c = 2^\circ\text{C min}^{-1}$ and $R_c = 10^\circ\text{C min}^{-1}$, respectively, and the solid lines represent the corresponding fitted lines.

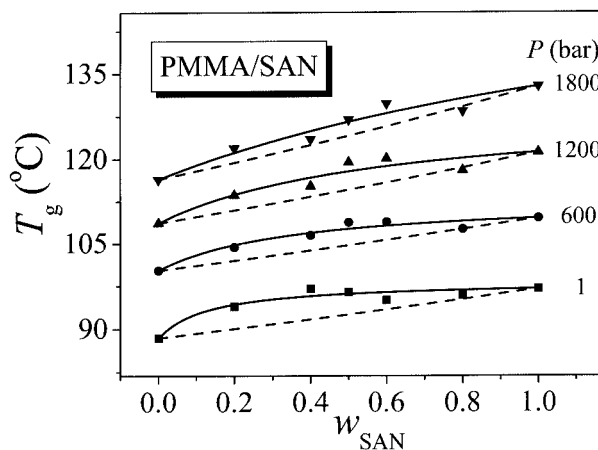


Figure 4 Pressure and composition dependencies of T_g for the PMMA/SAN system. The solid symbols represent the experimental data for T_g , and the solid and dashed lines represent the values fitted with the Gordon–Taylor equation and calculated with the Fox equation, respectively.

and circles represent the determined data of T_g at the cooling rates of 2 and 10°C min⁻¹, respectively, and the solid lines represent the corresponding fitted lines. The relationships between T_g and pressure at the corresponding cooling rates are also given in Figure 3. T_g increased linearly with the increase in pressure at a given cooling rate. Moreover, the values of T_g determined at a cooling rate of 10°C min⁻¹ were a little lower than those determined at 2°C min⁻¹ at the same pressures.

Pressure-dependent T_g 's of the PMMA/SAN blends

Figure 4 shows the pressure and composition dependencies of T_g for the PMMA/SAN system. The solid symbols represent the experimental data of T_g obtained from the PVT diagrams; the solid and the dashed lines represent the values fitted with the Gordon–Taylor equation and calculated with the Fox equation, respectively. The experimental data of T_g (at different pressures) could be fitted well by the Gordon–Taylor equation. However, the experimental data of T_g deviated positively from the values calculated with the Fox equation. Table II lists the values of k (at different pressures) in the Gordon–Taylor equation for the PMMA/SAN system; k tended to decrease with an increase in pressure.

TABLE II
Values of Parameter k (at Different Pressures) in the Gordon–Taylor Equation for the PMMA/SAN System

k	Pressure (bar)			
	1	600	1200	1800
	8.514	3.774	2.711	1.611

Figure 5 shows T_g of SAN100 and PMMA100 as a function of pressure. The solid squares and circles represent the experimental data of T_g for SAN100 and PMMA100, respectively, and the solid lines represent the corresponding fitted lines. The relationships between T_g and pressure are also given in Figure 5. T_g of SAN100 was a little higher than that of PMMA100 at a certain pressure, and T_g increased linearly with the increase in pressure.

Moreover, the increments of T_g with pressure for the PMMA/SAN system were also considered, and they are listed in Table III. The increments of T_g with pressure for all the samples were between 1.4 and 2.0°C/100 bar, within the range of 1.0–5.0°C/100 bar reported for some mixing systems.^{26–28}

CONCLUSIONS

On the basis of the obtained results and the discussion, the following conclusions can be drawn:

1. PVT diagrams determined via the isobaric cooling procedure could be used to evaluate T_g 's of samples at different pressures. With an increase in pressure, T_g 's increased linearly.
2. T_g of SAN100 decreased linearly with an increase in the cooling rate at a fixed pressure.
3. The relationships between T_g (at different pressures) and the composition of the PMMA/SAN systems could be well fitted by the Gordon–Tay-

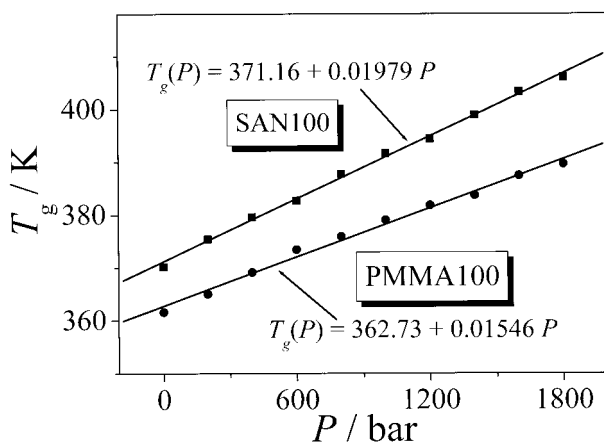


Figure 5 T_g of SAN100 and PMMA100 as a function of pressure. The solid squares and circles represent the experimental data for T_g of SAN100 and PMMA100, respectively, and the solid lines represent the corresponding fitted lines.

TABLE III
Increments of T_g to Pressure (P) for the PMMA/SAN System

	SAN content (wt %)						
	0	20	40	50	60	80	100
dT_g/dP (°C/100 bar)	1.56	1.56	1.46	1.69	1.93	1.81	1.99

lor equation. Moreover, the experimental data of T_g positively deviated from the values calculated with the Fox equation.

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