Article

Effects of Residual Solvent on Glass Transition Temperature
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The effects of residual solvent on the glass transition temperature (T_g) of poly(methyl methacrylate) (PMMA) were studied. A small amount of solvent in a film obtained by solution casting was found to remain even after vacuum evaporation for 30 h and compression-molding at 200 °C. The amount of residual solvent was less than 0.5 %, as revealed by gas chromatography. Therefore, this phenomenon is different from the plasticizing effect. A shift of the T_g to a lower temperature was attributed to strong ion-dipole interactions between the solvent molecules and the carbonyl group in PMMA molecules. Such interactions suppressed the associated states of PMMA, which greatly affected chain mobility.

Key Words: Glass transition temperature / Rheology / Thermal properties / Thermoplastics / Viscosity and viscoelasticity

1. INTRODUCTION

Poly(methyl methacrylate) (PMMA) is used in various functional applications in our daily life, such as optical films, plastic glasses, and paints. For practical applications to acrylic paints, enhancing the glass transition temperature (T_g) of PMMA is necessary to expand its applications.

Various rheological properties of PMMA have been evaluated by many researchers.¹⁻⁷⁾ These studies have shown that some rheological properties are considerably different from those of typical polymers such as polystyrene (PS). Masuda *et al.*¹⁾ showed that the ratio of entanglement compliance to steady-state compliance for monodisperse PMMA was considerably larger than typical values for other polymers. Osaki *et al.*⁵⁾ studied the ratio of two characteristic time constants obtained from the non-linear relaxation modulus, *i.e.*, τ_k/τ_s , where τ_k is the time for shrinkage of an extended chain and τ_s is the relaxation time of a chain with entangled molecular weight. They showed that the ratio for PMMA is approximately four times as large as that for PS. Furthermore, Plazek *et al.*³⁾ showed that PMMA does not follow the classic WLF equation and proposed that two mechanisms contribute to the glass-to-rubber transition.

It is believed that the unique rheological properties

derive themselves from intermolecular interactions in PMMA. For example, intermolecular interactions between stereoisomers, *i.e.*, syndiotactic PMMA (s-PMMA) and isotactic PMMA (i-PMMA), have a considerable effect on the rheological properties.⁸⁾

Intermolecular interactions in PMMA could be affected by various organic solvents, because of interactions between the solvent and carbonyl groups in PMMA. Thus, these effects can change the glass-to-rubber transition. Some reports have suggested that residual solvents and gases in the sample can affect the T_g of polar polymers. He *et al.*⁹⁾ found that PMMA and PS containing acetone show lower T_g . Rittigstein *et al.*¹⁰⁾ reported that the species of organic solvents used for spin coating have impact on T_g of PMMA-silica nanofiller composites. Moreover, Lin *et al.*¹¹⁾ reported that the PMMA/poly(styrene-co-maleic anhydride) (SMA) composite shows higher T_g and longer segmental relaxation time when using chloroform, methylethyl ketone and tetrahydrofuran as compared with the solution-cast film using *N,N*-dimethylformamide. They concluded that the existence of hydrogen bonding affects the chain conformation in the solution.¹²⁾ A similar result was also reported for solution-cast films prepared from mixture solvents of *m*-xylene and acetic acid.¹³⁾

In this paper, we investigated the effects of a small amount of solvent on the thermal properties of PMMA. Because most paints contain various kinds of solvents, including water, the information obtained in this study will be

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useful to industry for expanding the service temperatures of materials. Furthermore, these results demonstrate the importance of a complete drying process before measurements of physical properties of PMMA.

2. EXPERIMENTAL

2.1. Materials

A commercially available PMMA (Mitsubishi Chemical, Acrypet VH) was used as the polymer. The number- and weight- average molecular weights were $M_n = 58,000$ and $M_w = 120,000$, respectively, which were determined by size exclusion chromatography (Tosoh, HLC-8020) with chloroform as a solvent.

The solvents used in this study to dissolve PMMA pellets were butyl acetate, acetone, dichloromethane, and methanol. The boiling point and saturated vapor pressure at 20 °C of each solvent are summarized in Table I.

2.2. Sample Preparation

PMMA pellets (2 g) were completely dissolved in the organic solvents (30 g), *i.e.*, butyl acetate, acetone, dichloromethane, or a mixture of dichloromethane and methanol (weight fraction 90:10), and stirred for 40 h at room temperature. The solution was cast in a Teflon-coated container and dried at room temperature overnight in a draft chamber. The sample was further dried under the following two conditions: 30 h under vacuum at room temperature; and 30 h under vacuum at 160 °C. The solvents used and vacuum conditions of each sample are summarized in Table II.

These samples were compressed into a film with 300 μm thickness at 200 °C under 30 MPa for 1.5 min with the use of a compression-molding machine. Subsequently, the samples were quenched at 25 °C for 3 min. The pellets without any solvents were also compressed into a film after drying under vacuum at room temperature for 30 h as a reference sample

(R1). Furthermore, pellets without any added solvent were compressed under the same conditions after being evaporated for 30 h at 160 °C (R2). All the obtained films were free from voids.

2.3. Measurements

A differential scanning calorimeter (DSC, PerkinElmer, DSC 8500) was used to evaluate thermal properties at a heating rate of 10 °C/min from room temperature under a nitrogen atmosphere. Approximately 10 mg of the sample was encapsulated in an aluminum pan.

The temperature dependence of the oscillatory tensile moduli (storage modulus E' and loss modulus E'') was measured from 25 to 180 °C at a frequency of 10 Hz with the use of a dynamic mechanical analyzer (DMA, UBM, Rheogel-E4000). The heating rate was 2 °C/min.

The amount of residual solvent in each film was measured by gas chromatography (Shimadzu, GC-2014) after dissolution by stirring in dimethyl sulfoxide for 2 days and equilibration of the solution for 1 week. The amounts of solvents were quantified based on a calibration curve from the peak area of each solvent. The amount of dichloromethane could not be detected owing to its high volatility.

3. RESULTS AND DISCUSSION

Figure 1 shows the dynamic tensile moduli for the films obtained from the compression-molding using samples A, B, C, D, and R1. Samples A-D were prepared with the use of butyl acetate, acetone, dichloromethane, and the mixture of dichloromethane and methanol, respectively.

Although the films shared the same thermal history, *i.e.*, vacuum drying at room temperature for 30 h and compression-molding at 200 °C, the peak temperatures in the E'' curve, defined as $T_{g\text{-DMA}}$, were markedly different. In particular, the $T_{g\text{-DMA}}$ of sample A, prepared with butyl acetate as a

Table I Boiling point of each solvent and the saturated vapor pressure at 20 °C.

Solvents	Saturated vapor pressure at 20 °C (kPa)	Boiling point (°C)
Butyl acetate	1.3	126.3
Acetone	24.7	56.1
Dichloromethane	47.4	39.6
Methanol	13.0	64.7

Table II Solvent and vacuum conditions.

	Butyl acetate	Acetone	Dichloromethane	Dichloromethane/Methanol
RT under vacuum for 30 h	A	B	C	D
160 °C under vacuum for 30 h	E	F	G	H

solvent, was located at 93 °C, which was much lower than T_{g-DMA} of R1 (112 °C). This result suggests that the organic solvents remained in the films, although the films were prepared by compression-molding at 200 °C after dried under vacuum at room temperature for 30 h. Films having higher T_{g-DMA} values tended to show a large maximum value of E'' suggesting that the glass-to-rubber transition occurs over a relatively narrow temperature range. However, the films obtained from sample A showed a lower value of E' in the temperature range higher than 60 °C. This result indicates that the service temperature of PMMA products strongly depends on their preparation method.

Figure 2 shows DSC heating curves of the films measured at 10 °C/min. The heat flow changed stepwise for all samples owing to the glass-to-rubber transition; however, the transition was not clear for sample A. This result can be

Fig. 1 Temperature dependence of the dynamic tensile moduli at 10 Hz. The samples were treated by the following solvents prior to vacuum-drying at room temperature for 30 h. (red) butyl acetate, sample A, (blue) acetone, sample B, (green) dichloromethane, sample C, (orange) dichloromethane/methanol, sample D, and (black) no solvent, R1.

Fig. 2 The second heating curves of DSC at a rate of 10 °C/min. The samples were treated by various solvents prior to vacuum-drying at room temperature for 30 h.

Table III T_g 's of the sample films.

Samples	Solvents	T_{g-DMA} (°C)	T_{g-DSC} (°C)
R1	—	112	109
A	Butyl acetate	93	96
B	Acetone	100	105
C	Dichloromethane	101	104
D	Dichloromethane/Methanol	102	106

attributed to the broad distribution of relaxation times, as suggested in Fig. 1.

The glass transition temperatures evaluated by DSC, denoted as T_{g-DSC} , are summarized in Table III. As shown in the table, T_{g-DSC} and T_{g-DMA} featured similar trends.

The DMA and DSC measurements suggest that it is almost impossible to remove the solvent at room temperature even with exposure to vacuum conditions for 30 h following the compression-molding at 200 °C. Such strong absorption of solvents can be attributed to the dipole-dipole interactions of the solvents with the carbonyl groups in PMMA. In fact, Patra *et al.* detected the interaction between PMMA and polar solvents as a stretching vibration peak of the carbonyl group in FT-IR spectra.¹²⁾ A similar result was reported by Plazek *et al.*,³⁾ which showed that water molecules strongly absorbed to PMMA and act as a plasticizer, reducing the T_g .

As shown above, once the samples were dissolved in solvent, the T_g decreased even after compression-molding at 200 °C. The films contained a small amount of the residual solvent, which was difficult to remove. This result is also supported by the film's appearance; the films appeared as transparent films without any void formation, despite being exposed to high temperature (200 °C) and vacuum-drying conditions.

Figure 3 shows the dynamic tensile moduli for the films obtained by compression-molding after drying under vacuum for 30 h at 160 °C, *i.e.*, samples E to H.

The decrease of the T_g was not so obvious for these samples compared with the substantial changes of the dynamic tensile moduli shown in Fig. 1; however, a slight T_g shift was observed.

The amount of residual solvent in the films was measured by gas chromatography, as shown in Table IV.

Although the amount of dichloromethane was not characterized owing to its facile evaporation, we clarified that butyl acetate and acetone remained in the films obtained by compression-molding at 200 °C after vacuum-drying at room temperature for 30 h. Furthermore, these results showed that even a small amount of the solvents, less than 0.5 %, is enough to decrease the T_g .

This phenomenon cannot be explained by the plasticizing effect of the solvent. For the plasticizing effect, the T_g can be expressed as a volume/weight fraction of the solvent and polymer. The Gordon–Taylor (GT) equation,¹⁴⁾ as shown below, is typically used to express the T_g of a plasticized polymer:

$$T_g = \frac{x_1 T_{g,1} + k_{GT}(1-x_1)T_{g,2}}{x_1 + k_{GT}(1-x_1)} \quad (1)$$

where $T_{g,i}$ is the T_g of i component, x_i is the weight fraction of i , and k_{GT} is the difference in the thermal expansion coefficients between the glassy and rubbery states.

As shown in the GT equation, the amount of residual solvent was too low to affect the T_g , suggesting that the T_g shift could not be attributed to the conventional plasticizing effect. Thus, it is likely that some solvent molecules show strong electrostatic interactions with the PMMA and reduce the intermolecular interactions between neighboring PMMA chains and enhance segmental motion.

The T_g shift occurs also for residual water as reported previously^{3, 15, 16)}. The temperature dependences of the

dynamic tensile moduli for films prepared from R1 and R2 are shown in Fig. 4.

Although both films were obtained by compression-molding at 200 °C, the T_g values were different, *i.e.*, 112 °C for R1 and 118 °C for R2. The drying conditions before compression-molding greatly affected the dynamic mechanical properties. Because the film had no voids, water molecules were not evaporated during compression-molding. This result shows that prolonged heating at high temperature under vacuum conditions is necessary to remove moisture from a sample. In industry, PMMA is usually dried prior to melt-processing to avoid foaming owing to water evaporation. However, water molecules can remain in the material and reduce intermolecular interactions between neighboring PMMA molecules in a melt-processed product without forming voids.

These results demonstrate that the thermal properties, particularly T_g , strongly depend upon the solvent treatment, which must be considered for materials design and processing of solution-cast films and paints for acrylate polymers.

Fig. 3 Temperature dependence of the dynamic tensile moduli at 10 Hz. The samples were treated by the following solvents prior to vacuum-drying at 160 °C for 30 h. (red) butyl acetate, sample E, (blue) acetone, sample F, (green) dichloromethane, sample G, (orange) dichloromethane/methanol, sample H, and (black) no solvent, R2.

Fig. 4 Temperature dependence of the dynamic tensile moduli at 10 Hz. (open symbols) R1 and (closed symbols) R2.

Table IV Amounts of residual solvents measured by gas chromatography.

Sample	Solvents	Dry Temp. (°C)	Amount of solvent (ppm)
A	Butyl acetate	RT	3200
B	Acetone	RT	4100
C	Dichloromethane	RT	—
D	Dichloromethane/Methanol	RT	1500
E	Butyl acetate	160	Not detect
F	Acetone	160	100
G	Dichloromethane	160	—
H	Dichloromethane/Methanol	160	100

4. CONCLUSIONS

We studied the glass transition temperature of PMMA films obtained by compression-molding at 200 °C. In particular, the effect of drying processes prior to compression-molding were investigated in solution-cast films. For films that showed no voids, which might indicate the evaporation of solvent, a small amount of a solvent remained in the compressed films, which decreased the glass transition temperature. Because the amount of solvent was low, this was not a conventional plasticizing effect. The strong dipole-dipole interactions between the solvent molecules and the carbonyl groups of PMMA enhanced the segmental motion of PMMA by reducing interchain interactions and thus decreased the T_g . However, the origin of the T_g decrease has yet to be precisely characterized by other spectroscopic methods. Furthermore, this phenomenon should be considered in applications that involve processes with organic solvents, such as paint.

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