

# Miscibility of Polymethyl Methacrylate with Poly (Hydroxy Ether) of Bisphenol A

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## SYNOPSIS

The miscibility of polymethyl methacrylate (PMMA) with the poly (hydroxy ether) of bisphenol A (phenoxy resin) was studied and PMMA has been found to be miscible with phenoxy resin. PMMA/phenoxy blends were found to be clear and showed a single, composition-dependent glass transition temperature. The  $k$  parameter of the Gordon-Taylor equation can be taken as a measure of the strength of the specific interaction between the two polymers, and a low value of  $k = 0.3$  is found for the PMMA/Phenoxy blends. Fourier transform infrared (FTIR) showed the presence and nature of intermolecular interactions between the two polymers.

## INTRODUCTION

Polymethyl methacrylate (PMMA) is an amorphous polymer that has good optical clarity and good weatherability. Phenoxy resin (poly hydroxy ethers of bisphenol A) is the reaction product of epichlorohydrin with bisphenol A. It is relatively tough and is soluble in only a few solvents. PMMA has been reported to be miscible with polyvinyl chloride<sup>1,2,3</sup> and styrene-acrylonitrile copolymers, SAN.<sup>4,5</sup> Phenoxy resin has been reported to be miscible with poly( $\epsilon$ -caprolactone) (PCL).<sup>6</sup>

In this work, we describe the miscibility of PMMA with phenoxy resin. The miscibility of two polymers is generally established by the presence of a single glass transition temperature which is determined using mechanical or thermal methods, by observation of optical clarity, or by direct observation of the structure using optical or electron microscopy. The same techniques may be used to observe the phase separation which may take place on heating or cooling.

Fourier transform infrared (FTIR) spectroscopy also is a useful technique with which to study com-

patible polymer blends.<sup>6,7</sup> FTIR spectroscopy indicated that a shift in the hydroxyl band of phenoxy resin occurs in phenoxy/PCL blends. It was proposed that the miscibility of such blends is due to a specific interaction between the hydroxyl groups of phenoxy resin and the carbonyl group of PCL.<sup>4</sup> In this work, we will observe the shift in the hydroxyl band of phenoxy resin in PMMA/phenoxy blends. This shift and the driving force toward the miscibility in PMMA/phenoxy blends will be compared to those of phenoxy/PCL blends.

## EXPERIMENTAL

### Materials

The PMMA (Lucky, EG 890) employed is reported to have a number average molecular weight of 65,000. The phenoxy resin was supplied by Union Carbide (grade PKHC). It was quoted to have number average molecular weight of 25,000.

### Preparation of Blends

The two polymers were blended for about 30 s in a kneader (Buss Ko-Kneader Model MDK/E46, Buss AG, Basle, Switzerland). Barrel and die temperature was set to 265°C. The blends passed through a cooling water bath and were pelletized. The dynamic mechanical test specimens were injection molded.

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## Characterization

The sample was assessed for visual clarity. Dynamic mechanical measurements were performed to confirm the miscibility of the blends. A Rheometrics Mechanical Spectrometer, (RMS, Model 605, Rheometrics, Inc.), was used to measure  $T_g$ . The specimens (65 mm × 12 mm × 3.175 mm) were subjected to an imposed oscillatory frequency of 2 Hz. A temperature range of 40°C to 150°C was scanned at a heating rate of 2°C/min. A plot of  $G''$  (loss modulus) against temperature was constructed. Differential scanning calorimeter (DSC) measurements were carried out using a Perkin Elmer 7 series thermal analyzer under a nitrogen atmosphere with a heating rate of 20°C/min. The heat flow difference between 10 mg of a sample in an aluminum pan and a similar empty pan was recorded. The glass transition temperatures by DSC in this report were determined at the half height temperature of the heat capacity jump.

## FTIR Spectroscopy

The films of phenoxy resin and PMMA/Phenoxy blends were placed onto potassium bromide (KBr) windows at room temperature. Infrared spectra were obtained on a Digilab FTS-20/80 spectrometer. One hundred scans at a resolution of 4 cm<sup>-1</sup> were signal averaged.

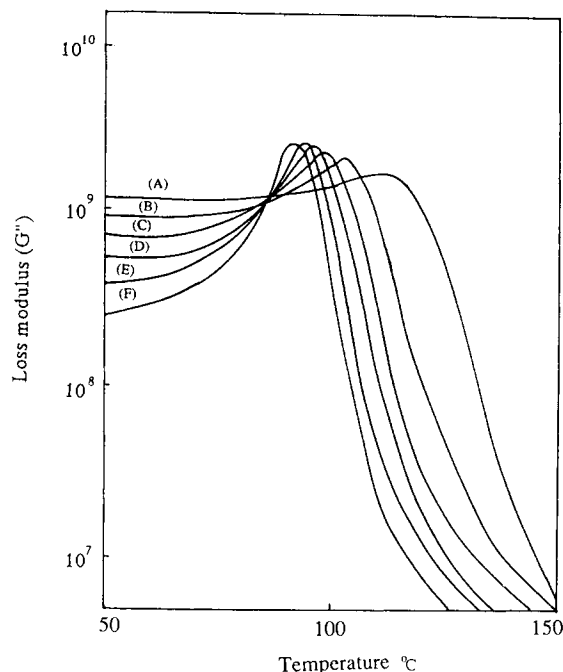
## RESULTS AND DISCUSSION

### Glass Transition Temperature Measurements

Figure 1 shows the RMS results for a series of blends. The  $T_g$ 's of phenoxy resin and PMMA are found, respectively, at 91°C and 112°C. All PMMA/phenoxy blends exhibit a single  $T_g$  intermediate between those of phenoxy resin and PMMA, and can be considered to be miscible. Figure 2 shows a plot of  $T_g$  against composition. The result is compared to the Fox equation<sup>8</sup>

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

where  $w_1$  and  $w_2$  are the weight fractions, and  $T_{g1}$  and  $T_{g2}$  are the glass transition temperatures of the two base polymers. The negative deviation of the  $T_g$  values from the Fox equation can be taken as evidence of relatively weak interaction between PMMA



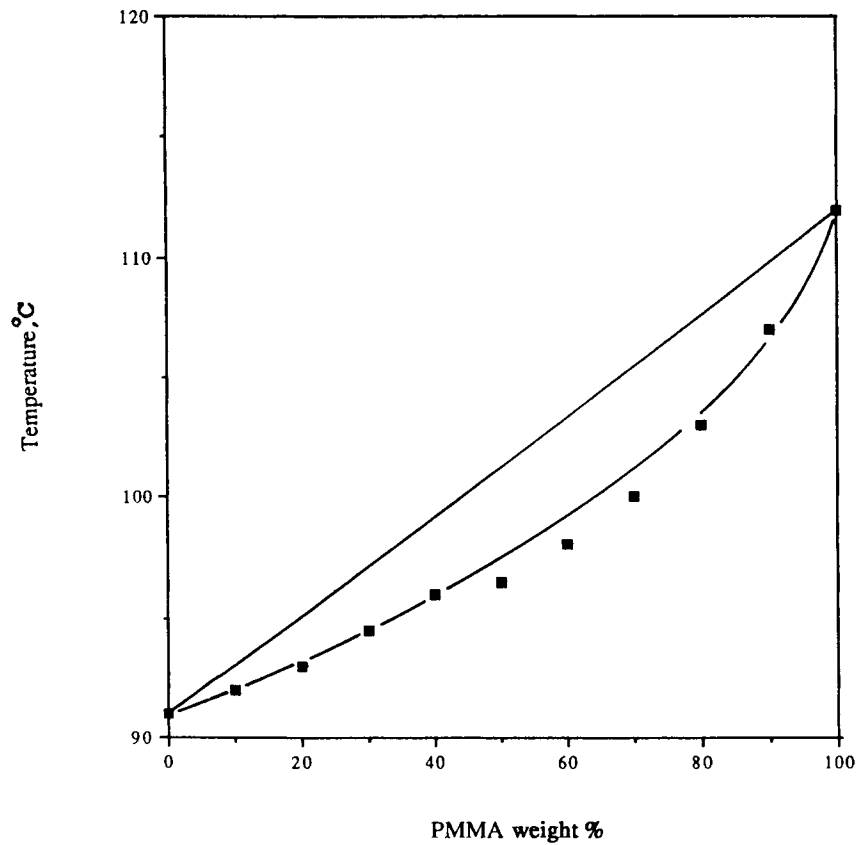
**Figure 1** Plots of loss modulus  $G''$  against temperature for blends of PMMA/phenoxy at the following weight ratios: (A) 100 : 0; (B) 80 : 20; (C) 60 : 40; (D) 40 : 60; (E) 20 : 80; (F) 0 : 100.

and phenoxy resin. Figure 3 shows the DSC results for the same blends. They also show a single composition-dependent glass transition temperature. Figure 4 shows a plot of DSC  $T_g$  against composition compared to the Fox equation. Negative deviation of the  $T_g$  values from the equation is again observed. In the Golden-Taylor equation,<sup>9</sup>

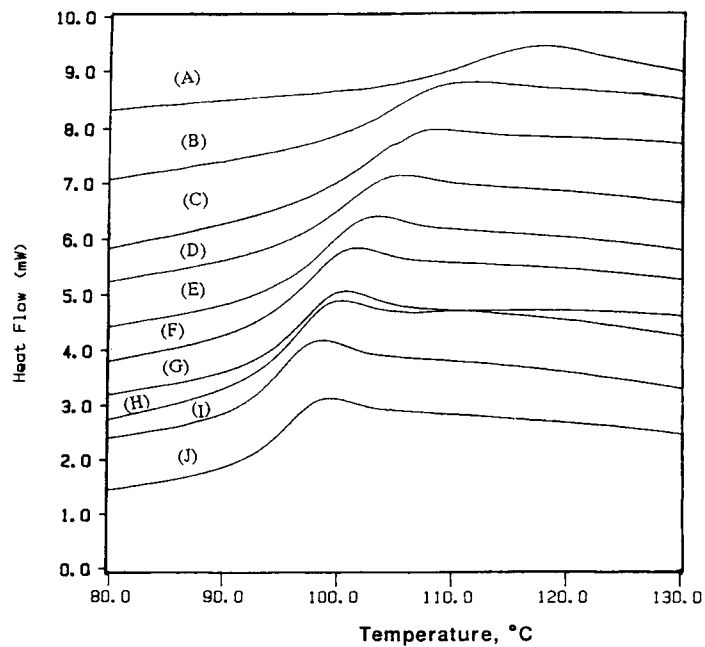
$$T_g = \frac{w_1 T_{g1} + k w_2 T_{g2}}{w_1 + w_2} \quad (2)$$

$k$  is an adjusting parameter related to the degree of curvature of the  $T_g$ -composition diagram. When  $k$  is unity, a straight line is obtained. When  $k < 1$ , the  $T_g$  of the blend is lower than expected. When  $k > 1$ , the  $T_g$  is higher than expected, and this suggests strong interactions. The lower line drawn in Figure 4 was obtained from equation (2) with  $k = 0.3$ . This suggests that the polymer-polymer interaction is not very strong.

It has been suggested<sup>10</sup> that the width of the transition at  $T_g$  could be indicative of the molecular state of mixing of the components of the blends. As shown in Figure 3, phenoxy resin exhibits a 7–9°C width at  $T_g$ , but PMMA exhibits a very broad transition of 14–18°C. The PMMA/phenoxy blends ex-



**Figure 2** Plot of  $T_g$  against composition for PMMA/phenoxy blends. The upper line is a theoretical plot based on the Fox equation.

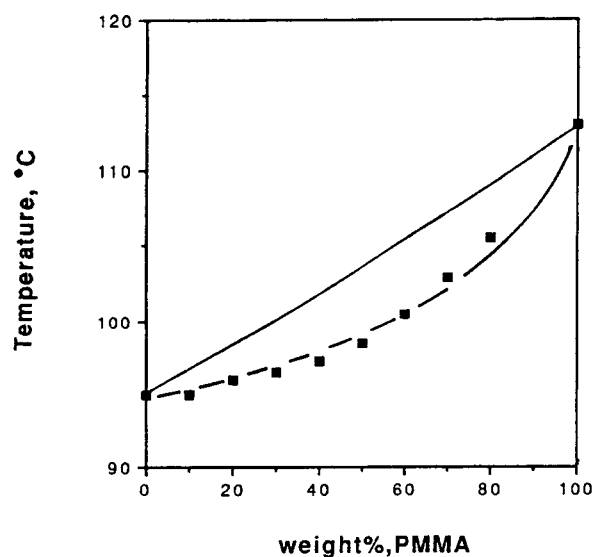


**Figure 3** DSC thermograms for PMMA/phenoxy blends of PMMA/phenoxy at (A) 100 : 0; (B) 80 : 20; (C) 70 : 30; (D) 60 : 40; (E) 50 : 50; (F) 40 : 60; (G) 30 : 70; (H) 20 : 80; (I) 10 : 90; and (J) 0 : 100 weight ratio.

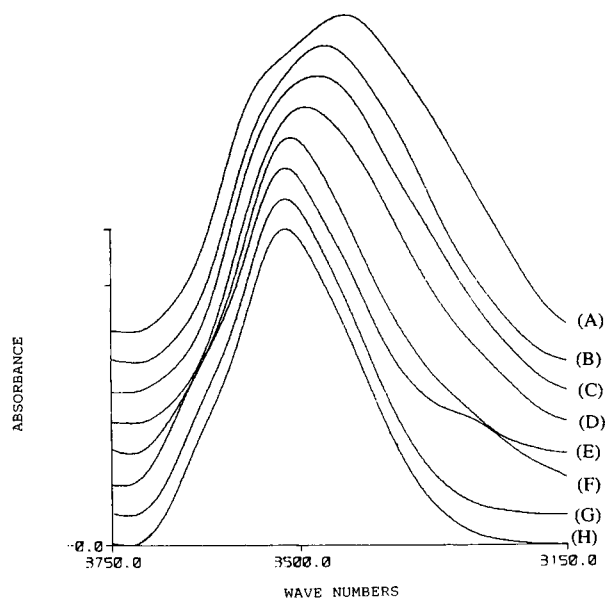
hibit transition widths intermediate between those of the pure components. The  $T_g$  transition widths of phenoxy/PMMA blends increase with increase in PMMA concentration. Since a large  $T_g$  transition zone is observed for pure PMMA, the widths of PMMA/phenoxy transition may not be taken as a good indication of the level of molecular mixing.

### FTIR Spectroscopy

Figure 5 shows detailed infrared spectra from 3150  $\text{cm}^{-1}$  to 3750  $\text{cm}^{-1}$  of pure phenoxy resin (denoted A) and PMMA/phenoxy blends containing 10, 20, 30, 40, 50, 60, and 70 weight percent PMMA (denoted B-H respectively), all recorded at room temperature. The spectrum in this region of pure phenoxy resin may be considered to be composed of two components. A broad band centered at 3440  $\text{cm}^{-1}$  is considered to be attributed to intermolecularly hydrogen-bonded hydroxyl groups (self-associated hydroxyl groups).<sup>6</sup> The minor contribution, observed as a shoulder at 3550  $\text{cm}^{-1}$ , is attributed to unassociated free hydroxyl groups. Upon mixing with PMMA, the broad hydrogen-bonded hydroxyl band of the phenoxy resin is observed to shift to higher frequencies as a function of increasing PMMA concentration. The relative concentration of free hydroxyl group also appears to decrease with



**Figure 4** Plot at  $T_g$  by DSC against composition for PMMA/phenoxy blends. The upper line is a theoretical plot based on the Fox equation.



**Figure 5** FTIR spectra recorded at 25°C of PMMA/phenoxy blends containing the following weight ratios: (A) 0 : 100; (B) 10 : 90; (C) 20 : 80; (D) 30 : 70; (E) 40 : 60; (F) 50 : 50; (G) 60 : 40; (H) 70 : 30.

PMMA concentration. The shift of the hydrogen-bonded hydroxyl band of phenoxy resin upon mixing with poly( $\epsilon$ -caprolactone) (PCL) has been observed by Coleman and Moskala.<sup>6</sup> This result was interpreted as evidence for a hydrogen bond between the hydroxyl and carbonyl groups of PCL. Similarly, we conclude that for the PMMA/phenoxy blends, free hydroxyl groups and self-associated hydroxyl groups become associated with PMMA carboxylic acid groups upon mixing, via hydrogen bonds. It is concluded that hydrogen bonding is a driving force for the miscibility of PMMA/phenoxy blends.

### CONCLUSION

PMMA/phenoxy was found to be a miscible system. PMMA/phenoxy blends were found to be clear and showed a single, composition-dependent glass transition temperature. Glass transition temperature increased with an increase of PMMA and decreased with a decrease of PMMA. The  $k$  parameter of the Gordon-Taylor equation is found to be 0.3 for the system. Fourier transform infrared (FTIR) showed that hydrogen bonding is a driving force for miscibility of PMMA and phenoxy resin.

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