

# Dielectric relaxation studies of bisphenol-A polycarbonate-*N,N'*-bis(3-methylphenyl)-1,1'-biphenyl-4,4'-diamine solid solutions

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The dielectric relaxation spectra of *N,N'*-bis(3-methylphenyl)-1,1'-biphenyl-4,4'-diamine (PPB)-polycarbonate (PC) solid solutions have been studied as a function of composition. The glass transition of these mixed systems varies monotonically with composition. Analysis of the apparent activation at the glass transition temperature ( $T_g$ ) show it to be composition dependent up to 50 vol% small molecules and composition independent above this composition. The data indicate that the small molecule has a greater effect on the  $T_g$  reorientation process of the PC than vice versa. The activation energy dependence on composition is discussed in terms of the fundamental WLF parameters. From 0 to 50% PPB dynamic behaviour is as expected, increasing small molecule concentration decreases  $T_g$  and the apparent glass transition activation energy. Above 50% small molecules, a possible  $T_g$  dependence of some of the WLF parameters is obtained. Line-shape analysis of the glass transition provided no information on the molecular dispersion. The sub- $T_g$  relaxations of this system indicate little, if any, small molecule-polymer interactions. It is shown that the addition of PPB eliminates the  $\beta$  relaxation of PC and reduces the  $\gamma$  relaxation intensity. In the former case, the disappearance of the  $\beta$  relaxation is correlated with a change of composition independence in the apparent activation energy of the glass transition. The latter is a dilution effect.

(Keywords: dielectric relaxation; glass transition; composition)

## INTRODUCTION

Plasticizers are important in the polymer industry and can be used to modify polymer properties. These modifications form the subject of a variety of dynamic studies<sup>1-3</sup>. The plasticizer can play the role of mechanical property modifier and can also produce other desired properties. Examples of this are the addition of *n*-butyl-4,5,7-trinitrofluorenone [BuTNF] and bis[4-(diethylamino)-2-methylphenyl]phenylmethane [BDETPM] to polycarbonate (PC)<sup>4,5</sup>. These two materials not only plasticize PC, but also make it capable of transporting electrons and holes, respectively.

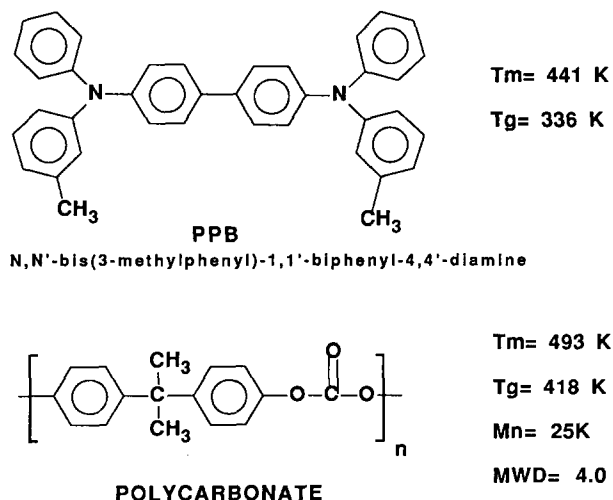
We have been interested in the effects of plasticizers on the molecular relaxation of PC<sup>4-7</sup>. Our studies have involved using plasticizers that are molecularly similar as well as dissimilar to PC. For molecularly similar molecules, it was shown that the glass transition temperature ( $T_g$ )-composition relationship could be described by either a  $T_g$  versus  $1/M_n$  or a standard polymer diluent correlation, and that the apparent activation energy,  $E_{app}$ , for  $T_g$  and its changes with composition were correlated with local mode motions in the polymer backbone.

For molecules dissimilar to PC, results varied with structure. In BDETPM mixtures, results were similar to the above, while BuTNF exhibited relaxational data that could only be described by an interactive complex between the small molecule and a portion of the polymer chain.

In the studies cited (with the exception of the BuTNF), it was found that as the localized motion in the PC backbone was affected by addition of a plasticizer, the  $E_{app}$  for  $T_g$  also changed. In order to further understand this process, the following study was undertaken.

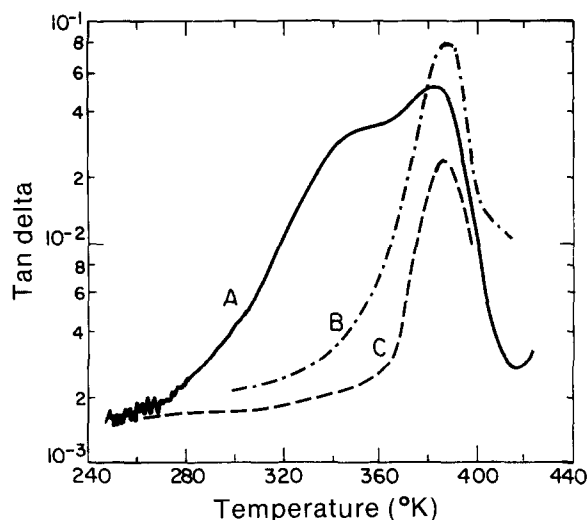
## EXPERIMENTAL

The thermal data were obtained using a Perkin-Elmer DSC-II (scanning rate = 2 K m<sup>-1</sup>). The structures and physical constants of the materials used are shown in Scheme 1. Films for dielectric experiments were cast from 10% solutions (g solid ml<sup>-1</sup> solvent) of the components



Scheme 1

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**Figure 1** Tan  $\delta$  versus temperature for a 40/60 PPB-PC film. Drying conditions: A, 312 K, 20 h,  $1.33 \times 10^{-1}$  Pa; B, 373 K, 18 h,  $1.33 \times 10^{-1}$  Pa; C, heat-quench cycle, 473 K, 1-2 s. Room temperature, data taken at 120 Hz

in methylene chloride,  $\text{CH}_2\text{Cl}_2$ . The solutions were doctor-bladed onto ball-grained aluminium, air-dried, and then vacuum dried (312 K, 48 h). The PC used in these studies had  $M_n = 10\,580$  and  $M_w/M_n = 2.5$ . Composition data are reported in *N,N'*-bis(3-methylphenyl)-1,1'-biphenyl-4,4'-diamine (PPB)-PC weight percentages.

Dielectric samples were electroded with evaporated gold and tested in spring-loaded sample cells. Samples were isolated from the environment in a stainless steel box sealed with Teflon. Temperature calibration was carried out with a thermocouple mounted within 1 cm of the sample (accurate to  $\pm 2$  K).

Two dielectric set-ups were used in these studies: a scanning dielectric device described previously<sup>4,8</sup> and a General Radio 1615-A capacitance bridge with standard accessories. The former system permits continuous acquisition of dielectric data at variable scanning rates from liquid nitrogen temperature to 473 K. The programme rate for these experiments was  $0.9 \text{ K min}^{-1}$ .

## RESULTS AND DISCUSSION

### *Anomalous relaxation behaviour and retained solvent*

Unlike other small molecule systems we have studied dielectrically<sup>4,6</sup>, PPB-PC exhibits unusual dielectric behaviour when studied after the normal 312 K drying for 2 days. This unusual behaviour is shown in *Figure 1* (curve A) where it is seen that two apparent relaxations are taking place in the vicinity of the glass transition of the mixed system. Although the data shown is for a 40/60 mixture, similar curves were observed in all mixture compositions. Originally, these were thought to be due to phase separations leading to relaxations attributed to the mixture components<sup>9-11</sup>. Phase separation was discounted for two reasons: the low temperature peak occurred below the  $T_g$  of pure PPB (340 versus 360 K); and high temperature thermal cycling of the film resulted in elimination or reduction of the low temperature component.

The question naturally arises as to the nature of the low temperature, thermally removable relaxation. Pos-

sible explanations for the relaxation are: (1) retained solvent; (2) sorbed water; and (3) inhomogeneities in the morphological character of the samples. Phase separation of the solid solution constituents can be eliminated as relaxations due to the pure components should be observed. Water can be eliminated as samples exposed to long periods of 100% relative humidity do not exhibit the low temperature relaxation.

Entrapped solvent or an unusual morphology that shifts or creates a new relaxation are the remaining explanations. We chose to eliminate the latter because the intensity of the anomalous relaxation is sometimes greater than that of the true  $T_g$  (high temperature) relaxation. This would indicate more dipolar material with a much larger dipole participating in the relaxation, i.e. entrapped solvent.

An upper limit for the amount of entrapped solvent can be estimated from the dielectric data. The change in dielectric constant at a given relaxation is a function of the number of dipoles participating in the relaxation<sup>11</sup>. The Onsager relation was used to estimate this number<sup>12</sup>:

$$\mu_0^2 = \frac{3kT(2\epsilon_r + \epsilon_u)(3)^2}{4\pi N(3\epsilon_r)(\epsilon_u + 2)} \quad (1)$$

where  $\mu_0$  is the dipole participating in the relaxation,  $k$  is Boltzmann's constant,  $T$  is the absolute temperature,  $N$  is the dipole density per unit volume, and  $\epsilon_r$  and  $\epsilon_u$  are the relaxed (low frequency) and unrelaxed (high frequency) dielectric constants. Equation (1) was derived for a condensed phase of non-interacting dipoles and may not be appropriate for the particular system being studied. Equation (1) can be rearranged to solve for  $N$ . Assuming that  $\text{CH}_2\text{Cl}_2$  is the only molecule participating in the relaxation and that  $\delta\epsilon(\epsilon_r - \epsilon_u) \approx 0.26$ ,  $N$  is calculated to be  $2.5 \times 10^{19} \text{ cm}^{-3}$ . The number of molecules or monomer units  $\text{cm}^{-3}$  of PPB and PC can be calculated, assuming a density of one, to be  $1.95 \times 10^{21}$ . Therefore, the upper limit of  $\text{CH}_2\text{Cl}_2$  concentration is  $\approx 1.3\%$ . This is not an unreasonable value for a sample that has never been vacuum treated. The same calculation has been applied to a 40/60 PPB-PC film pumped at  $1.33 \times 10^{-1}$  Pa at 312 K for 19 h and yielding a solvent content of 0.13%.

The above values can only be considered an upper limit. There is no reason to suspect that a solvent molecule will relax independently of the surroundings, and in fact a combined motion of solvent-small molecule or solvent-polymer might be expected. The fact that an almost critical temperature is required for removal of the anomalous peak suggests a rather strong interaction between  $\text{CH}_2\text{Cl}_2$  and PPB (possibly some form of charge transfer). In an attempt to verify the entrapped solvent hypothesis, a 40/60 PPB-PC sample that had been heated and quenched was placed in a small desiccator at room temperature with a  $\text{CH}_2\text{Cl}_2$  saturated atmosphere for 19 h. The loss curve for this sample is similar to *Figure 1* (curve A). A weak peak appeared near 320 K, and the absolute value of  $\tan \delta$  had increased almost an order of magnitude.

We have also noted that solvent cast PC films do not exhibit the anomalous peak when subjected to standard 312 K,  $1.33 \times 10^{-1}$  Pa drying conditions. The data suggest that  $\text{CH}_2\text{Cl}_2$  has an affinity for the PPB. This conclusion is strengthened by the hypothesis that aryl-

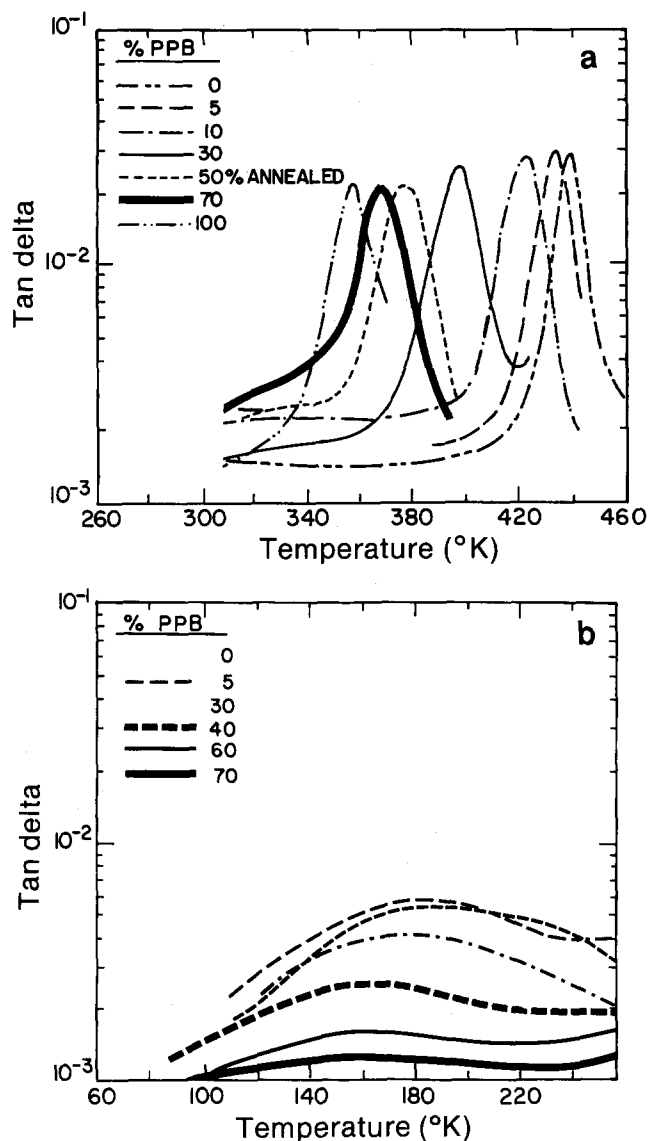


Figure 2 Tan  $\delta$  versus temperature for various compositions of PPB-PC. (a) High temperature and (b) low temperature region. Data taken at 120 Hz

amines could form weak charge transfer complexes with chlorinated hydrocarbon solvents<sup>13</sup>.

The above discussion points out the necessity for solvent removal in order that the true nature of the PPB-PC solid solution can be studied. Because of the observed solvent effects, all data presented below have been obtained from samples prepared either by a heat-quench technique or by pumping at elevated temperature (350 K or higher). With these techniques, the data were reproducible and indicated apparently homogeneous and stable blends of the components.

Dielectric results

A plot of tan  $\delta$  versus temperature for the various compositions is shown in Figure 2. Although 10 compositions were run, less are included in the figure for clarity. Figure 3 contains a plot of  $T_g$  (as determined from the peak in dielectric loss as a function of temperature at 120 Hz) versus composition, and Figure 4 is a transition map for the glass transition of the blends. Figure 5 is a plot of the  $E_{app}$  of  $T_g$  versus composition.

The  $\alpha$  ( $T_g$ ) relaxation

It is seen from Figure 3 that the glass transition of these solid solutions varies monotonically with composition. Plotting this data as a volume fraction of PPB produces an almost identical plot which does not exhibit a break or an inflection that Kovacs<sup>14</sup> postulated would occur in a polymer when the free volume is 'eliminated' by the addition of a liquid. This indicates that free volume exists throughout the entire composition range.

There is no indication of heterogeneous relaxation of the two components near  $T_g$  indicating that the micro Brownian motion that is associated with  $T_g$  occurs in both components in identical temperature frequency regimes.

The  $T_g$  data is easily fit by the Gordon-Taylor equation<sup>15</sup> (equation (2)) with a constant  $K$  value of

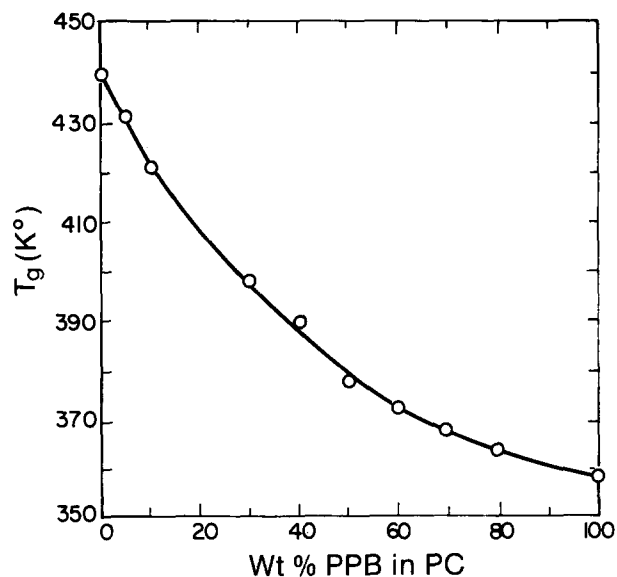


Figure 3 Glass transition temperature (120 Hz) versus composition for PPB-PC

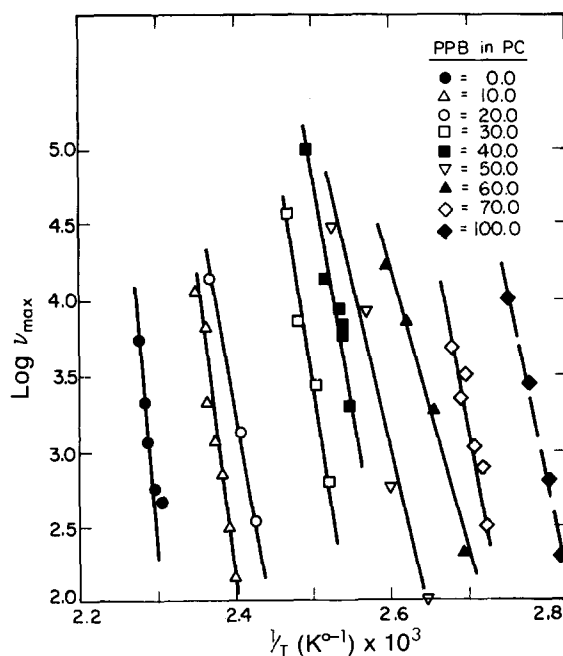


Figure 4  $\log v_{max}$  (at  $T_g$ ) versus inverse temperature for PPB-PC

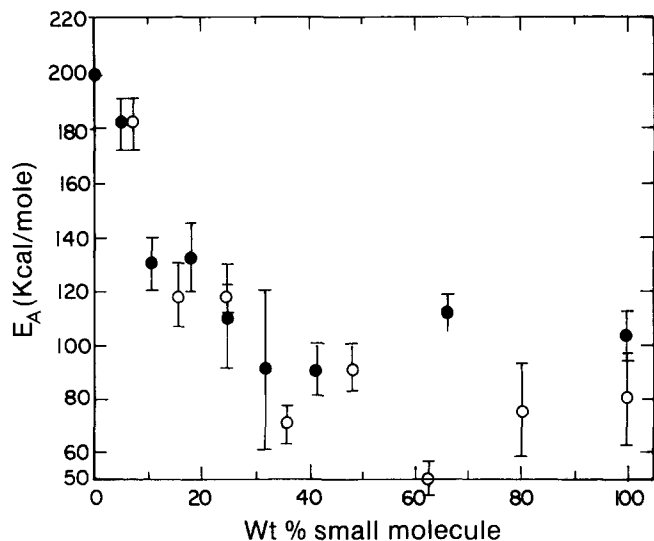


Figure 5 Activation energy ( $T_g$ ) versus composition for PPB-PC (●) and bisphenol-A diphenyl carbonate-Lexan (○)

$2.60 \pm 0.1$ :

$$T_g = \frac{x_1 T_{g1} + x_2 K T_{g2}}{x_1 + K x_2} \quad (2)$$

where  $x_i$  is the weight or volume fraction of component  $i$ ,  $T_{g1}$  is the glass transition temperature of pure component  $i$  and  $K$  is related to coefficients of expansion. The fit is shown in Figure 2 as a solid line.

Figure 4 shows  $T_g$  to be Arrhenius activated (in the frequency regime studied) for all compositions. This apparent Arrhenius effect is not unlike that observed in many homopolymeric PCs and indicates that a much wider frequency regime is needed to observe WLF type relaxation curves. The  $E_{app}$  values as a function of composition (Figure 5) indicate there are two composition regions of thermally activated relaxation: from 0 to ~40% PPB and from ~40 to 100% PPB. In the latter case, the activation energies appear composition independent at  $\sim 418 \pm 104 \text{ kJ mol}^{-1}$ . In the former case, the energies show classic plasticization effects in that  $T_g$  is shifted to lower temperatures and  $E_{app}$  decreases with increasing small molecule composition. The data are not unlike that obtained for bisphenol-A diphenyl carbonate-PC solid solutions<sup>6</sup>. Both sets of data are plotted in Figure 5 and exhibit similar characteristics.

A more interesting picture of the two small molecule systems is obtained when the  $E_{app}$  values for  $T_g$  are plotted versus volume fraction of small molecule. These results are shown in Figure 6. Within the limits of error of our measurement, both systems exhibit a change to composition-independent activation energies above 50 vol% small molecules. We surmise from the data that when matrix inversion takes place and the small molecule becomes the major volume component all reorientation barriers for the system become similar to those of the small molecule.

The data can be considered in terms of the WLF formalism<sup>16-18</sup>. In the WLF notation,  $E_{app}$  can be calculated as:

$$E_{app} = 2.303 R C_1^0 C_2^0 T^2 / (C_2^0 + T - T_0)^2 \quad (3)$$

where  $R$  is the universal gas constant,  $T_0$  is an arbitrary reference temperature, usually  $T_g$ ,  $T$  is the absolute

temperature, and  $C_2^0$  and  $C_1^0$  are functions of the fractional free volume and coefficient of expansion of the system being studied. At  $T_g$ , equation (3) becomes:

$$E_{app} = 2.303 R C_1 T_g^2 / C_2^0 = \sim R T_g^2 \alpha_f / f_g^2 \quad (4)$$

where  $f_g$  is the fractional free volume at  $T_g$  and  $\alpha_f$  is the coefficient of expansion of the free volume. Equation (4) predicts a linear relationship between  $E_{app}$  and  $T_g^2$ . If we assume that the dielectric measurements provide values near equilibrium, values of  $E_{app}$  versus  $T_g^2$  can be plotted. These are shown in Figure 7 for the systems cited. Both sets of data provide essentially identical slopes in the concentration range 0-50% small molecules.

This slope is  $(8.8 \pm 1.3) \times 10^{-3} \text{ kJ mol}^{-1} \text{ K}^{-2}$  which means that the ratio:

$$\frac{\alpha_f}{f_g^2} = \frac{8.8 \times 10^{-3}}{R} \approx 1 \text{ K}^{-1} \quad (5)$$

is composition independent from 0 to 50% small molecules. The value attained for  $\alpha_f / f_g^2$  is very reasonable

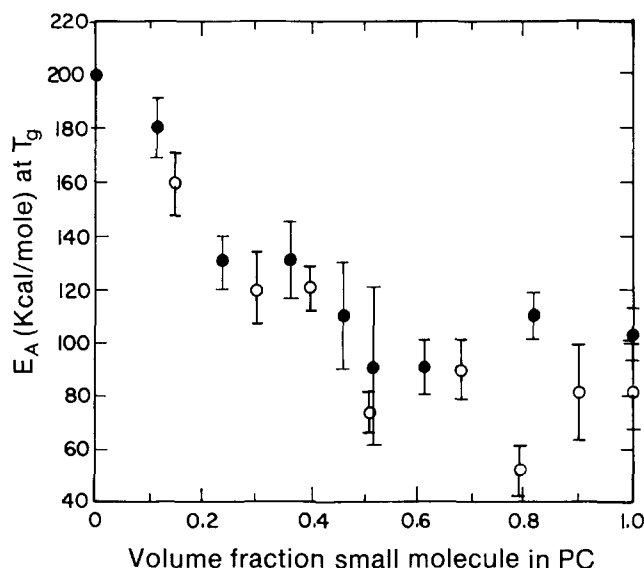


Figure 6 Activation energy ( $T_g$ ) versus volume fraction PPB (●) and bisphenol-A diphenyl carbonate (○) in PC blend

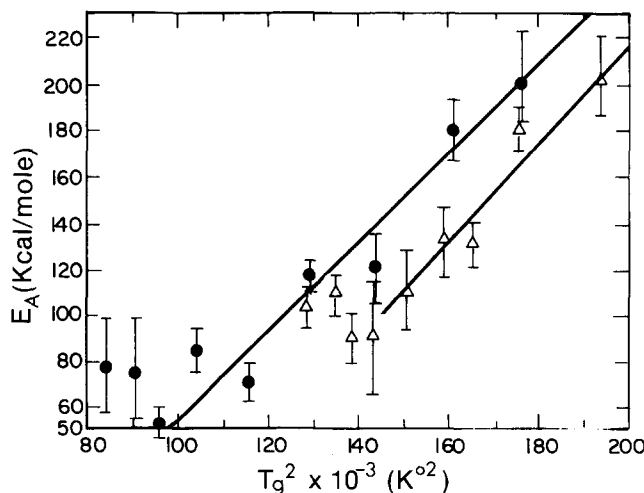


Figure 7 Activation energy ( $T_g$ ) versus  $T_g^2$  for PPB-PC (●) and bisphenol-A diphenyl carbonate-Lexan (Δ)

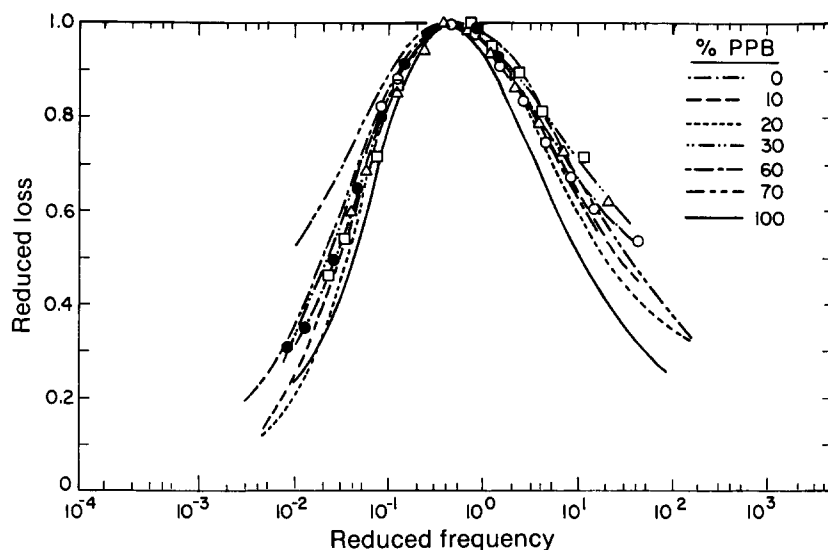


Figure 8 Reduced loss versus reduced frequency for various mixtures of PPB-PC at the glass transition

in terms of the measured value for coefficients of expansion and calculated values of  $f_g$  (ref. 19).

If the activation energy is considered in the range 50–100% small molecules, the plot of activation energy versus  $T_g^2$  has essentially zero slope implying that:

$$\frac{RT_g^2\alpha_f}{f_g^2} = \text{constant} \quad \text{or that} \quad \frac{\alpha_f}{f_g^2} \sim \frac{1}{T_g^2} \quad (6)$$

Because of the experimental error in the measurement of  $E_{app}$ , it is difficult to verify or disclaim a  $T_g$  dependence for either  $f_g$  or  $\alpha_f$ . The ratio of  $T_g^2$  of 100%:50% PPB is only 1.1 and that of 100%:50% bisphenol-A-diphenylcarbonate is 1.37. In the latter case, only a 17% change in  $f_g$  would account for the observed result. It is sufficient to note that, when the small molecule becomes the matrix in these solid solutions, the  $E_{app}$  for  $T_g$  apparently becomes composition independent which, in turn, implies that either  $\alpha_f$  or  $f_g$  or both become functions of the blend  $T_g$  such that  $\alpha_f/f_g^2 \sim 1/T_g^2$ .

A line-shape analysis of the  $T_g$  relaxations as a function of composition shows all mixtures (within the limits of error of our measurements) to be identical. A plot of reduced loss versus reduced frequency is shown in Figure 8 where it is seen that no trend in the reduced line shape is observed. This is unlike the system bisphenol-A-diphenylcarbonate-PC where line narrowing was observed as the small molecule concentration was increased<sup>6</sup>.

#### The sub- $T_g$ relaxations

If the temperature regime below the glass transition is considered (Figure 2), the combined  $\beta$  (220 K) and  $\gamma$  (160 K) relaxations of PC, which have been assigned to combined phenyl-carbonyl motion and carbonyl motion, respectively<sup>18–24</sup>, are observed to decrease in intensity with increased PPB concentration.

The  $\beta$  disappears with the addition of 30% PPB and  $\gamma$  intensity is continually reduced through 70% PPB (Figure 9). If the data in Figure 5 are considered and the  $E_{app}$  of  $T_g$  is correlated with the compositional dependent of the  $\beta$  relaxation intensity, an effect similar to that noted in earlier systems studied is observed<sup>5–7</sup>, i.e. at the composition where the  $\beta$  relaxation is no longer observed,

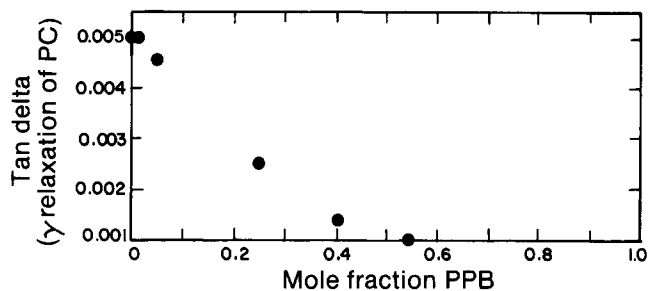


Figure 9 Tan  $\delta$  for the  $\gamma$  relaxation in PC versus mole fraction PPB

~30 wt% PPB, the  $E_{app}$  of  $T_g$  becomes composition independent. It appears that the barrier controlling the localized dynamics of the PC backbone can be correlated with those associated with  $T_g$ . In the case of PC, this is a combined phenyl-carbonyl interaction. Above 70% PPB, the films could not be measured at low temperature since they fractured upon cooling. The reduction in intensity of the  $\gamma$  relaxation without shifting to lower temperatures and the linearity of tan  $\delta$  with composition indicate that dilution of the PC by PPB does not affect the local potential barriers in the polymer that control the carbonyl motion. Within this temperature range, the data indicate that no sub- $T_g$  relaxations are apparent for PPB.

A weak relaxation has also been observed near 300 K (not shown). This relaxation is not observed in either pure component, but increases in intensity with increasing PPB content in the mixed system. There are two explanations for the relaxation: it is due to retained solvent or it is due to an anomalous  $\beta'$  relaxation that has been observed in oriented (stressed) PC<sup>25–27</sup>. In the latter case, it was found that freshly moulded PC, as well as oriented PC, exhibited a weak relaxation below  $T_g$  (323–373 K, depending on the degree of orientation). This relaxation was not characteristic of PC in its equilibrium state because it could be eliminated by thermal annealing above  $T_g$ . It could be possible that in creating the PPB-PC solid solution, the  $\beta'$  relaxation was induced.

We, however, favour the former explanation for the

observed relaxation. The intensity of the relaxation increases with increased PPB content but is too low in temperature to be associated with the  $T_g$  of pure PPB. If the relaxation were associated with pure PC or a PPB-PC complex, the intensity of the relaxation would be expected to go through, at best, a maximum where the PPB-PC ratio is maximized as a function of monomer molar composition. Furthermore, annealing the samples at low temperatures does not eliminate the relaxation. Additionally, if the relaxation were associated with stressed PC caused by casting the solid solution, it would be expected to be observed in the bisphenol-A diphenyl carbonate-PC relaxation spectrum and it is not. Conversely, a strong interaction between PPB and  $\text{CH}_2\text{Cl}_2$  was already demonstrated. If the relaxation is associated with an interactive complex, it would be expected to increase with PPB concentration. This is, in fact, the case. Also, a heat-quench cycle would be expected to strain the sample and produce the  $\beta'$  relaxation, but it has been shown above that this is not so. We therefore conclude that the weak relaxation near 300 K is associated with a  $\text{CH}_2\text{Cl}_2$ -PPB complex. Since thermally cycled samples do not exhibit a measurable dielectric increment associated with the relaxation, the concentration of the species must be smaller than those calculated earlier.

## CONCLUSIONS

The dielectric relaxation spectra of PPB-PC solid solutions have been studied as a function of composition. The glass transition of these mixed systems varies monotonically with composition. Analysis of the apparent activation at  $T_g$  shows it to be composition dependent up to 50 vol% small molecules and composition independent above this composition. The data indicate that the small molecule has a greater effect on the  $T_g$  reorientation process of the PC than vice versa. The activation energy dependence on composition is discussed in terms of the fundamental WLF parameters. From 0 to 50% small molecules dynamic behaviour is as expected; increasing small molecule concentration decreases  $T_g$  and the apparent glass transition activation energy. Above 50% small molecule, a possible  $T_g$  dependence of some of the WLF parameters is obtained. Line-shape analysis of the glass transition provided no information on the molecular dispersion. The system is compared to solid solutions of bisphenol-A diphenyl carbonate-PC which exhibits similar glass transition effects.

The sub- $T_g$  relaxations of this system indicate little, if any, small molecule-polymer interactions. It is shown

that the addition of PPB eliminates the  $\beta$  relaxation of PC and reduces the  $\gamma$  relaxation intensity. In the former case, the disappearance of the  $\beta$  relaxation is correlated with a change to composition independence in the apparent activation of the glass transition. The latter case is correlated with a dilution effect.

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