Conclusions

Copolymers of styrene with pClS exhibit relaxation spectra, due to cooperative main-chain rotation above their T_g's, of widths characteristic of many flexible chain polymers and glass-forming liquids. Cole–Cole circular arc parameters do not change with composition but there is a slight increase in dipole correlation parameters (Kirkwood "g") with decreasing chlorostyrene content.

On blending copolymers of compositions (58.5–67.8% pClS) with PPO very broad relaxation spectra are obtained. In general this is interpreted as arising from a range of local environments differing in concentration. The range of local concentrations required to cause this spectral broadening is evaluated and model calculations then give good agreement with experimental results. In addition to the broadening, a characteristic higher second peak or shoulder is observed in phase-separated systems. This is interpreted as a Maxwell–Wagner–Sillars process. In the copolymer of critical composition (67.1% pClS) this second peak and the overall breadth are dependent on thermal history. The inference is that an upper consolute temperature (~180 °C) exists for this particular copolymer blend. Fast cooling from above this temperature produces less well defined phase structure.

The locus of maximum dielectric loss is linear against log frequency for the copolymers alone and the compatible blend, but curvature results in the case of incompatible blends. This is primarily due to the presence of the high frequency overlapping dispersion region.

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Dielectric Relaxation Studies of Bisphenol A–Diphenyl Carbonate/Lexan Polycarbonate Solid Solutions

John M. Pochan,* Harry W. Gibson, Michael F. Froix, and DarLyn F. Hinman

Xerox Corporation, Webster, New York 14580. *Received June 27, 1977*

ABSTRACT: The T_g and sub-T_g relaxations in solid solutions of Lexan polycarbonate and bisphenol A–diphenyl carbonate (MLEX) have been studied dielectrically. The T_g's of the mixed system obey the Fox equation and act as a polymer/diluent system exhibiting a single correlated motion. The $\alpha(T_g)$ relaxation appears Arrhenius activated. These apparent activation energies are composition dependent for 0 to 50 vol % MLEX and exhibit plasticization effects. Above 50% MLEX, the energies are composition independent. These results are discussed in terms of intra- and intermolecular interactions. The solid solution cannot be described as a mixture of high and low molecular weight polymers. The sub-T_g relaxations reflect the T_g analysis. The addition of either component to the other causes the β relaxation (phenylcarbonyl motion) to disappear with the γ relaxation (carbonyl motion) being a molar averaging of the γ relaxation of the pure components. The sub-T_g relaxations are uncorrelated.

The effect of plasticizers on polymer properties is industrially important and forms the subject of a variety of dynamic studies.[1-14] In these studies, various plasticizer–polymer combinations have been used, including polar polymer–nonpolar plasticizer, polar plasticizer–nonpolar polymer, etc. The studies typically show the glass-transition temperature, T_g, of the polymer to be plasticized. In some cases involving a polar plasticizer, the dynamic T_g exhibits uncorrelated structure where the relaxations of the individual components are perturbed by their counterpart.[3,5,6,11] An example is the system poly(vinyl acetate)/benzyl benzoate[3] where (1) at low plasticizer concentrations a plasticized polymer T_g occurs, (2) at low polymer concentrations an antiplasticized plasticizer T_g occurs, and (3) at intermediate compositions overlapping but independent relaxations from both components occur. Würstlin[3] proposed that at low plasticizer concentrations, the plasticizer molecules were bound to the polymer chains via dipole–dipole interactions. He further postulated that a critical composition exists where the polymer becomes completely "solvated" by the plasticizer and that above this composition relaxations due to pure plasticizer became evident. Luther and Weisel[6] and Thurn and Würstlin[5] were later

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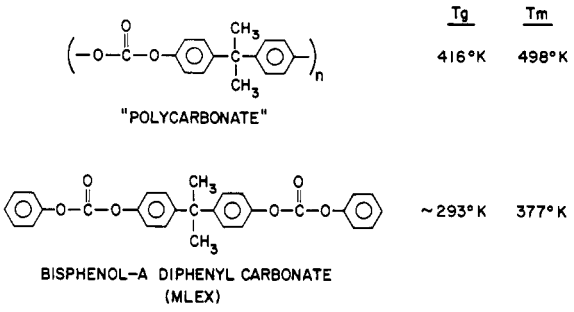

Figure 1. Chemical structures and thermal properties of the components of the studied system.

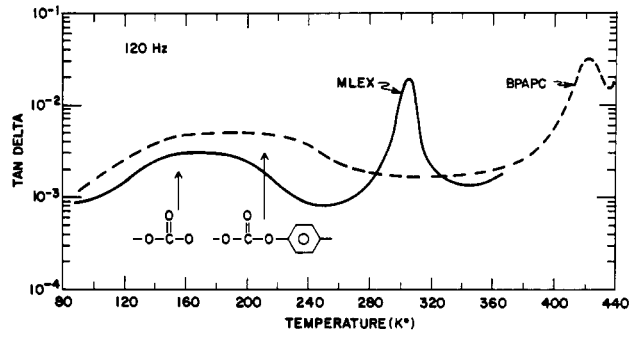

Figure 2. Tan δ vs. temperature for MLEX and BPAPC at 120 Hz.

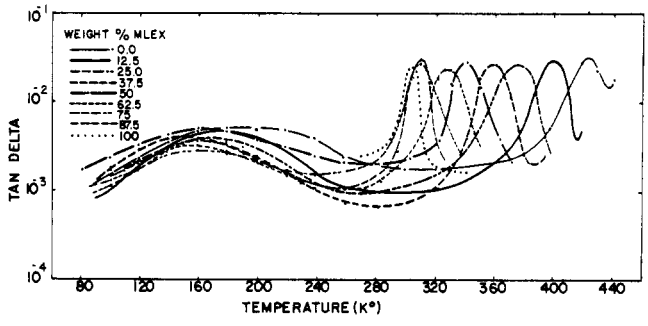

Figure 3. Tan δ vs. temperature for solid solutions of MLEX and BPAPC at 120 Hz.

able to show that the observed relaxations were due to the superposition of the two symmetric loss peaks of the pure components. These loss peaks exhibited the effect of one component on the other but did not exhibit a correlated motion. Hains and Williams[15] strengthened the argument for bound plasticizer molecules with their study on polystyrene (PS) (nonpolar)/di-*n*-butyl phthalate (polar) solid solutions.

In the previous work, the mixed system was usually studied by measuring the effect on the dynamics of the glass transition. If dipole/dipole interactions were strong enough to provide bound plasticizer molecules, it might be expected that the sub-T_g relaxations of such systems would also exhibit characteristics of the bound system. We previously showed this in solid solutions of *n*-butyl 4,5,7-trinitrofluorenone-2-carboxylate (BuTNF)/Lexan polycarbonate.[12] In that system, only a correlated β relaxation exists at intermediate composition ranges. This motion involves the entire BuTNF molecule as well as a localized motion of the combined carbonate phenyl structure of the polymer. We thought this occurred because of the strong electron-withdrawing character of the trinitrofluorenone moiety. Both the α and the γ relaxation of polycarbonate were plasticized by the monomer, with the $\alpha(T_g)$ relaxation exhibiting a noncorrelated motion (relaxations due to both components).

In the above study, a chemically dissimilar molecule was added to polycarbonate to observe its effects on the dynamics of T_g and sub-T_g relaxations of the mixed system. We now report a dielectric study on the T_g and sub-T_g relaxations of solid solutions of the structurally similar systems: bisphenol A–diphenylcarbonate and Lexan polycarbonate. The study was undertaken to ascertain differences between this system and the structurally dissimilar system discussed above.[12]

Experimental Section

The structure and thermal properties of the materials used in this study are shown in Figure 1. T_g's and T_m's were determined with a Perkin-Elmer DSC-II. The polycarbonate used was Lexan 145 (M_n = 10 580, mol wt dis = 2.5) and shall be referred to as BPAPC. The bisphenol A–diphenyl carbonate (MLEX for monomeric Lexan) synthesis is given below.[16]

To a stirred solution of 68.4 g (0.300 mol) of bisphenol A, 50 mL of pyridine, and 2000 mL of benzene, 100 g (0.637 mol) of phenyl chloroformate was added dropwise over a period of 1 h. After being stirred at room temperature for 17 h, the reaction mixture was washed with 300 mL of water and three 50-mL portions of 10% HCl. Ether (200 mL) was added and the solution was washed with 100 mL of water, two 50-mL portions of 10% NaOH, and four 100-mL portions of water. After drying with Na_2SO_4 the solution was evaporated to yield 139 g (98%) of a white solid, mp 92–104 °C. Several recrystallizations from benzene–hexane afforded a colorless solid, mp 103.0–104.0 °C (lit.[6] mp. 101–102 °C). Analysis calculated for $C_{29}H_{24}O_6$: C, 74.35; H, 5.16. Found: C, 74.71; H, 4.68. NMR ($CDCl_3$) δ 1.60 (s, 6 H, CH_3), 7.1–7.3 (18 H, arom H); IR ($CHCl_3$) 1785 cm^{-1} (C=O).

Films for dielectric studies were prepared by casting 10% (grams of solids/mL of solvent) CH_2Cl_2 solutions of the components on ballgrained aluminum. The samples were air dried and then vacuum dried (10^{-3} mmHg, 313 K) for at least 24 h. The films were approximately 10 μm thick. Gold electrodes were evaporated on the exposed surfaces of the samples and they were used in spring-loaded sample cells. Samples were isolated from the environment in a stainless steel box sealed with Teflon. Temperature calibration was done with a thermocouple mounted within a centimeter of the sample and was accurate to ±2 K.

Two dielectric apparati were used in these studies: a scanning dielectric device described previously[12,17] and a General Radio 1615-A capacitance bridge with standard accessories. The former system permits continuous acquisition at variable scanning rates of dielectric data from liquid-nitrogen temperature to ~473 K. Program rate for these experiments was 0.9 K/min. The latter instrument was used to obtain data for line shape studies and transition map plots.

DSC scans of all samples indicated only one glass transition which did not change within the time frame of our experiment (1–2 weeks) and our limits of error (±2 K). At compositions greater than 50 wt % MLEX, very small endotherms due to crystalline MLEX were observed. Once melted, these endotherms did not reappear within our experimental time frame. Within the limits of error of our measurements, T_g was not shifted by melting these minute crystallites. These data indicate stable solid solutions.

Results and Discussion

Shown in Figure 2 are tan δ vs. temperature for pure MLEX and BPAPC. The α(420 K), β(~220 K), and γ(~160 K) relaxations are shown for the BPAPC. Combined dielectric,[18–20] mechanical,[21–23] and NMR[24,25] studies indicate that α is a microbrownian motion associated with the glass transition, β is a combined phenyl ring carbonyl motion, and γ is a carbonyl motion. These are indicated in Figure 2. The curve for MLEX indicates three apparent relaxations also: the α(~300 K), the β(~190 K), and the γ(~160 K). We assign the α to the glass transition as calorimetric data taken on a DSC-II indicate a second-order relaxation in this temperature region. By analogy with BPAPC the β and γ are assigned motions similar to those in the polymer. With the β relaxation occurring in MLEX at a slightly lower temperature than that of the polymer, it would appear that the molecular constraints in the polymer create intramolecular potentials that cause the

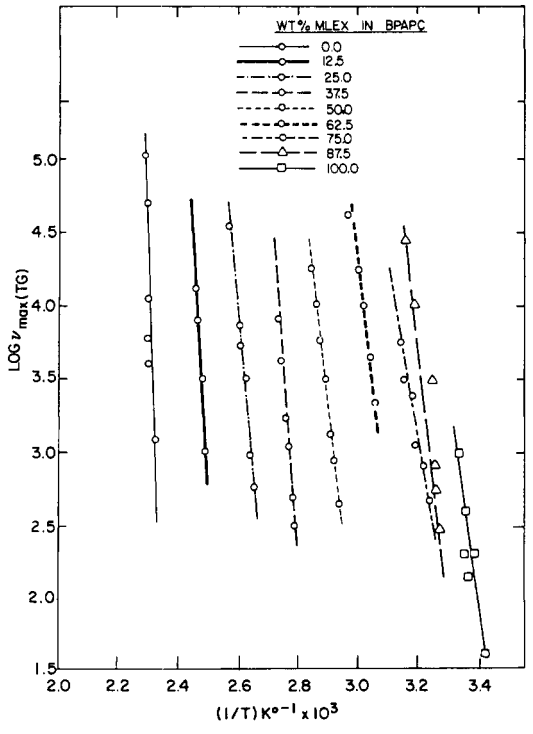

Figure 4. Log ν_{max} vs. $1/T$ (K^{-1}) for the glass transition of various mixtures of MLEX with BPAPC. Compositions are in weight percent.

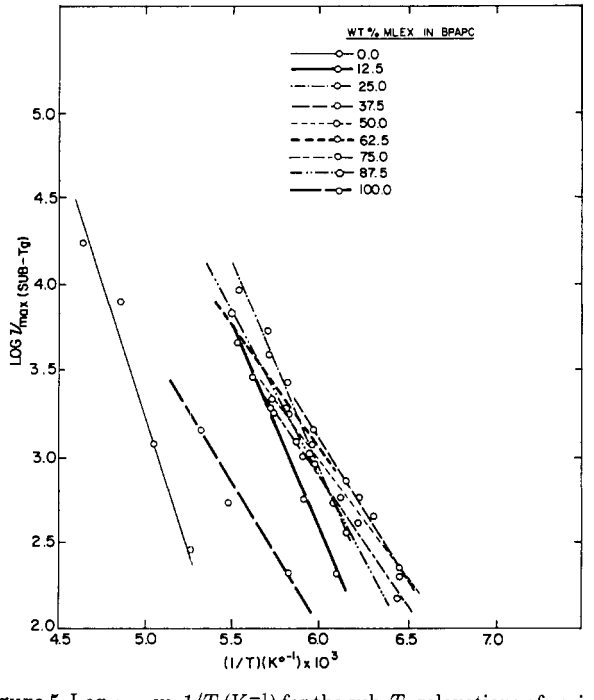

Figure 5. Log ν_{max} vs. $1/T$ (K^{-1}) for the sub-T_g relaxations of various mixtures of MLEX with BPAPC. Compositions are in weight percent.

combined phenyl carbonyl motions to occur at a higher temperature. This might be expected since the end groups in the monomer system are not constrained. Tan δ (at T_g) for the monomer system is slightly lower than that of BPAPC and this would also be expected on the basis of dipole densities which are higher in the polymer case (assuming the densities are similar).

Dielectric data for the solid solutions and pure materials are shown in Figure 3. Transition maps for the T_g and sub-T_g relaxations are shown in Figures 4 and 5 and the activation

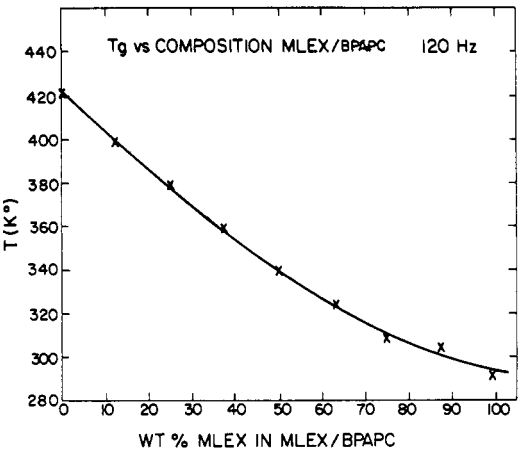

Figure 6. T_g vs. composition. T_g obtained from dielectric tan δ maximum at 120 Hz.

Table I
T_g Activation Energies (MLEX/BPAPC) [a]

Wt % MLEX	E_a, kcal/mol	Wt % MLEX	E_a, kcal/mol
0.0	200.0 ± 29.0	62.5	86.5 ± 4.6
12.5	181.4 ± 4.6	75.0	49.4 ± 4.1
25.0	116.2 ± 11.4	87.5	74.1 ± 15.1
37.5	116.2 ± 1.6	100.0	77.8 ± 17.0
50.0	72.8 ± 1.6		

[a] MLEX = bisphenol A–diphenyl carbonate.

Table II
Sub-T_g Activation Energies (MLEX/BPAPC) [a]

Wt % MLEX	E_a, kcal/mol	Possible assignment
0.0	17.7 ± 1.1	Combined β–γ
12.5	11.3 ± 0.6	Combined β–γ
25.0	11.0 ± 0.5	Combined β–γ
37.5	6.7 ± 0.5	γ
50.0	5.5 ± 1.6	γ
67.5	6.9 ± 0.5	γ
75.0	6.0 ± 0.6	γ
87.5	8.5 ± 0.5	γ
100.0	8.1 ± 0.6	γ

[a] MLEX = bisphenol A–diphenyl carbonate.

energies and assignments are listed in Tables I and II. Temperature position of T_g, as obtained from the dielectric plots, vs. composition is shown in Figure 6.

The $\alpha(T_g)$ Relaxation. In Figure 3 it is seen that only one relaxation is observed at the glass transition for the mixed system. This differs from our previous data[12] with BuTNF/BPAPC and indicates that the motions of the polymer and monomer associated with T_g occur in the same temperature region. It is seen in Figure 6 that T_g varies continuously with composition. Replotting the data in terms of volume percent of MLEX (using a density of 1.2 for the polycarbonate[26] and an estimated density of 1 for the MLEX) produces an almost identical curve and does not exhibit a break or inflection point that Kovacs[27] postulated would occur in a polymer when the WLF free volume is eliminated by the addition of a liquid.

If the system is considered a mixed polymer system, i.e., if the MLEX can be considered a low molecular weight polycarbonate, then a correlation of the obtained T_g's with the calculated M_n^{-1} would be expected. This is plotted in Figure 7 where it is seen that the curve is not continuous as expected, but consists of two intersecting straight lines. Extrapolation of these lines to infinite M_n provides different values for T_g's

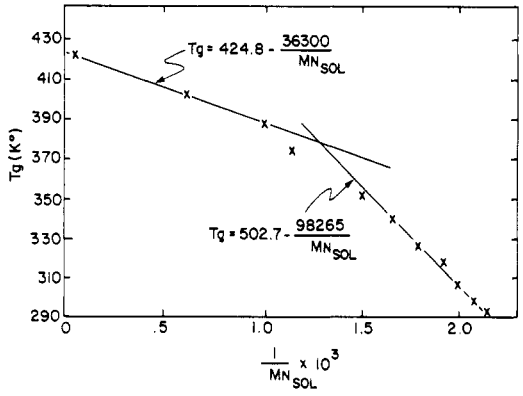

Figure 7. T_g vs. M_n^{-1} for MLEX/BPAPC mixtures.

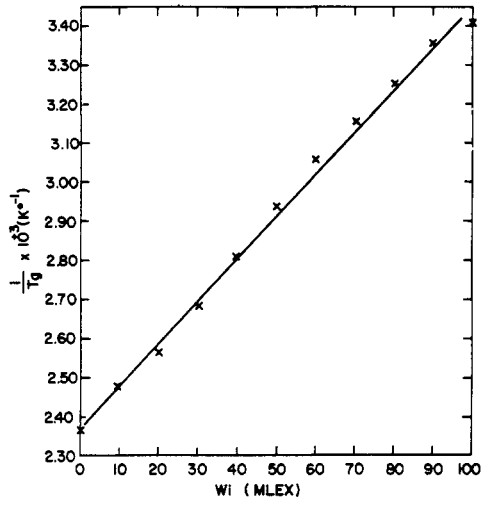

Figure 8. T_g^{-1} vs. weight fraction MLEX in MLEX/BPAPC mixtures.

of the polycarbonate, with the low percent MLEX extrapolating to the measured polycarbonate T_g value and the high percent MLEX curve extrapolating to a much higher value. These extrapolated T_g's could be an indication of differences in the high molecular weight polymer conformation in the two ranges of composition of the solid solution. The result does indicate that the mixtures cannot be considered polycarbonate mixtures since they do not obey the M_n^{-1} dependence.

The T_g composition results do obey the Fox equation

$$\frac{1}{T_g} = \frac{1}{T_{g2}} + W_1\left(\frac{1}{T_{g1}} - \frac{1}{T_{g2}}\right) \quad (1)$$

where the T_g's are of the pure components and W_i is the weight fraction of individual components. This equation assumes free volume dominance of T_g as well as free volume additivity. A plot of $1/T_g$ vs. weight fraction MLEX is shown in Figure 8. An excellent correlation of the data is obtained. We have applied the equation to a number of polymer/diluent systems with identical results[30,31] and our data indicate that the MLEX/BPAPC system can be considered a solid solution of polymer/diluent. In fact, our data are very similar to those of polystyrene plasticized by styrene and poly(methyl methacrylate) plasticized by its monomer.[32]

It is seen in Figure 4 that all the blends exhibit Arrhenius activation energies within the experimental frequency–temperature domain. This is not unlike the results obtained for other homopolymeric polycarbonates[18] and indicates that a much higher temperature (frequency) is needed to observe the WLF type relaxation curves. The apparent activation

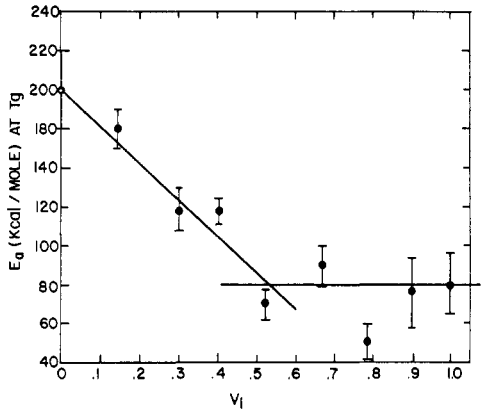

Figure 9. Arrhenius activation energy for the glass transition vs. volume fraction (V_i) MLEX for MLEX/BPAPC mixtures.

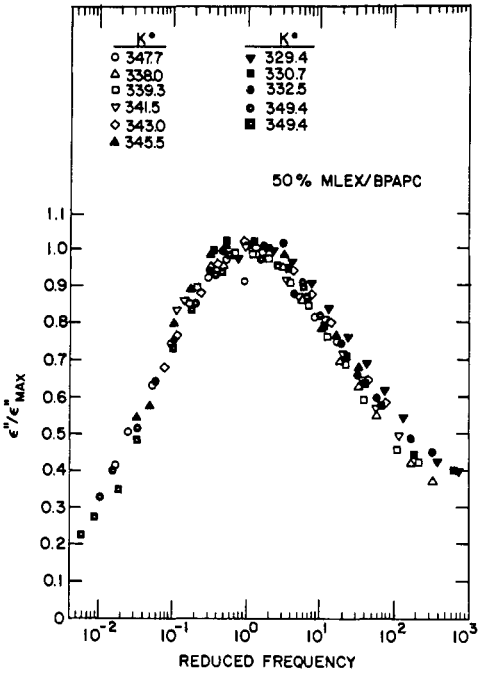

Figure 10. ($\epsilon''/\epsilon''_{max}$) vs. ($\nu/\nu_{max}$) for a 50/50 MLEX/BPAPC near the glass transition.

energies (E_a) as a function of volume fraction (Figure 9) also indicate that there are two regions of thermally activated relaxations: (1) above approximately 50 MLEX loading and (2) below this value. In the former case, the apparent activation energy is insensitive to composition (70 ± 20 kcal/mol) while in the latter case the relaxations appear plasticized in that E_a decreases with increasing MLEX composition and T_g decreases. We believe the scatter in the data is due to variations in the microscopic morphology of the systems and that even though the individual errors in the activation measurements are small, an average error of 20 kcal/mol compensates for any sample to sample variation in data.

A line shape analysis of the T_g relaxation provides insight into the molecular mechanism of the relaxation in these mixed systems. Figure 10 is a plot of reduced loss vs. reduced frequency for a 50/50 MLEX/BPAPC film. For all the temperatures studied, the curves are almost totally superimposable. All samples studied provided similar data, indicating that the T_g distribution of relaxation times for individual samples did not vary with temperature. The best fit of each composition curve is plotted in Figure 11. A single relaxation time curve

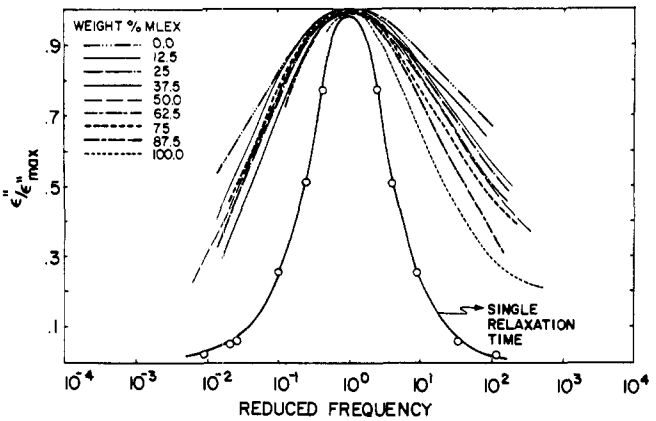

Figure 11. $(\epsilon''/\epsilon''_{max})$ vs. (ν/ν_{max}) at various compositions of MLEX/BPAPC. Continuous curve is a single relaxation time curve.

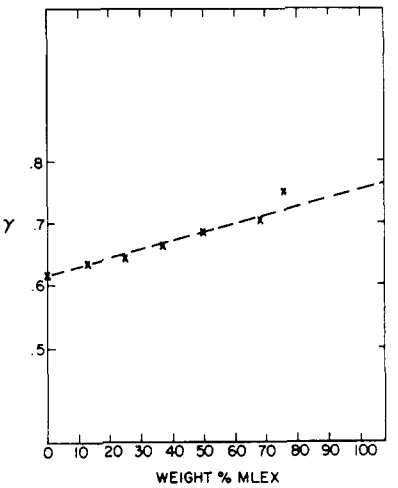

Figure 12. Cole–Davidson γ vs. composition for MLEX/BPAPC T_g.

is also included in the plot for comparison. Obviously, increasing the MLEX concentration decreases the line width, especially at higher frequencies. The skewed distribution at higher frequencies (high frequency broadening) is characteristic of many polymer systems and has been addressed theoretically by Davidson and Cole.[33] In their analysis, the frequency dependence of ϵ is given by:

$$\frac{\epsilon^*(\omega) - \epsilon_\mu}{\epsilon_r - \epsilon_\mu} = \frac{1}{(1 + i\omega\tau_1)^\gamma} \qquad (2)$$

$$0 \leq \gamma \leq 1$$

whereas the single relaxation time curve is:

$$\frac{\epsilon^*(\omega) - \epsilon_\mu}{\epsilon_r - \epsilon_\mu} = \frac{1}{1 + i\omega\tau} \qquad (3)$$

where $\epsilon^*(\omega)$ is the complex dielectric constant, ϵ_μ is the high-frequency "unrelaxed" dielectric constant, ϵ_r is the zero-frequency "relaxed" dielectric constant, ω is the angular frequency of measurement, and τ is the relaxation time associated with a given relaxation. Equation 2 is unlike eq 3 in that the maximum in the distribution of relaxation times is not at $\omega\tau = 1$ and that the Cole–Cole plot for the equation provides a curve that approaches the abscissa along a straight line. The angle between this line and the abscissa is $\gamma\pi/2$. The Davidson–Cole analysis thus provides a measure of the high-frequency "skewedness" of a relaxation, i.e., for $\gamma = 1$, a characteristic single relaxation time curve is obtained. This analysis has been done for the MLEX/BPAPC system and the results are shown in Figure 12 where it is seen that γ varies smoothly from ~0.62 for BPAPC to an extrapolated value of ~0.74 for MLEX. These results could be interpreted in terms of a single distribution of relaxation times of the correlated motion of MLEX and BPAPC at the glass transition, with the distribution becoming more liquid-like at higher MLEX concentrations. It has been shown, however, that when two or more relaxation regions overlap, relaxation curves result which can be fitted to the Davidson–Cole equation.[34] Our data have therefore been analyzed in an alternate fashion.

The reduced plot for BPAPC and MLEX was molar averaged (using eq 4) for each of the mixtures to see if the data could be matched,

$$(\epsilon''/\epsilon''_{max})_{total} = \chi_{MLEX}(\epsilon''/\epsilon''_{max})_{MLEX} + (1 - \chi_{MLEX})(\epsilon''/\epsilon''_{max})_{BPAPC} \qquad (4)$$

where χ_i is the mole fraction of each component and the values of $\epsilon''/\epsilon''_{max}$ are obtained for each component at each frequency. Within the limits of error of our measurements, the curves generated by this technique are identical to those of Figure 11. It can therefore be concluded that although empirical distributions such as the Davidson–Cole fit the experimental data, the relaxation can be explained as the overlap between two relaxations that are occurring within the limits of error at identical temperatures.

This interpretation coupled with the T_g and activation energy data provide the following molecular interpretation of the T_g of the mixtures in this system. When the low T_g material (MLEX) is added to BPAPC the glass transition of the composite shifts in a uniform manner between the T_g's of the individual components. The relaxation appears to be correlated in nature, i.e., only a single component is observed at all compositions. Line shape analysis indicates that although only one T_g is observed, the relaxation can be interpreted as an overlap of the relaxations of the pure components at identical temperatures. The activation energies do not exhibit a continuous change with composition as the T_g does, but show a significant drop in E_a when MLEX is first added to BPAC (0 → 50 vol %) and then remain relatively constant. The constituents of the mixture are chemically similar and preferential interactions of the MLEX with the BPAPC chain would not be expected. It is therefore postulated that the addition of the MLEX to BPAPC causes intra- or interchain interactions to diminish, thus lowering the effective E_a of T_g. This continues to occur until these interactions are not controlling the reorientation process at the glass transition (above 50 vol % MLEX). The interactions, then, are polymer intrachain, polymer chain/molecule, and molecule/molecule. Since the activation energy of pure MLEX and a 50/50 blend are identical, it must be considered fortuitous that the E_a's remain constant as very little intramolecular interaction would occur in the MLEX. It can therefore be reasoned that above 50 vol % MLEX composition polymer intrachain, polymer chain–MLEX and MLEX–MLEX interactions that control the reorientation process of the blends at T_a are either identical or the MLEX–MLEX interactions are the significant interaction controlling the entire matrix at T_g. The former explanation appears more plausible.

The T_g data can be considered in terms of the WLF formalism.[35] In the WLF notation, the apparent activation energy at T_g can be calculated as

$$E_a = 2.303RC_1^0C_2^0T^2/(C_2^0 + T - T_0)^2 \qquad (5)$$

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 eq 5 becomes

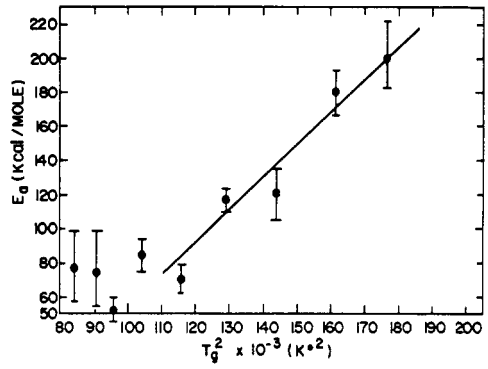

Figure 13. Apparent activation energy for T_g vs. T_g^2 for MLEX/BPAPC mixtures.

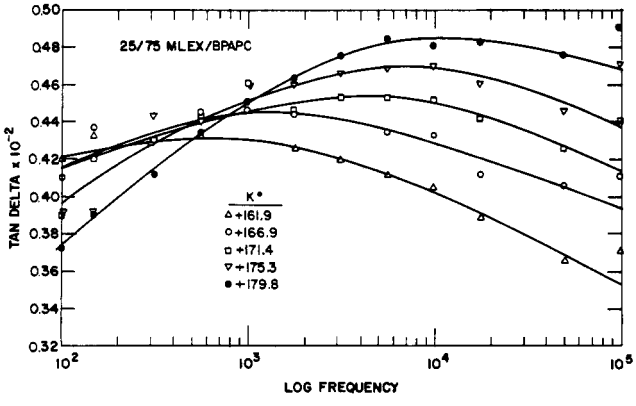

Figure 14. Tan δ vs. log frequency at low temperatures for a 25/75 MLEX/BPAPC (weight percent) film.

$$E_a = 2.303RC_1{}^gT_g{}^2/C_2{}^g \simeq RT_g{}^2\alpha_f/f_g{}^2 \quad (6)$$

where f_g is the fractional free volume at T_g and α_f is the coefficient of expansion of f. Equation 6 predicts a linear relationship between E_a and $T_g{}^2$. If it is assumed that the dielectric measurements provide E_a values at equilibrium, then values of E_a vs. $T_g{}^2$ can be plotted. As is seen in Figure 13, a linear relationship is obtained in the 0 to 50% MLEX range. The slope is $\sim(2.1 \pm 0.3) \times 10^{-3}$ kcal mol^{-1} K^{-2}, which means that the ratio

$$\alpha_f/f_g{}^2 = 2.1 \times 10^{-3}/R \simeq 1 \text{ K}^{-1} \quad (7)$$

and is composition independent from 0 to 50% MLEX. Whether α_f and f_g remain constant cannot be determined, but it can be concluded that the compositional variation does not affect their ratio. The value of 1 K^{-1} for $\alpha_f/f_g{}^2$ is reasonable in terms of measured values for coefficients of expansion and calculated values of f_g.[35]

If the E_a's are considered in the 50 to 100% MLEX range, the plot of E_a vs. $T_g{}^2$ has essentially zero slope, implying that if the WLF formalism holds,

$$RT_g{}^2\alpha_f/f_g{}^2 = \text{constant or } T_g{}^2 = Kf_g{}^2/\alpha_f \quad (8)$$

Because of the experimental error involved in the measurement of $E_a(T_g)$, it is difficult to verify or disclaim a T_g dependence of either f_g or α_f. The ratio of $T_g{}^2$ (100% MLEX) to $T_g{}^2$ (50% MLEX) is only 1.37 and a change of only 17% in f_g would be required for this change.

At this time, it is sufficient to note that when the monomeric compound becomes the matrix, the E_a becomes composition independent.

The Sub-T_g Relaxations. An example of the sub-T_g relaxations is shown in Figure 14. It is seen that the intensity of the relaxation increases with increasing temperature. A plot

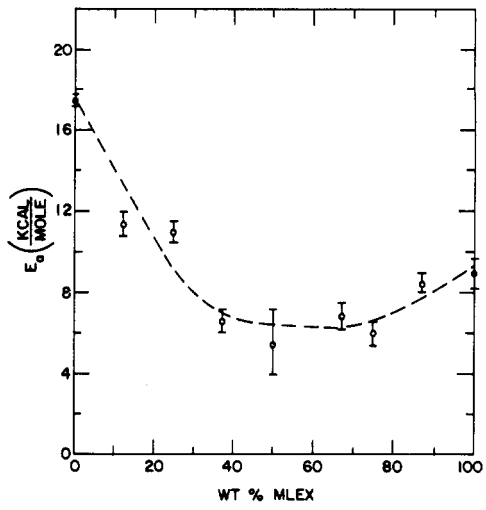

Figure 15. Sub-T_g activation energy vs. composition for MLEX/BPAPC mixtures.

of reduced dielectric loss vs. reduced frequency indicates, however, that the distribution of relaxation times is not changing. The data are similar to that of Ishida and Matsuoka for the β relaxation in amorphous BPAPC.[20]

The data in Figures 2 and 3 for the sub-T_g relaxations in the solid solutions indicate that the β relaxation in BPAPC is eliminated (either plasticized or disappears) or merges with the γ relaxation with the addition of MLEX. At 37.5% MLEX, the low-temperature relaxation spectra is symmetric and has been assigned to the γ (carbonyl motion) relaxation (see Table II). Once the β relaxation is eliminated, the γ relaxations for the blends occur in identical temperature–frequency regimes (see Figure 5). The activation energies as a function of composition are shown in Figure 15 and Table II. The activation energy data indicate that the combined β–γ relaxation appears to shift to lower temperature (this is probably due to the decreased intensity of the β relaxation). Once the β relaxation is eliminated, the γ relaxation provides activation energies almost identical to those obtained by Aoki and Brittain[36] for the γ relaxation via thermally stimulated discharge measurements in BPAPC. The β, γ, and δ relaxations in BPAPC have been assigned to combined phenyl ring carbonyl motions, carbonyl motions, and methyl group rotations, respectively. The δ is not dielectrically active and thus eliminating the β relaxation should provide activation energies similar to those obtained elsewhere. It appears that the activation energies for the carbonyl motion in MLEX and BPAPC are almost identical in that there is little change in the activation energy with composition between 37.5 and 75.0% MLEX. Above 75% MLEX the activation energy again rises to ~8.5 kcal/mol. This is taken as an indication that the β relaxation for MLEX becomes active within this narrow composition range. It thus appears that the β relaxation in both constituents is easily affected by the alternate constituent. The combined phenyl ring carbonyl motion is thus easily plasticized or affected by additional components, whereas the carbonyl motion in both components is basically identical and not affected by molecular weight. The observed relaxations thus appear to be an average of the two pure materials with the β relaxation eliminated from MLEX or BPAPC by the addition of the other component.

In comparing the T_g and sub-T_g data, it is apparent that $E_a(T_g)$ becomes compositionally independent (>37.5% MLEX) at the same composition that the β relaxation is no longer observed. This implies that the phenyl carbonyl motion or structure is important in determining the potential fields controlling the glass transition of the mixed system up to

37.5% MLEX. Above this composition, other forces, which appear to be composition independent, control T_g. It appears from these data that chain conformations control the glass transition activation energies at low MLEX loadings, and that these forces are reduced, or eliminated, at high MLEX concentrations.

In Summary. The dielectric relaxations of solid solutions of bisphenol A-diphenyl carbonate (MLEX)/Lexan polycarbonate (BPAPC) have been studied as a function of composition. The T_g of the solutions is a continuous function of composition indicating no loss of "excess" free volume upon the addition of the MLEX to BPAPC. The T_g data have been interpreted in terms of a free volume additivity equation used to explain many polymer/diluent systems. Although a single relaxation distribution is observed for the glass transition, indicating possible correlated polymer/small molecule motions, the data can be interpretated in terms of a molar averaging of the individual relaxations occurring at identical temperatures. The T_g's are Arrhenius activated and exhibit composition independence above 50 vol % MLEX. Below this value the apparent activation energies exhibit plasticization effects. The activation energies indicate that MLEX has a greater effect on the energies involved in the BPAPC reorientations at T_g than vice versa. This effect is explained in terms of the removal of localized motion in the polymer and its effect on intra- and interchain interactions as well as polymer–molecule interactions.

The sub-T_g relaxations reflect the T_g relaxation analysis. MLEX and BPAPC exhibit similar molecular relaxations: $T_g(\alpha)$, combined phenyl ring carbonyl motion (β), and carbonyl motion (γ). The addition of MLEX to BPAPC or BPAPC to MLEX causes the β relaxation to disappear and at intermediate compositions the relaxations appear to be a molar averaging of the γ relaxations of the pure components and are thus uncorrelated. The activation energies for these relaxations reflect this behavior.

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Pyroelectricity in Polymer Blends of Poly(vinylidene fluoride)

H. Lee, R. E. Salomon, and M. M. Labes*

Department of Chemistry, Temple University, Philadelphia, Pennsylvania 19122.

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ABSTRACT: Polymer blends of poly(vinylidene fluoride) with both poly(methyl methacrylate) and poly(vinyl fluoride) were prepared and evaluated for pyroelectric activity. Percent crystallinity and extent of α, β, γ, and amorphous phases were evaluated by both x-ray diffraction and infrared spectroscopy. The correlations observed are supportive of a dipole-reorientation model for pyroelectricity.

Pyro- and piezoelectricity in poly(vinylidene fluoride) (PVF_2) are thought to be due to the existence of an oriented dipolar structure induced by "poling" polymer films in a high dc field ("dipole-reorientation" model),[1-5] or to the existence of a nonhomogeneous space charge distribution ("space-charge" model),[6-10] or both phenomena superimposed.[11,12] The purpose of this study was to vary the crystallinity and phases of PVF_2 by blending it with poly(vinyl fluoride) (PVF) and poly(methyl methacrylate) (PMMA) and attempt to correlate pyroelectric behavior with the extent of crystalline phase present. If such a correlation exists, it would be hard to rationalize it in terms of a space-charge model, i.e., further credence would be added to the dipole-reorientation model.

Morphological studies[13-19] have shown that there are three crystalline forms of PVF_2. The α form (form II) has the trans-gauche-trans-gauche' configuration[16] and the β form (form I) has the planar zigzag conformation.[19] The structure of the γ form (form III) is not established. However, there are

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