Communications to the Editor

Dielectric Behavior of a Polycarbonate/Polyester Mixture upon Transesterification

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Dielectric relaxation spectroscopy provides a sensitive measure of the local environment surrounding molecular dipoles.[1] In the examination of polymers, it is customary to record the complex dielectric constant $\epsilon^*(\nu) = \epsilon'(\nu) + i\epsilon''(\nu)$ as a function of frequency ν. The form of the spectra can often be related to aspects of specimen structure. For example, the distribution of local environments that arise due to concentration fluctuations in polymer blends[2] and diblock copolymers[3] has been characterized using this technique. Further information concerning the dipolar magnitude as well as local geometric constraints can also be obtained through accurate measurement of the dielectric dispersion magnitude $\Delta\epsilon = \epsilon'(0) - \epsilon'(\infty)$. Studies which measure $\Delta\epsilon$ for polymers[1,4] are less common due to the broadness of polymer relaxations and the limited spectral range of most dielectric spectrometers. Using suitable instrumentation, however, $\Delta\epsilon$ can be measured and interpreted. In this paper, we describe significant changes to the dielectric behavior in mixtures of polycarbonate and an amorphous polyester copolymer as the specimens are annealed at different temperatures. The variations in $\Delta\epsilon$ are related to structural changes which are a result of transesterification and phase separation processes.

Transesterification has been discussed in a recent review.[5] The interplay between the transesterification and phase separation has been examined by Yoon et al.[6] They used small-angle neutron scattering (SANS) to demonstrate that a mixture of polycarbonate and a polyester copolymer became homogeneous as the specimen transesterified to form random copolymers at temperatures above 220 °C, while phase separation dominated at lower temperatures (160 °C < T < 180 °C). In addition, successive cycles of transesterification followed by phase separation were possible as long as the transesterification was only partially complete. In the current study, the same materials as those in Yoon et al. are used,[6] and the structural information obtained from their scattering experiments is used to interpret our results.

Specifically, Bisphenol A polycarbonate (PC) with M_w = 20 000−25 000 (Aldrich Chemical Co.)[7] and poly(oxymethylene-1,4-cyclohexylenemethyleneoxyterphthaloyl)$_x$-*co*-(oxyethyleneoxyterephthaloyl)$_y$ (PET−PCHT) polyester copolymer with x:y = 64:36 (Eastman Chemical Co.) were utilized in the study described herein. A 1:1 mixture by weight was dissolved in dichloromethane, precipitated in methanol, and then dried in a vacuum oven at 70 °C for several days. Thin films between 0.2 and 0.3 mm were formed by melt pressing between Kapton polyimide sheets at 160 °C and then placing them between 3.6-cm-diameter copper plates. Subsequent annealing near 160 or 220 °C was performed in a vacuum oven.

The dielectric measurements were performed with a precision time-domain spectrometer developed and built at NIST.[8] The device accurately measures the charge response of the specimen to a 100-V step pulse over a period of 10 μs to 2900 s. A Laplace transform of the data into the frequency domain yields the complex capacitance function $C^*(\nu) = C'(\nu) + iC''(\nu)$ where the accessible frequency ν ranges between 10^{-4} and 10^4 Hz. The specimen temperature, T, was controlled within 0.03 °C using an oven. $C^*(\nu)$ is converted to $\epsilon^*(\nu)$ using the formula $\epsilon^*(\nu) = \epsilon_{\mathrm{ref}}C^*(\nu)/C'(\infty)$, where $C'(\infty)$ is the extrapolated high-frequency capacitance and ϵ_{ref} is a reference permittivity. Using the two-fluid method at 22 °C with $\nu = 1$ kHz,[9] ϵ_{ref} was measured to be 3.0, 3.4, and 3.2 for the pure PC, pure polyester, and unannealed 1:1 mixtures, respectively. For the given measurement conditions, ϵ_{ref} corresponds to a permittivity within the β-relaxation. Consequently, the fractional error in our measurements is given by $\Delta\epsilon_\beta/\epsilon_{\mathrm{ref}}$, where $\Delta\epsilon_\beta$ is the dispersion strength of the β-relaxation. Using literature values for $\Delta\epsilon_\beta$,[1,4] the uncertainty is estimated to be ±6%.

Several loss spectra of the α-relaxation for the unannealed 1:1 specimen taken at different temperatures are plotted in Figure 1. For each scan the frequency of maximum loss, $\nu_{\max}$, was determined by spline interpolation. The temperature dependencies of $\nu_{\max}$ are shown in Figure 2. For all of the specimens examined, $\nu_{\max}(T)$ follows the Williams−Landel−Ferry form[10] expected near a glass transition. For the unannealed mixture, the $\nu_{\max}$ data fall in the range of 80−110 °C, a range slightly greater than that for pure polyester. Upon annealing at 220 °C for 2 h, this range shifts to higher temperatures (110−130 °C) such that the spectra are nearly halfway in between the values for the pure PC and polyester components. Finally, with further annealing at 156 °C, the $\nu_{\max}$ data shift to lower temperatures by about 4 °C.

We have estimated T_g from the dielectric measurements as the temperature corresponding to $\nu_{\max}(T_g)$ = 0.1 Hz. As shown in Table 1, the T_g's determined by dielectric spectroscopy are consistent with those from differential scanning calorimetry (DSC) using a ramp rate of 10 °C/min. Using DSC, we observed two T_g's for the unannealed 1:1 specimen which are close to those for the pure polyester and PC components. With the dielectric measurement, however, we see only a single T_g near that for the pure polyester. We expect a second T_g arising from PC should also exist. However, it is most likely masked by the large conductivity at elevated temperatures arising from residual catalyst in the polyester fraction.

Upon annealing, there are dramatic changes to the dielectric dispersion magnitude, as shown by several representative plots of $\epsilon''(\nu)$ vs $\epsilon'(\nu)$ in Figure 3. For convenience, a Havriliak−Negami expression[11] with a

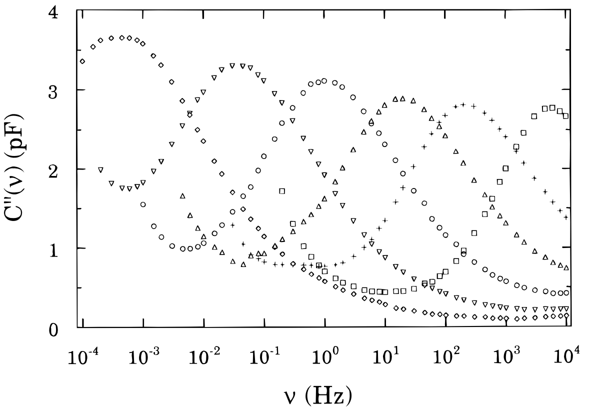

Figure 1. Loss spectra for the unannealed 1:1 specimen. The spectra were measured at 79.6 (◇), 84.6 (▽), 89.6 (○), 94.5 (△), 99.6 (+), and 109.6 °C (□). The experimental errors are in all cases less than the symbol sizes.

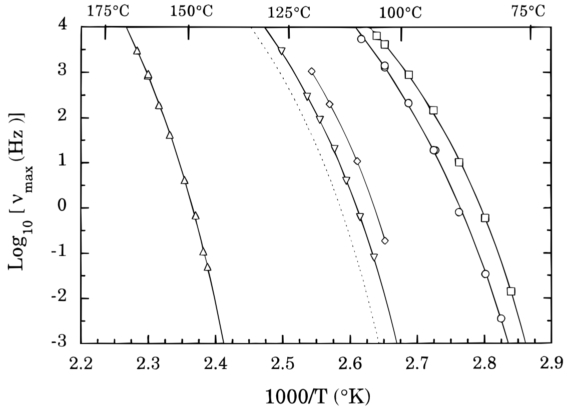

Figure 2. Plot of ν_{max} vs $1/T$ (K) for pure polycarbonate (△), pure polyester (□), a 1:1 mixture melt pressed (○), a 1:1 mixture after annealing for nearly 2 h at 220 °C (▽), and a 1:1 mixture after 15 h of annealing at 156 °C (◇). The solid lines are fits to the Williams−Landel−Ferry (WLF) expression,[10] while the dotted line represents the average of the WLF fits to the pure components.

Table 1. Glass Transition Temperatures (°C) As Determined by DSC and from the Temperature Where the Dielectric Loss Maximum Is at ν_{max} = 0.1 Hz

specimen	% PC/% polyester	T_g(DSC)	T_g(dielectric)	$\Delta\epsilon^0$
polycarbonate	100/0	145 ± 1	147 ± 1	0.47 ± 0.02
unannealed mixture	50/50	85 ± 1 131 ± 2	86 ± 1	0.30 ± 0.03
+2 h at 220 °C	50/50	106 ± 1	107 ± 1	0.67 ± 0.02
+15 h at 156 °C	50/50		103 ± 1	0.56 ± 0.02
polyester	0/100	82 ± 1	82 ± 1	1.07 ± 0.02

conductivity term

$$\epsilon^*(\nu) = \epsilon(\infty) + \frac{\Delta\epsilon}{[1 + (2\pi i\nu\tau)^{\alpha}]^{\gamma}} + \frac{i\sigma_0}{2\pi\nu} \tag{1}$$

was used to describe the data, where $\Delta\epsilon = \epsilon'(0) - \epsilon'(\infty)$ is the dispersion magnitude, τ is the relaxation time, σ_0 is the conductivity, and the exponents α and γ are representative of the broadening and asymmetry of the loss curve, respectively. While good fits were obtained using a Marquardt least-squares algorithm,[12] there were systematic deviations of the data from eq 1. Therefore, the fits were used to visually estimate $\Delta\epsilon$ and its uncertainty. In order to interpret the changes in $\Delta\epsilon$, we have assumed that $\Delta\epsilon$ scales inversely with temperature in our measurement range[13] and normalized values defined by $\Delta\epsilon^0 = T\Delta\epsilon/T^0$ where T^0 = 390 K are reported in Table 1.

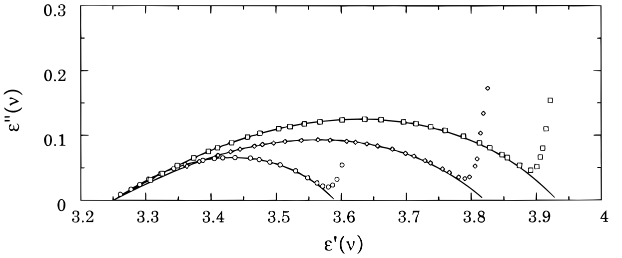

Figure 3. Cole−Cole plots for 1:1 mixtures of polycarbonate and polyester for the specimens measured at 89.6 °C (○), annealed for 2 h at 220 °C and measured at 115.4 °C (□), and further annealed for 15 h at 156 °C and measured at 116.6 °C (◇). The solid lines are the fits to eq 1. Note the sharp increase in $\Delta\epsilon$ upon annealing at 220 °C and the slight decrease upon further annealing at 156 °C.

Upon annealing at 220 °C, $\Delta\epsilon^0$ increases sharply from 0.30 to 0.67. Then, upon further annealing at 156 °C, $\Delta\epsilon^0$ decreases to 0.56. Throughout our experiments, the exponents α and γ are essentially unmodified by these annealing treatments and remained close to α = 0.5 ± 0.1 and γ = 0.7 ± 0.1 for each of the three data sets considered here. These values of α and γ are typical of the broad relaxations observed for polymers.[11]

Both calorimetric and dielectric determinations of T_g provide an assessment of specimen homogeneity. As noted above, the results for the unannealed 1:1 mixture are very close to those for the pure components. This implies that the specimen consists of polyester-rich and PC-rich domains, and, in the dielectric measurement, the local environment of the relaxing polyester segments is predominately polyester. Indeed, previous investigations by time-dependent studies of phase separation using SANS,[6] light microscopy, and NMR[13] all indicate that phase separation is present in the unannealed mixture. Yet, in the unannealed mixture, the T_g's are not equal to the pure component values: the lower T_g is 3 °C greater than that for pure polyester and the larger T_g is about 15 °C less than that for pure PC. This suggests that there is mixing within the domains. The mass fraction w_a of component a may be estimated by rewriting the Fox equation[14] as

$$w_a = \frac{T_{a,0}(T_a - T_{b,0})}{T_a(T_{a,0} - T_{b,0})} \tag{2}$$

where T_a is the T_g observed in the mixture for the phase rich in component a and $T_{a,0}$ and $T_{b,0}$ are the pure component values. According to eq 2, the PC-rich domains contain 19% polyester, while the polyester-rich domains contain 5% PC. From this, the total mass fraction of the polyester-rich domains is computed to be 41%. This preferential solubility of polyester in polycarbonate was also observed by of Kim and Burns.[15]

For the unannealed mixture, the measured dispersion magnitude of $\Delta\epsilon^0$ = 0.30 is about 25% of the pure PET−PCHT value of $\Delta\epsilon^0$ = 1.07.[16] Since the dispersion is due only to the polyester dipoles within the polyester-rich domains, estimated as 39% of the total mass, a value of $\Delta\epsilon^0$ = 1.07 × 39% = 0.42 is calculated. Even though this exceeds the measured values by 40%, the solubility of polyester in PC partially accounts for the differences in the dispersions of pure polyester and unannealed mixture. In addition, it is possible that the small fraction of less mobile polycarbonate within the polyester-rich domains hinders the motion of neighboring polyester segments, thereby limiting the ability of the polyester dipoles to fully relax. From our measurements alone, however, it is difficult to further describe this effect.

Upon annealing at 220 °C for 2 h, the changes in T_g and the near doubling of $\Delta\epsilon^0$ suggest significant structural changes. The resulting T_g, which is in between those of the pure components, indicates a large degree of mixing. Therefore, it appears that transesterification leading to random copolymers has occurred. This is also consistent with the previously noted decrease in scattered neutron intensity in the earlier SANS measurements.[6] The increase of $\Delta\epsilon^0$ to 0.67 upon annealing at 220 °C implies that either the number or the strength of the relaxing dipoles has increased. In fact, this is close to the average value of 0.77 one might expect for a 1:1 mixture of the pure polyester and PC components which have $\Delta\epsilon^0 = 1.07$ and $\Delta\epsilon^0 = 0.47$, respectively. For the 1:1 mixture, the maximum value from a contribution of polyester dipoles only is $\Delta\epsilon^0 = 1.07 \times 50\% = 0.535$. Since this is less than the observed value of $\Delta\epsilon^0 = 0.67$, there must be an additional contribution from the polycarbonate segmental dipoles.

Upon further annealing for 15 h at 156 °C, $\Delta\epsilon$ decreases slightly to 0.56 and the single T_g falls by about 4 °C. In the earlier SANS study,[6] the scattering increased when the transesterified specimen was further annealed at lower temperatures, indicating a heterogeneous phase structure. This is the direct opposite of what happens from annealing at 220 °C, which results in homogeneity. Consequently, this suggests that the decrease in both T_g and $\Delta\epsilon$ corresponds to an increase in heterogeneity and also demonstrates that the transesterification is not complete. This is in accord with the temperature cycling experiments of Yoon et al.[6] which demonstrate incomplete transesterification.

In summary, large changes in $\Delta\epsilon$ of PC/polyester mixtures are observed upon transesterification. Our measurements of $\Delta\epsilon$ permit a more comprehensive interpretation of specimen homogeneity than from a determination of T_g alone. In combination with the structural information from SANS,[6] our results yield a consistent physical picture where $\Delta\epsilon$ increases or decreases as the phase structure becomes homogeneous or heterogeneous, respectively. Thus, the dielectric response can be used to characterize different phase morphologies. Further investigations of different mixture compositions are in progress.[16]

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