Modeling Intercomponent Mixing Effects in Rubber-Modified Glassy Polymers

RALPH E. TAYLOR-SMITH* and RICHARD A. REGISTER†

Department of Chemical Engineering, Princeton University, Princeton, New Jersey 08544

SYNOPSIS

A phenomenological model is presented to assess the effects of phase mixing on storage modulus vs. temperature data in polymer blends comprising a continuous glassy matrix and discrete rubbery inclusions. An extension of the Kerner–Dickie model, it is developed for systems of low-dispersed phase content with a moderate degree of intermixing, and compared with experimental data for six blends of polystyrene or lightly hydroxylated polystyrene with poly(ethyl acrylate) at 90/10 and 70/30 w/w compositions. Phase mixing is induced in this system through intercomponent hydrogen bonding. The model successfully represents data for the four blends of lowest interphase content, but fails for the other two. The model can evidently provide a good description of blends where the bulk of each component resides in a pure phase, but fails when the mixed interphase constitutes the majority of the material. © 1995 John Wiley & Sons, Inc.

INTRODUCTION

Isochronal linear viscoelastic properties have been successfully represented for numerous multiphase polymer systems, using a variety of conceptually simple mechanical models.[1-4] With appropriate modifications, such models can also represent data from block copolymers or polymer blends where some degree of phase mixing exists.[5-10] Cohen and Ramos[5] studied binary and ternary blends of an isoprene–butadiene diblock copolymer with either or both of the corresponding homopolymers. They found that data from dynamic mechanical thermal analysis (DMTA) could be well represented by a form of the Takayanagi model.[1] For the ternary blend case, model predictions proved very sensitive to the location of the diblock copolymer in the system, providing a tool to assess the compatibilizing activity of such copolymers. Diamant et al.[6] used an extension of the Nielsen model[2] to characterize the interphase in styrene–butadiene–styrene triblock

copolymers, prepared by casting from a variety of solvents. Their modeling results provided detailed information concerning the effect of solvent type on the volume fraction of mixed material, or interphase, and the composition profile across the interphase. In a similar vein, Annighöfer and Gronski[7] modeled DMTA data from specially designed triblock copolymers, where the endblocks were styrene and isoprene and the midblock was a random styrene–isoprene copolymer of variable length. Phase mixing between the styrene and isoprene endblocks was modified by controlling the length of the midblock. The interfacial thickness extracted from DMTA modeling agreed well with independent experimental determinations via small-angle X-ray scattering and densitometric transmission electron microscopy.[8]

Recently, we have used a modification[9] of the Takayanagi model[1,10] to represent data from 50/50 w/w blends of polystyrene, PS, and poly(ethyl acrylate), PEA. The extent of mixing between components was adjusted by introducing variable levels of phenolic hydroxyl groups onto the polystyrene chains, yielding lightly hydroxylated polystyrene (HPS). The model gave a very satisfactory representation of DMTA data, namely, storage modulus E' and loss tangent tan δ vs. temperature. For sys-
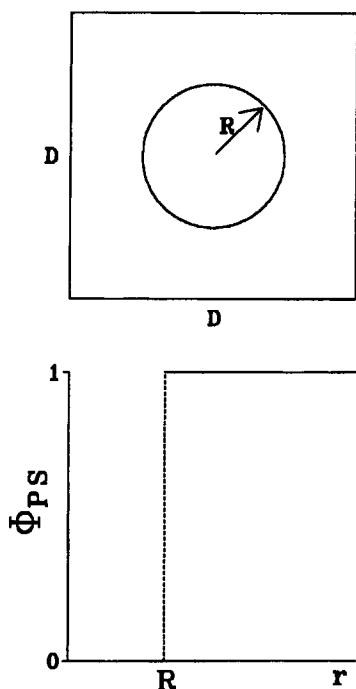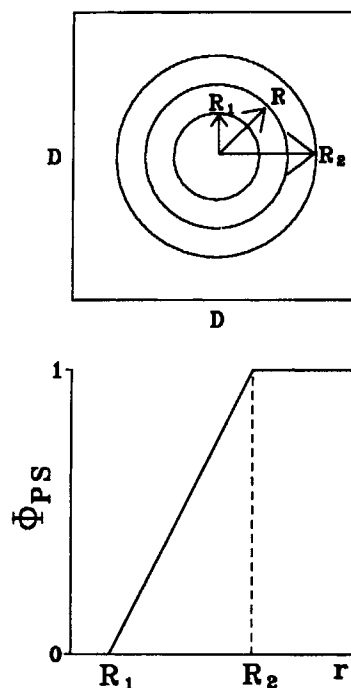

Figure 1 Schematic of the microstructure represented by the original Kerner–Dickie model, where, in our case, the matrix is PS. Top sketch illustrates a cross-section of the system morphology; bottom sketch maps the normalized PS segment concentration (Φ_{PS}) over the cross-section.
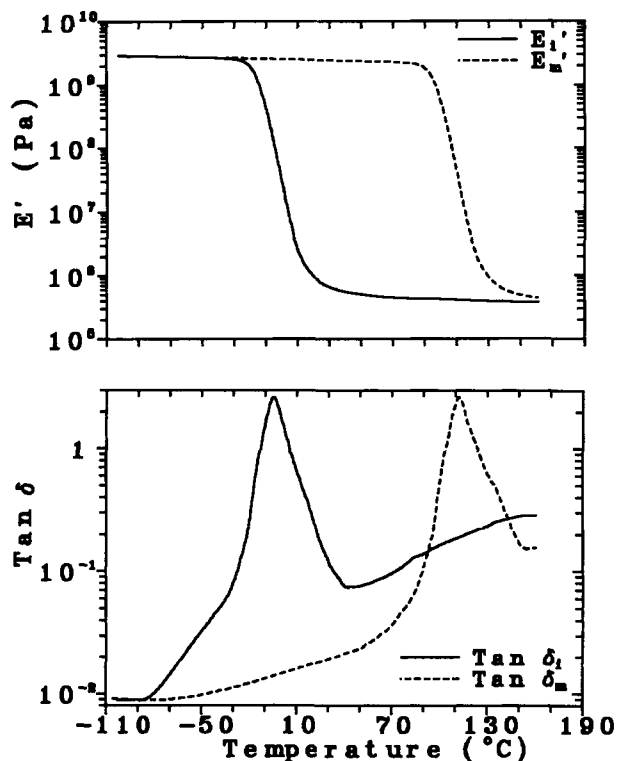
tems of low functionalization level, the model provided a measure of the volume fraction of interfacial material in the blend while for highly functionalized systems, where no pure HPS or PEA remained, the model provided an estimate of the amplitude of concentration variations in the system. However, the model assumes cocontinuity of the two phases and, thus, is only successful in representing data for blends with compositions near 50/50. As many blends of practical interest have very asymmetric compositions—particularly rubber-toughened plastics, with a glassy matrix and rubber inclusions—we develop here a model that provides similar information for the asymmetric case. The model is based on the pioneering work of Kerner,[11] who derived expressions for the bulk and shear moduli of an isotropic composite comprising noninteracting spherical particles distributed within a homogeneous matrix. His simple closed-form equations involve only the volume fraction of inclusions and the moduli and Poisson's ratio of the inclusions and matrix.

Dickie[12] used the correspondence principle—the substitution of complex dynamic moduli for the analogous elastic quantities in the Kerner equa-

tion—to extend the model to the dynamic case. Comparisons between the model and experimental DMTA data by Dickie and co-workers[12,13] constitute the most comprehensive application of the Kerner theory to heterogeneous polymer blends. For systems comprising glassy inclusions in a rubbery matrix, the model does not represent experimental data well; Dickie discusses possible origins of these discrepancies.[12] By contrast, for systems of the rubbery inclusions/glassy matrix type, general features and trends exhibited in experimental data were consistently reproduced by the Kerner–Dickie equation. However, modulus values were typically overestimated when the volume fraction of inclusions was equated to the known volume fraction of rubber. Better quantitative agreement was obtained by defining a "mechanically effective" dispersed phase volume fraction, V_{ME}, empirically selected to match the measured modulus values. For a blend comprising a glassy poly(methyl methacrylate) matrix and rubbery poly(butyl acrylate) inclusions, Dickie's values for V_{ME} were $\sim$ 20% greater (relative basis) than the volume fraction of rubber.[3] He attributed this discrepancy to partial phase inversion of the system: occlusion of a fraction of the majority com-

Figure 2 Schematic of the microstructure represented by the modified Kerner–Dickie model, where mixing is allowed. Material between R_1 and R_2 constitutes the mixed interphase.
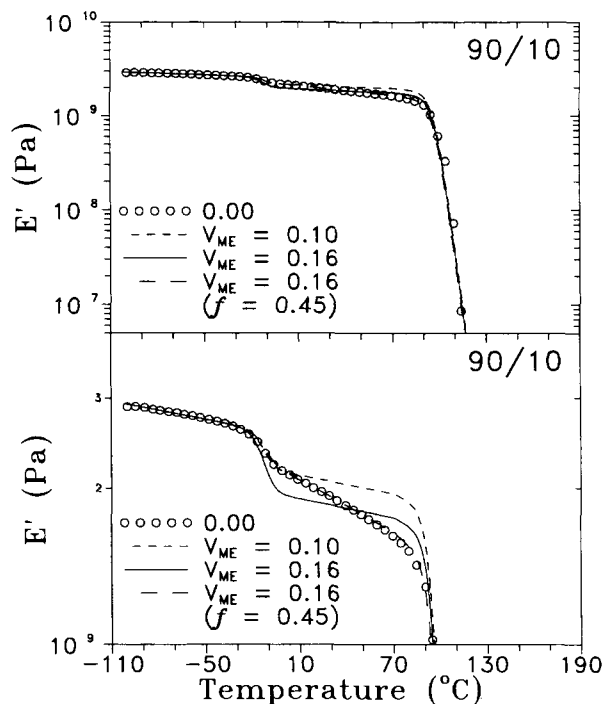
Figure 3 Input DMTA data (E'—top panel; tan δ—bottom panel) for the models: (—) PEA inclusions, (---) PS matrix.

material should exhibit broadened glass transitions when compared with a physical blend of identical composition, wherein little phase mixing occurs.

In our previous work on 50/50 HPS/PEA blends,[9,14] we observed a similar broadening of the glass transitions as the HPS functionalization level increases, and incorporated the mechanical response of the interphase into the Takayanagi model, following methods developed previously.[7,10] Here, we modify the Kerner–Dickie model in an analogous, though simpler, fashion. The portion of the interphase with $T_g < T$ is considered as part of the rubbery inclusions, while the remainder is assigned to the matrix. Because the interphase has a continuous composition gradient, this yields a temperature-dependent volume fraction of inclusions. We compare the model with experimental E' data from DMTA for 90/10 and 70/30 w/w HPS/PEA blends, where the HPS functionalization level ranges from zero to 3.72 mol %. In 50/50 blends, our earlier studies showed that 3.72 mol % substitution produced the most extensive interfacial mixing consistent with

ponent by the minority, forming a composite dispersed phase of greater volume fraction than the rubber alone. Such composite inclusions are well known in high-impact polystyrene, for example.

Dickie and Cheung[13] investigated polymer–polymer composites prepared via a two-stage emulsion polymerization, where methyl methacrylate was polymerized onto a crosslinked butyl acrylate seed latex. They were unable to adequately represent DMTA data for these systems with the Kerner–Dickie model, because the experimental glass transitions in the composites were broader than those exhibited by the two pure components. However, data from simple blends of the homopolymers, of similar composition, could be adequately fit by the model. The Kerner–Dickie approach treats the components as immiscible, so no relaxation modes between the glass transition temperatures (T_g) of the two pure components are predicted for the blends, nor are the transitions greatly broadened. The two-stage emulsion polymerization could produce materials with a composition gradient where, between the rubbery core and the glassy shell, a substantial interphase of mixed material exists. Such a

Figure 4 Comparison of experimental E' data for the 90/10 unfunctionalized blend (O) with predictions from the unmodified Kerner–Dickie model: (---) $V_{ME} = V_{PEA} = 0.10$, (—) $V_{ME} = 0.16$. Also shown are the predictions of the modified model (– –) with $V_{ME} = 0.16$ and $f = 0.45$. Bottom panel gives an expanded view.
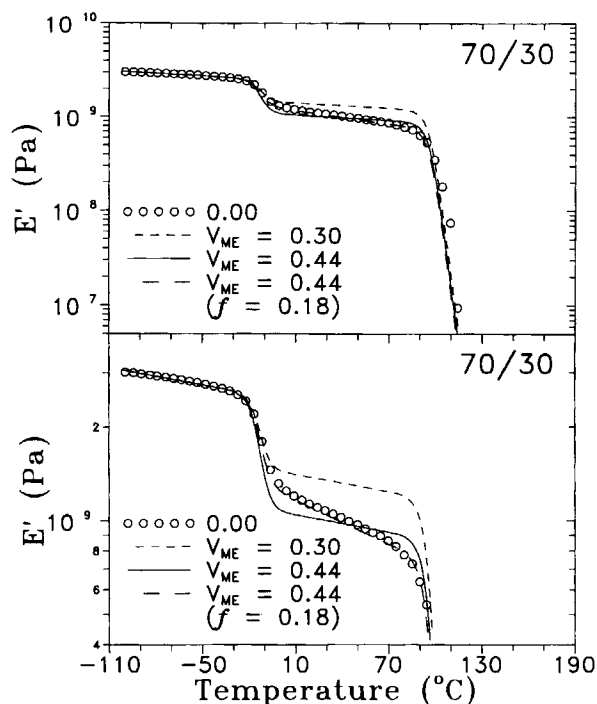
Figure 5 Comparison of experimental E' data for the 70/30 unfunctionalized blend (O) with predictions from the unmodified Kerner–Dickie model: (---) $V_{ME} = V_{PEA} = 0.30$, (—) $V_{ME} = 0.44$. Also shown are the predictions of the modified model (- -) with $V_{ME} = 0.44$ and $f = 0.18$. Bottom panel gives an expanded view.

pure domain centers,[9] and resulted in greatly enhanced stress–strain behavior.[14]

EXPERIMENTAL SECTION

The synthesis and characterization of materials utilized in this study has been described previously.[14,15] Briefly, these materials are blends of PEA with one of a series of p-hydroxyl-functionalized polystyrenes (HPS) of differing functional group content. The polymers were blended in dilute solution, freeze dried, and finally compression molded into films above the glass transition temperature of the HPS component. Acquisition of the DMTA data, using a Rheometrics RSA-II in tensile mode at 1 Hz, has also been previously described.[9,14] The measured E' values for the functionalized blends at a given composition were scaled by a factor near unity (±0.1) to ensure that the moduli matched those of the corresponding unfunctionalized blend at temperatures below −50°C. This accounts for errors in determining the sample cross sections; samples were always

kept thin enough so that compliance of the RSA-II transducer could be accurately accounted for. Additional information on these blends, including uniaxial tensile stress–strain curves and small-angle x-ray scattering data, can be found elsewhere.[15]

MODEL DEVELOPMENT

The viscoelastic form of the Kerner–Dickie equation,[12] written in terms of the temperature-dependent complex modulus E^*, is:

$$E_c^* = \frac{\gamma\{(1 - V_{ME})E_m^* + \beta(\alpha + V_{ME})E_i^*\}}{(1 + \alpha V_{ME})E_m^* + \alpha\beta(1 - V_{ME})E_i^*}E_m^* \quad (1)$$

where

$\alpha = 2(4 - 5v_m)/(7 - 5v_m)$
$\beta = (1 + v_m)/(1 + v_i)$
$\gamma = (1 + v_c)/(1 + v_m)$
$v = $ Poisson's ratio
$V_{ME} = $ mechanically effective volume fraction of inclusions.

Subscripts c, m, and i refer to the composite, matrix, and inclusions, respectively. Note that the various E^* quantities in eq. (1) are all complex; that is, they contain both real (E') and imaginary ($E'' = E'\tan\delta$) parts. To actually compare eq. (1) with experimental E' or $\tan\delta$ data, it is necessary to algebraically resolve the real and imaginary components of E_c^*.

Figure 1 schematizes the microstructure assumed in the original Kerner–Dickie model; discrete spheres of the minority component (here, PEA) are dispersed within a continuous matrix of the majority component (here, PS). The plot at the bottom graphs the composition profile of the system, as a function of the distance r from the center of the inclusion; in the Kerner–Dickie model, where interfacial mixing is not allowed, there is a discontinuity in composition (Φ_{PS}) at the inclusion radius R.

To incorporate phase mixing effects into the Kerner–Dickie model, we consider the inclusions to possess a core–shell morphology consisting of a core of pure minority component (radius R_1) and a shell of mixed material (outer radius R_2), with a linear composition gradient extending from pure minority component at R_1 to pure matrix at R_2. This structure
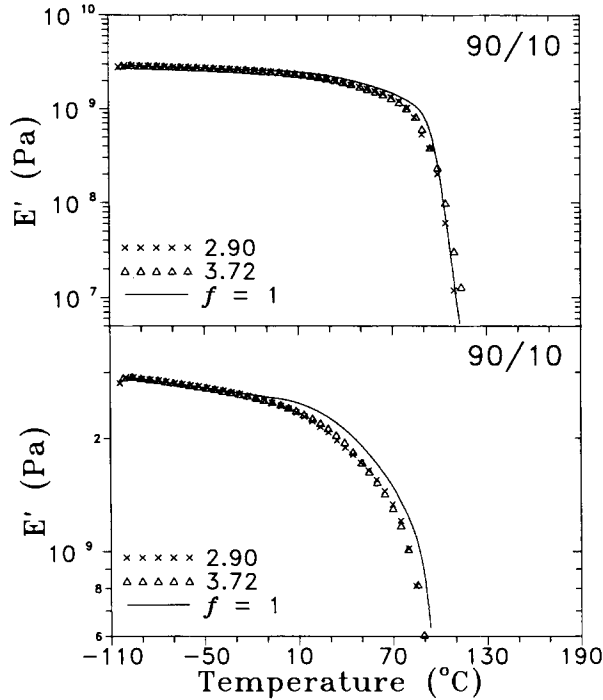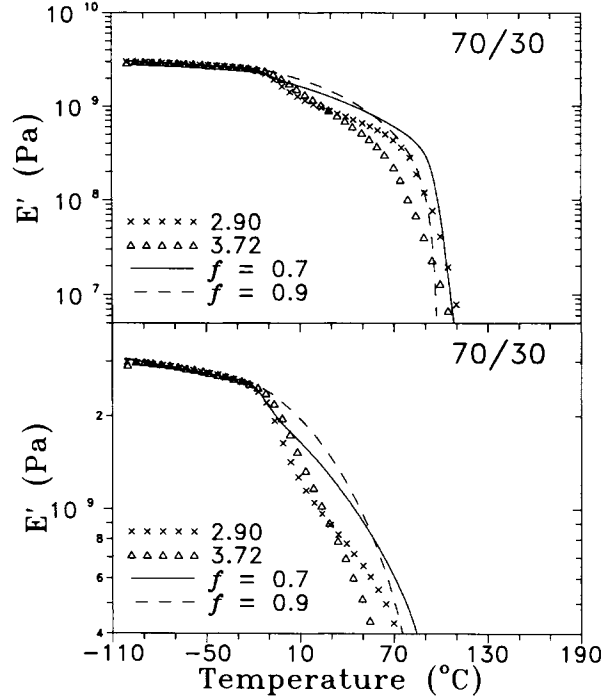
Figure 6 Comparison of experimental E' data for the 90/10 functionalized blends [($\times$) 2.90 mol % HPS functionalization; (Δ) 3.72 mol %] with the prediction from the modified model (—) with $V_{ME} = 0.16$ and $f = 1$. Bottom panel gives an expanded view.

Figure 7 Comparison of experimental E' data for the 70/30 functionalized blends [($\times$) 2.90 mol %; (Δ) 3.72 mol %] with the prediction from the modified model with $V_{ME} = 0.44$: (—) $f = 0.7$ and (---) $f = 0.9$. Bottom panel gives an expanded view.

is schematized in Figure 2. Because the Kerner equation considers only two types of material—matrix and inclusions—it cannot represent the continuous gradation of material properties resulting from the continuous composition profile in Figure 2. Thus, we divide the mixed material (between R_1 and R_2) into two parts: at a given temperature T, all mixed material with a glass transition temperature $T_g < T$ is treated as having the viscoelastic response of PEA, while all material with $T_g > T$ is considered to have the viscoelastic response of PS. The T_g for material with a given Φ_{PS} is found from the Fox equation.[16] This approach yields a temperature-dependent volume fraction of inclusions and should capture the effect of phase mixing on the modulus.

For a partially mixed system, with some of both the minority (PEA) and majority (PS) components still remaining in pure phases, the degree of intercomponent mixing can be represented by the fraction of the total PEA contained within the shell interphase, denoted f:

$$(1 - f)V_{ME} = (4\pi/3)(R_1/D)^3 = (4\pi/3)\mathcal{R}_1^3 \quad (2)$$

In eq. (2), V_{ME} denotes the mechanically effective volume fraction of inclusions *in the absence of any phase mixing*, which should be equal to the volume fraction of PEA if the inclusions are noninteracting and do not occlude any matrix material. As discussed below, V_{ME} is obtained by fitting the unfunctional-
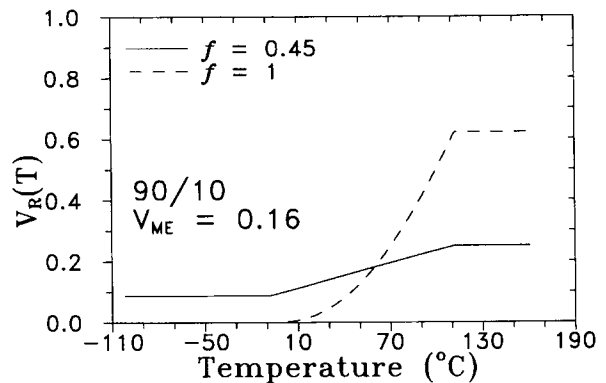
Figure 8 Temperature dependence of the effective volume fraction of rubber calculated from the modified model for the 90/10 blends: (—) unfunctionalized blend, (---) 2.90 and 3.72 mol % functionalized.
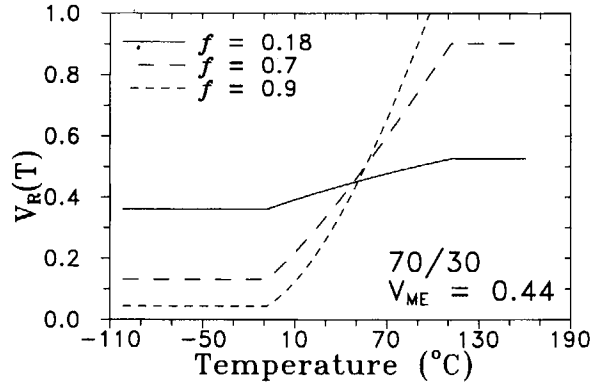
Figure 9 Temperature dependence of the effective volume fraction of rubber calculated from the modified model for the 70/30 blends: (—) unfunctionalized blend, (- -) 2.90 mol % functionalized, (---) 3.72 mol % functionalized.

ized blend data to the original Kerner–Dickie equation, which does not allow for phase mixing. Because the Kerner–Dickie model does not incorporate any effect of particle size—the only morphological parameter is the volume fraction of inclusions—we nondimensionalize all lengths by D, which is the length of the side of a cube containing a single inclusion. $\mathcal{R}_1$ is, thus, the nondimensional form of R_1, and $\bar{r}$ is the nondimensional form of the radial distance variable r.

$\mathcal{R}_2$ denotes the outer limit of the interphase; its value is set by mass balance on the component forming the inclusions:

$$f V_{\mathrm{ME}} = \frac{1}{D^3} \int_{R_1}^{R_2} (1 - \Phi_{\mathrm{PS}}) 4\pi r^2 dr$$
$$= \frac{\pi(\mathcal{R}_2^4 - 4\mathcal{R}_1^3 \mathcal{R}_2 + 3\mathcal{R}_1^4)}{3(\mathcal{R}_2 - \mathcal{R}_1)} . \quad (3)$$

If all the PEA is contained within the interphase, $f = 1$ and $\mathcal{R}_1 = 0$. Under these conditions, the linear composition gradient extends from the particle center out to the surrounding matrix, and the mixed interphase (outer radius $\mathcal{R}_2$) has four times the volume V_{ME} that an inclusion would have in the absence of phase mixing ($f = 0$; radius R_1 in Fig. 1). Strictly speaking, the mass balance in eq. (3) only holds if the inclusions do not occlude any matrix material, and V_{ME} equals the volume fraction of PEA (V_{PEA}). For composite inclusions, where $V_{\mathrm{ME}} > V_{\mathrm{PEA}}$, the balance in eq. (3) is correct provided the occlusions are evenly distributed from $0 \leq \bar{r} \leq \mathcal{R}_2$.

With the assumption of a linear composition gradient between R_1 and R_2, the Fox equation can be used to determine the radius $\bar{r}_T$, which corresponds to a position within the graded interphase where $T_g = T$, for any temperature $T_{g,\mathrm{PEA}} < T < T_{g,\mathrm{PS}}$. The densities of PS and PEA are quite similar,[9] so volume fractions can be used in place of weight fractions in the Fox equation, yielding:

$$\bar{r}_T / \mathcal{R}_1 = 1 + \left(\frac{\mathcal{R}_2}{\mathcal{R}_1} - 1 \right)$$
$$\times \left[\frac{T_{g,\mathrm{PS}}}{T_{g,\mathrm{PS}} - T_{g,\mathrm{PEA}}} - \frac{(T_{g,\mathrm{PS}})(T_{g,\mathrm{PEA}})}{(T_{g,\mathrm{PS}} - T_{g,\mathrm{PEA}})T} \right] \quad (4)$$

This equation is solved for $\bar{r}_T$ at a given T; the volume fraction of rubbery material within the system at T is given by:

$$V_R = (4\pi/3)\bar{r}_T^3 \quad \text{for} \quad T_{g,\mathrm{PS}} < T < T_{g,\mathrm{PEA}} \quad (5)$$

Because the composition profile is flat for $\bar{r} < \mathcal{R}_1$ and $\bar{r} > \mathcal{R}_2$, in these regions V_R is given by:

$$V_R = (4\pi/3)\mathcal{R}_1^3 \quad \text{for} \quad T < T_{g,\mathrm{PEA}} \quad (6)$$
$$V_R = (4\pi/3)\mathcal{R}_2^3 \quad \text{for} \quad T > T_{g,\mathrm{PS}} \quad (7)$$

We emphasize that our model assumes pure domain centers; that is, $\Phi_{\mathrm{PS}} = 0$ at $r = 0$ in Figure 2. Calculations were performed utilizing eq. (1) with V_{ME} replaced by V_R. In principle, the Poisson's ratios v in eq. (1) are temperature-dependent, complex quantities; however, very little information is available on $v^*(T)$. Fortunately, calculations by Dickie[13] indicate that the predicted dynamic moduli are rather insensitive to the value used for Poisson's ratio, so we take v to be exclusively real and set $v_c = v_m = v_i = 0.5$ at all temperatures. For the T_g values of the pure components, we use the tan δ maxima found[9,14] in a 50/50 unfunctionalized blend ($T_{g,\mathrm{PEA}} = 265$ K; $T_{g,\mathrm{PS}} = 385$ K).

The complex modulus of the inclusions, E_i^*, was assumed equal to that of PEA, which was measured experimentally.[9] The modulus of the matrix E_m^* was obtained by shifting the PEA data to higher temperature by $T_{g,\mathrm{PS}} - T_{g,\mathrm{PEA}} = 120°\mathrm{C}$, and scaling E_m^* vertically to match E_i^* below $-50°\mathrm{C}$. The components of E_m^* and E_i^* —namely, E' and tan δ ($=E''/E'$) are shown in Figure 3. This approach parallels our previous work[10] on 50/50 w/w blends; though the shapes of the E^* vs. T curves are not precisely identical for PS and PEA, or for HPS of different

functionalization level, we found the discrepancy to be inconsequential.[9] For materials with greatly different E^* vs. T curves, it would be preferable to measure the viscoelastic response of both constituents and use these directly. As discussed in the Experimental section, the E' data in Figure 3 were scaled by a factor near unity to ensure a match to the blend data at low temperatures.

Unfortunately, this scheme for incorporating mixing effects does a poor job of describing tan δ data. Experimentally, tan δ values increase for temperatures between the two pure-component T_g values as a result of phase mixing.[14,15] However, we consider the mixed interphase to be divided between the glassy and rubbery phases. Although this is successful in representing E' data—materials near T_g have E' values between those of glass and rubber— it fails for tan δ or E'', which both peak at T_g. Calculations show that the Kerner–Dickie model gives tan δ predictions very close to that of the matrix material[12] for all temperatures above the inclusion T_g, and this undesirable feature is retained in our modified version. Therefore, we have considered only the E' data in optimizing the fit of our model to experimental data. Moreover, since the Kerner– Dickie model does not work well when the matrix is rubbery, the model predictions become unreliable as T approaches the glass transition of the matrix. Hence, we have optimized our model fits for $T < 90°C$.

RESULTS AND DISCUSSION

Before fitting the functionalized blend data, values for V_{ME} are required. These were obtained by fitting the unmodified Kerner–Dickie model, eq. (1), to E' vs. T data for the unfunctionalized (0.00 mol %) HPS/PEA blends, with a temperature-independent V_{ME} as the only adjustable parameter. Results for the 90/10 and 70/30 blend compositions are shown in Figures 4 and 5. In these plots, the dashed curve is the prediction obtained assuming that V_{ME} equals the volume fraction of PEA; this assumption yields E' predictions which exceed the experimental data for all T between $T_{g,PEA}$ and $T_{g,PS}$. As in the work of Dickie, better agreement with the data in this intermediate plateau region was obtained by selecting a mechanically effective dispersed phase volume fraction slightly greater than V_{PEA}, shown as the solid curves in Figures 4 and 5. Because the unmodified model predicts a flatter plateau than observed experimentally, adjusting V_{ME} can only pro-

duce agreement at a single temperature. We chose to match model and experiment at the arithmetic mean of $T_{g,PS}$ and $T_{g,PEA}$ (52°C). Choosing match points anywhere near the center of the plateau resulted in equally good fits when allowing for mixing in our modified model, with only slight differences in the parameters.

Using the V_{ME} values from the solid curves in Figures 4 and 5, we applied our modified model to the unfunctionalized blend data, with f as the only adjustable parameter. Figures 4 and 5 show the excellent fits obtained to the E' data with the modified model, over the whole range of temperature. Best-fit values obtained were $f = 0.45$ for the 90/10 blend and $f = 0.18$ for the 70/30 blend. This indicates that substantial phase mixing is present even in the unfunctionalized blends. This result is not unexpected, because we have previously noted that the solubility parameters of PS and PEA are very similar.[14]

This approach—keeping V_{ME} fixed (at 0.16 or 0.44, depending on composition) and allowing f to vary—was extended to the functionalized blends. At the 90/10 composition, experimental data at the two functionalization levels (Fig. 6) nearly superimpose, and an adequate representation of both data sets is obtained with $f = 1$. If V_{ME} was also allowed to vary, the fit could be improved slightly over selected temperature ranges; the best fit to the functionalized 90/10 blends for $T < 90°C$ was obtained with $V_{ME} = 0.21$ and $f = 1$, though this worsened the agreement at higher temperatures. The modest disagreement evident in Figure 6 can be attributed to our assumption of a linear gradient between R_1 and R_2. This provides a single description of the blend data in terms of only two parameters, V_{ME} and f, and gives the integral in eq. (3) a simple analytical solution. More complex interfacial profiles could be accommodated by using appropriate expressions for Φ_{PS} in eq. (3), but unless the shape of the interphase composition profile is known in advance, any improvement of the fit to the E' data would come at the expense of additional adjustable parameters. We have chosen to retain the simple linear composition profile, and to obtain V_{ME} from fits of the unmodified Kerner–Dickie model to the unfunctionalized blend data; thus, only one parameter is allowed to float in any particular fit.

For the 70/30 blend data (Fig. 7), a good representation was not obtained for either of the data sets. Although the model captures the qualitative shape of the data, the best fits (at $f = 0.7$ and 0.9, respectively, for the 2.90 and 3.72% HPS/PEA

data) are quantitatively poor. As with the functionalized 90/10 blends, better (though still not excellent) fits over selected ranges of temperature could be obtained if both V_{ME} and f were allowed to vary; best-fit combinations of $V_{ME} = 0.57$, $f = 0.58$ (for the 2.90% data) and $V_{ME} = 0.62$, $f = 0.60$ (for the 3.72% data) were found. Examination of our modified model, as depicted in Figure 2, shows that the representation should fail as the product $f V_{ME}$ nears 0.25. For $f = 1$ and $V_{ME} = 0.25$, the mixed interphase (radius R_2) occupies the *entire* volume of the cube of edge D; nonetheless, it is treated as a discrete inclusion. Clearly, this is a physical impossibility. This conundrum is brought out more clearly in Figures 8 and 9, in which the effective volume fraction of rubber V_R is plotted vs. temperature for all five of the model fits. For the 70/30 functionalized blends (Fig. 9), V_R nears or reaches unity *before* the polystyrene T_g. For the 70/30 functionalized blends, even when both V_{ME} and f were allowed to float, the best fit obtained had a value of $f V_{ME}$ similar to that obtained when V_{ME} was held fixed at 0.44. Examination of Figures 4–7 shows that a good fit is obtained with our modified model for $f V_{ME} \simeq 0.08$ (unfunctionalized blends), a reasonable fit is produced at $f V_{ME} = 0.16$ (90/10 functionalized blends), and a poor fit is generated for $f V_{ME} > 0.25$ (70/30 functionalized blends). These results indicate that our modified model can properly represent phase-mixing effects on E' when most of the material exists in pure phases, but fails when most of the material occupies a mixed interphase.

CONCLUSIONS

The Kerner–Dickie phenomenological model, which represents DMTA data for polymer blends with glassy matrices and rubbery inclusions, was modified to allow for interfacial mixing between components. The modification allows for a temperature-dependent volume fraction of rubbery inclusions, assuming a linear composition gradient across the interphase. The model was evaluated by comparing its predictions with experimental E' data for blends of PEA with HPS, where phase mixing is controlled through intercomponent hydrogen bonding. For the functionalized 90/10 w/w HPS/PEA blends, a good representation of the data was obtained with the assumption that all of the PEA within the system exists within the mixed interphase. It was also possible to quantify the degree of phase mixing occurring in the unfunctionalized materials; roughly 45 and 18% of the PEA must be mixed at the 90/10 and 70/30 compositions, respectively. However, only a poor representation of the functionalized 70/30 blends could be obtained, due to extensive phase mixing. We conclude that the model can properly assess the extent of phase mixing when most of the components exist in pure phases, but not when the interphase constitutes the majority of the material.

REFERENCES

1. M. Takayanagi, H. Harima, and Y. Iwata, *J. Soc. Mater. Sci. Jpn.*, **12**, 389 (1963).
2. L. E. Nielsen, *Rheol. Acta*, **13**, 86 (1974).
3. R. A. Dickie, in *Polymer Blends*, vol. 1, D. R. Paul and S. Newman Eds., Academic Press, New York, 1978.
4. J. D. Ferry, *Viscoelastic Properties of Polymers*, 3rd Ed., John Wiley & Sons, New York, 1980.
5. R. E. Cohen and A. R. Ramos, *J. Macromol. Sci.-Phys.*, **B17**, 625 (1980).
6. J. Diamant, D. S. Soong, and M. C. Williams, in *Contemporary Topics in Polymer Science*, vol. 4, W. J. Bailey and T. Tsuruta, Eds., Plenum Press, New York, 1982.
7. F. Annighöfer and W. Gronski, *Colloid Polym. Sci.*, **261**, 15 (1983).
8. F. Annighöfer and W. Gronski, *Makromol. Chem.*, **185**, 2231 (1984).
9. R. E. Taylor-Smith and R. A. Register, *J. Polym. Sci., Part B: Polym. Phys.*, **32**, 2105 (1994).
10. T. Hashimoto, Y. Tsukahara, K. Tachi, and H. Kawai, *Macromolecules*, **16**, 648 (1983).
11. H. Kerner, *Proc. Phys. Soc.*, **69B**, 808 (1956).
12. R. A. Dickie, *J. Appl. Polym. Sci.*, **17**, 45 (1973).
13. R. A. Dickie and M. Cheung, *J. Appl. Polym. Sci.*, **17**, 79 (1973).
14. R. E. Taylor-Smith and R. A. Register, *Macromolecules*, **26**, 2802 (1993).
15. R. E. Taylor-Smith, Ph.D. Thesis, Princeton University, 1994.
16. T. G. Fox, *Bull. Am. Phys. Soc.*, **1**, 123 (1956).