Dynamic Properties of NR/EVA Polymer Blends: Model Calculations and Blend Morphology

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ABSTRACT: The dynamic mechanical properties of blends of natural rubber (NR) and the ethylene-vinyl acetate copolymer (EVA), a thermoplastic elastomer, were investigated in terms of the storage modulus and loss tangent for different compositions, using dynamic mechanical thermal analysis (DMTA) covering a wide temperature range. Mean-field theories developed by Kerner were applied to these binary blends of different compositions. Theoretical calculations were compared with the experimental small strain dynamic mechanical properties of the blends and their morphological characterizations. Predictions based on the discrete particle model (which considers one of the components as a matrix and the other dispersed as well-defined spherical inclusions embedded in the matrix) agreed well with the experimental data in the case of 30/70 NR/EVA but not in the case of 70/30 NR/EVA blends. A 50/50 blend, where a cocontinuous morphology was revealed by SEM studies, was found to be approximately modeled by the polyaggregate model (where no matrix phase but a cocontinuous structure of the two is postulated). © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 72: 165–174, 1999

Key words: polymer blends; dynamic mechanical properties; NBR; EVA; Kerner model; polyaggregate model morphology; viscoelastic behavior

INTRODUCTION

Polymers and the blends made from them are viscoelastic in nature. Hence, the investigation of viscoelastic properties plays a major role in characterizing polymer blends regarding their mechanical behavior, structure-property relationships, and so on. Dynamic mechanical analysis has proved to be an effective tool in the characterization studies of viscoelastic materials. In a cyclic deformation field, the oscillatory strain wave results in an oscillatory stress response

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with a phase lag (δ) in between, which is a measure of the viscous contribution. The resulting viscoelastic parameters are expressed as¹

 E^* (complex modulus) = E' (elastic modulus) + iE'' (loss modulus)

$$\tan \delta = E''/E'$$

Presently, application of theoretical models which aim at understanding and predicting the mechanical behavior and morphology of the blends from the individual component characteristics has gained importance.^{2–8} Dynamic mechanical analysis has proved to be an effective tool in this

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regard. The computation technique to predict the viscoelastic properties is based on the analogy between viscosity and elasticity. The multicomponent theories generated for elastic systems have been adapted for viscoelastic materials through the elastic–viscoelastic correspondence principle.

A number of approaches are found in the literature to determine the composite properties from those of the components. Each approach has its merits and demerits. The empirical methods are based on the approximation of experimental data like analytical curve fitting. The hydrodynamic approach does not reflect the dependence of the effective properties on the elastic properties of the filler, the latter being assumed to be completely rigid. Methods of elasticity theory and geometrical models of the composite medium constitute the most widely accepted approach.⁷ For polymeric materials, dynamic mechanical analysis has proved to be an effective tool because the theories for elastic systems can be easily adapted for viscoelastic materials in the case of a steadystate harmonic condition. For the linear viscoelastic matrix and inclusion, the time-dependent elastic constants are replaced with corresponding complex viscoelastic constants obtained from dynamic experiments in the steady-state harmonic condition. When dynamic experiments are carried out at constant frequency, the steady material response is independent of the time (duration) of the measurement. $^{9-15}$

Models of importance in the study of polymeric blends and composites can be categorized as mechanical coupling models, self-consistent models, and bounding and semiempirical models. Selfconsistent models, namely, Kerner and Vander Poel and the empirical modifications thereof, allow study of the mechanical behavior with respect to the morphology/structure and, hence, find importance in mechanical properties versus morphological investigations.^{15–35}

The models have lately been used for predicting dynamic mechanical properties with respect to morphological aspects of the rubber/rubber blends.^{36–38} Thermoplastic elastomers (TPE) have gained importance in recent years since they possess properties of both thermoplastics and rubbers. Very little work has been reported on the use of models for studying the dynamic data of TPE systems. In this article, we discuss the applicability of Kerner's models for predicting the dynamic properties of NR/EVA blends. In our earlier article, we examined the applicability of the models to the NBR/EVA and NR/ 1,2-PBD systems.^{39,40}

THEORETICAL

The two cases considered in Kerner's expressions¹⁵ are composites with discrete particles in a matrix and polyaggregates without any matrix. The polyaggregate or the packed grain model where no separate matrix phase is postulated is assumed to represent a cocontinuous morphology of the blends.

Discrete Particle Model

The assumptions underlying this model are that spherical inclusions of varying size are randomly distributed in the volume of the matrix. The phase surfaces are in direct contact (bonded physically or chemically), that is, there is no slip at the phase interface, but interactions between particles are ignored. The model gives the overall average response of the material to loads (or deformation) rather than localized variation in material characteristics.

The Kerner equation for the shear modulus for a multicomponent system is given by

$$\frac{G}{G_m} = \frac{\sum G_i \phi_i / \{(7 - 5\mu_m)G_m + (8 - 10\mu_m)G_i\} + \phi_m / 15(1 - \mu_m)}{\sum G_m \phi_i / \{(7 - 5\mu_m)G_m + (8 - 10\mu_m)G_i\} + \phi_m / 15(1 - \mu_m)}$$
(1)

which for a binary blend of viscoelastic materials can be adapted for the complex Young's modulus through the correspondence principle and the relation $E^* = 2(1 + \mu^*)G^*$, where $\mu^* (= \mu' + i\mu'')$ is the viscoelastic Poisson ratio. Here, μ^* is assumed as μ (a real quantity), that is, the elastic Poisson ratio. Dickie⁹ showed that the error in assuming μ as a real quantity is negligible.

The transformed equation is represented as

$$\frac{E^{*}}{E^{*}_{m}} = \gamma \frac{(1-\phi_{i})E^{*}_{m} + \beta(\alpha+\phi_{i})E^{*}_{i}}{(1+\alpha\phi_{i})E^{*}_{m} + \alpha\beta(1-\phi_{i})E^{*}_{i}}$$
(2)

where

its variation with temperature, taken into consideration for computations, is as was used by Mazich et al. $^{\rm 38}$

The relation is given below:

$$\mu(T) = \frac{0.17\{(\log E'(\text{glass}) - \log E'(T)\}}{\{\log E'(\text{glass}) - \log E'(\text{rubber})\}} + 0.32$$
(3)

E', E'', and tan δ for the blends are computed using a Fortran program. The equation due to Kerner has been found to represent dynamic data on a variety of systems of the soft inclusions/hard matrix type.^{2,3,9}

Polyaggregate Model

Here, no separate matrix phase is contemplated. Particles of each component are suspended in a third component. As the concentration of the third component approaches zero, particles of each component will pack together in the volume of the material.

The model is represented by two coupled governing equations for the bulk (K) and the shear modulus (G):

$$\frac{(K_1^* - K^*)\phi_1}{(3K_1^* + 4G^*)} + \frac{(K_2^* - K^*)\phi_2}{(3K_2^* + 4G^*)} = 0$$
(4)

$$\frac{(G^* - G_1^*)\phi_1}{(7 - 5\mu)G^* + (8 - 10\mu)G_1^*} + \frac{(G^* - G_2^*)\phi_2}{(7 - 5\mu)G^* + (8 - 10\mu)G_2^*} = 0 \quad (5)$$

Equations (4) and (5) are expressed in terms of the dynamic Young's modulus (E^*) through the equations $E^* = 2(1 + \mu^*)G^*$ and $K^* = E^*/3(1 - 2\mu)$. The transformed equations with complex parameters are resolved into real and imaginary parts as follows:

Eq (4):
$$f(E^*) = g(E', E'', \text{ and } \mu)$$

+ $ih(E', E'', \text{ and } \mu) = 0$ (6)

Eq (5):
$$f(E^*) = u(E', E'', \text{ and } \mu)$$

+ $iv(E', E'', \text{ and } \mu) = 0$ (7)

From eqs. (6) and (7), we have four sets of equations by equating the real and imaginary parts of



Figure 1 Temperature dependence of storage modulus of NR/EVA blends including pure components.



Figure 2 Temperature dependence of loss tangent of NR/EVA blends including pure components.

each to zero. These equations are functions of E', E'', and μ . Since μ is assumed to be real, we have only three variables to solve (i.e., E', E'', and μ). For this reason, we ignore the imaginary part of eq. (4) or (6), leaving three equations to solve. The Newton–Raphson method^{38,39,41} was used to solve the simultaneous equations from (7).

The increments in E' and E'', that is, $\Delta E'$ and $\Delta E''$ are defined as

$$\Delta E' = \frac{v \partial u / \partial E'' - u \partial v / \partial E''}{D} \tag{8}$$

$$\Delta E'' = \frac{u \partial v/\partial E' - v \partial u/\partial E'}{D} \tag{9}$$

where

$$D (determinant) = \partial u / \partial E' \partial v / \partial E'' - \partial u / \partial E'' \partial v / \partial E'$$
(10)

Convergence is attained with the expressions

$$E_{i-1}' = E_i' + \Delta E' \tag{11}$$

$$E_{j-1}'' = E_j'' + \Delta E'' \tag{12}$$

The real part of eq. (6) is expressed as quadratic in μ . The values of E' and E'' obtained from eq. (7) are substituted in the real part of eq. (6) to solve for a new value of μ . The value of μ thus obtained (generally it falls between 0.32 and 0.5) is used for the final convergence of E', E'', and μ for subsequent iterations to converge. Solution of the coupled system of eqs. (4) and (5) was obtained by convergence of all variables E', E'', and μ .

Initial estimates for E', E'', and μ (assumed real) are obtained from the values of the components, weighted by their volume fractions. The temperature dependence of μ of the components, that is, $\mu_1(T)$ and $\mu_2(T)$ in the blend, is determined from the relation as mentioned earlier in eq. (3). The details of the procedure have been dealt with in our earlier article.³⁹

EXPERIMENTAL

The details of the experimental methods of blend preparation and the determination of the storage



Figure 3 Computed and experimental storage modulus data for 30/70 NR/EVA blend.

modulus and loss tangent have been described elsewhere.⁴² The blends were prepared in a laboratory model intermix (Shaw Intermix KO) at a temperature of 60° C using a rotor speed of 60 rpm. The compositions chosen for the present study were 30/70, 50/50, and 70/30 NR/EVA.

Dynamic mechanical measurements were carried out on a DMTA machine (Polymer Laboratories) consisting of a temperature programmer and controller. This instrument measures the dynamic moduli (both storage and loss moduli) and the damping of a specimen under an oscillatory load as a function of temperature. The experiments were conducted in a uniaxial tension mode from -80 to 20° C at a frequency of 10 Hz. Further details of the raw materials, mixing, and property evaluation are as reported earlier.⁴²

RESULTS AND DISCUSSION

The experimental data for viscoelastic parameters are shown in Figures 1 and 2. Based on the peak values of tan δ , the T_g of NR was found to occur around -46° C and that of EVA around -10° C. The homopolymer NR showed a sharp rise in the loss tangent and drop in E' corresponding to the glass transition of the material. EVA does not show any such abrupt rise or fall in the tan δ value or E' at its characteristic glass transition zone. In the case of EVA, a rise in tan δ occurs followed by plateauing and E' exhibits a gradual decrease around the T_g region.

The blends exhibit two transitions corresponding to each of the components as shown below:

NR/EVA	$T_{{\mathscr G}_{ m NR}}\left(^{ m o}{ m C} ight)$	$T_{g_{\mathrm{EVA}}}\left(^{\mathrm{o}}\mathrm{C} ight)$
100/0	-46.3	
70/30	-46.3	_
50/50	-50.0	-10.9
30/70	-51.7	-10.1
0/100	—	-10.0

30/70 NR/EVA Blend

When the experimentally obtained properties of the 30/70 NBR/EVA blend are compared with the computed data for both *discrete particle* and *polyaggregate models*, it is observed from Figures 3 and 4 that predictions based on the discrete par-



Figure 4 Computed and experimental loss tangent data for 30/70 NR/EVA blend.

ticle model assuming EVA as the matrix provide a close match to the experimental data for both E'and tan δ . Differences between the predicted and experimental data are observed at temperatures above -30° C, that is, from the low-temperature through the transition-temperature regions, the model has worked well. At the very low temperature zone, the molecular movements are frozen and both the components behave like elastic solids. In the transition-temperature region past the glass transition temperature, the segmental mobility of the polymer backbone only sets in. Thus, at both low temperature and in the transition zone, a good match is observed; deviation occurs at a higher temperature where long-range rubbery relaxations also are expected to contribute. We observe that the discrete particle model (EVA as the matrix) predicts storage modulus values slightly higher than does the experimental data at temperatures above -30°C. A satisfactory match between the experimental data and the predictions has also been seen in the case of the polyaggregate model. It is interesting to note that the discrete particle model assuming either EVA or NR as the matrix and the polyaggregate model predictions give excellent agreement with the experimental data below the T_g .

In the case of the loss tangent data also, the discrete particle model (assuming EVA as the matrix) approximately matches the experimental data. The match is excellent below T_g , and at T_{g} , there is a small difference in the location of the peak. The experimental peak occurs at a slightly higher value than the predicted one. Although the predicted values are marginally lower than the experimental data, they clearly indicate the trend of the experimental results, that is, the two transitions corresponding to the NR and EVA peaks around -52 and around -10° C, respectively, in the blend. It may be noted that earlier investigations⁴² based on SEM analysis of a 40/60 NR/EVA blend indicated NR particles dispersed in a matrix of EVA, and beyond 50-60 parts of NR in the blend, a cocontinuous morphology of the two resulted. Thus, a larger volume fraction of EVA in the 30/70 NR/EVA blend coupled with the SEM findings supports the prediction that EVA is the matrix in which particles of NR are dispersed. Hence, the predictions of the discrete particle model with EVA as the matrix are quite satisfactory. The lack of fit assuming NR (having a low volume fraction and a high melt vis-



Figure 5 Computed and experimental storage modulus data for 50/50 NR/EVA blend.



Figure 6 Computed and experimental loss tangent data for 50/50 NR/EVA blend.



Figure 7 Computed and experimental storage modulus data for 70/30 NR/EVA blend.

cosity) as the matrix is in accordance with expectations.

For the 30/70 blend, it is also observed that except for the transition region the polyaggregate model's predictions are as good as those of the discrete particle model assuming EVA as the matrix. The polyaggregate model predicts a shift in the transition peak as compared to the experimental tan δ data and slightly overestimates the experimental data. However, the closeness of the polyaggregate calculations to the experimental data is difficult to reconcile on the basis of SEM findings that suggest that the 30/70 blend would be a dispersed-phase morphology. A possible explanation is the volume fraction of the "packed grains" of the major component, namely, EVA. The number of grains of EVA are sufficiently large enough to form a matrix for the grains of NR.

50/50 NR/EVA Blend

The data for the 50/50 blend is in conformity with increase in the NR content as revealed in the storage modulus and loss tangent values compared to 30/70 NR/EVA blend (Figs. 1 and 2). The

loss tangent data show a higher NR peak, but no appreciable change in the shoulder corresponding to EVA as compared to 30/70 NR/EVA blend. Theoretical calculations of the dynamic properties based on packed grain and discrete particle models are presented in Figures 5 and 6.

It is observed that discrete particle model calculations considering either EVA or NR as the matrix are markedly different from the experimental data. Calculations based on the polyaggregate model are somewhat closer to the experimental results. Up to -20°C, the polyaggregate predictions for the E' data are lower than the experimental data. Above -20° C, the reverse is true. Similar trends are observed in the case of loss tangent data. Earlier studies by Alex et al.⁴² indicated a cocontinuous morphology for the 50/50 NR/EVA blends. In view of the assumptions for the polyaggregate model, the greater agreement with the experimental observations indicates the applicability of this model. However, the small deviations below and above -30°C need to be rationalized.

It may be noted from the tan δ -temperature curve (Fig. 6) that the discrete particle model with EVA as the matrix matched reasonably well to



Figure 8 Computed and experimental loss tangent data for 70/30 NR/EVA blend.

the experimental data, but underestimated the tan δ values above T_g . The latter model also predicted the location of the tan δ peak to within a few degrees. However, comparison of the predictions of the models and experimental data for the storage modulus indicated a closer match for the polyaggregate model for the 50/50 blend.

70/30 NR EVA Blend

The experimental data for the 70/30 NR/EVA blend (Figs. 1 and 2) reflect the increase in the volume fraction of the NR phase compared to the 50/50 blend. This is manifested in lower E' values and a higher tan $\delta_{\rm max}$ for the NR phase. Moreover, there is no shift in the T_g value (-46.3°C) for the component NR in the blend as shown above.

Considering the larger volume fraction of NR in the blend, the discrete particle model with NR as the matrix should match the data. Also, previous investigation of the morphology of the blend revealed aggregates of EVA domains dispersed in a matrix formed by NR.⁴²

The predicted values and experimental results for the storage modulus and loss tangent at different temperatures for the 70/30 NR/EVA blend for different models are given in Figures 7 and 8. A comparison of the predicted values and experimental results for the storage modulus as well as the loss tangent for the 70/30 NR/EVA blend indicates that discrete particle model predictions are in close agreement to the experimental data, especially from low temperature to the T_g region. Above the T_g , the match is poor for both the storage modulus and tan δ . The predictions for the tan δ data match the location of the T_g but gives a higher peak value compared to the experimental data.

The discrete particle model predicts higher tan δ values at the transition region and lower values at the temperature region around -30° C onward. Whereas the polyaggregate model matches the experimental data at both below and above the T_g region, the model overestimates the tan δ data at T_g , but to a lesser extent when compared to the discrete particle model. Calculations assuming EVA as the matrix do not match the experimental results. The minor deviation of the model with NR as the matrix can be explained from morphological considerations. In the blend, aggregates of EVA are distributed in a matrix formed by NR. It may be recalled that the model assumed single-dispersed spherical particles.

CONCLUSIONS

The Kerner models for discrete particle and polyaggregate systems were used to predict the viscoelastic properties of NR/EVA polymer blends over a temperature range encompassing the glass transition temperature regions of the individual components. Comparison of the experimental data and the predictions indicated good agreement for the 30/70 NR/EVA blend in the case of the discrete particle model. This is supported by SEM studies. For the 50/50 composition, the polyaggregate model provided a closer match, indicating its applicability for the blend. SEM studies revealed cocontinuous morphology for the blend. For the 70/30 NR/EVA blend, discrete particle predictions did not agree with the experimental data beyond the glass transition region. The deviations are explained on the basis of larger domains of EVA particles dispersed in the NR matrix.

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