Macromol. Symp. ***2001**, 169, 237-242*

Actual Viscoelastic Characterization of the Interphase in a Compatibilized Thermoset/Thermoplastic Blend through Reverse Mechanical Modeling

*Didier Colombini, Gérard Merle, Nicole Albérola**

Laboratoire Matériaux Polymères et Composites U.M.R.-C.N.R.S.-5041
Université de Savoie - Le Bourget du Lac - 73376 Cedex - France

SUMMARY: The viscoelastic properties of an *in-situ* compatibilized thermoset/thermoplastic blend were investigated. A reverse mechanical modeling was used to predict (1) the actual viscoelastic characteristics of the *in-situ* synthesized interphase in the blend and (2) the evolution of these actual characteristics as a function of the thermal history of the polymer blend. Thus, predicted data revealed a significant increase of the ability of the molecular mobility in the interphase area after a refreshing thermal treatment be applied to the blend. Lastly, the frequency dependence of the predicted relaxation of the interphase component was also studied.

Presentation

The study of the interphases in multiphased materials (polymer blends and composites) remains an important subject of research, and it is well known that the interphase properties strongly affect the properties of such materials.

The compatibilized thermoset/thermoplastic blend used in this study contains 1.5 wt% of a reactive compatibilizer based on poly(styrene-b-ethylene-co-butene-b-styrene) in a thermoset epoxide-amine network in which 10wt% of a high-T_g thermoplastic are dispersed.

First, morphology and viscoelastic properties of the compatibilized polymer blend were investigated1). Mechanical spectrometry revealed an additional loss peak at about 333K at 1Hz in the compatibilized ternary blend spectrum which was detailed as a "micromechanical transition". According to Eklind and Maurer2,3), such a transition, which did not correspond to a relaxation of one of the pure components was predicted through mechanical modeling to depend on the Poisson's ratio and the volume fraction of the interphase. The occurrence of the "micromechanical transition" on mechanical spectra was then shown to be significantly influenced by the thermal history of the sample1). Precisely, a "refreshing" thermal treatment for 30 minutes at 20°C above the glass transition temperature of the epoxy network was applied to the samples which were initially left at least 18 months in classical laboratory conditions before our first experiments. Both the magnitude and the

CCC 1022-1360/00/$ 17.50+.50/0

temperature location of the interphase relaxation in mechanical spectra were shown to be modified by the applied thermal treatment. Thus, after "refreshing" thermal treatment, the interphase relaxation occurred at a lower temperature ($\Delta T \sim 5°C$) and its magnitude significantly increased. Such results point out that the viscoelastic behavior of such an interphase relaxation is strongly affected by the conditions of confinement of the components in the interphase zone. However, these viscoelastic characteristics are not experimentally accessible. Indeed, as a consequence of the reactive functions of the used compatibilizing agent, the actual component of the resulting *in-situ* synthesized interphase region can not be separately synthesized. Model interphase components were even synthesized and their viscoelastic properties were investigated1). Since the definition of the "micromechanical transition" mainly results from theoretical simulations, these properties were then used in a direct mechanical modeling4) but did not lead to an additional peak in the resulting theoretical mechanical spectra of the blend. In a "direct" mode, mechanical modeling consists to predict the viscoelastic properties of a blend from the knowledge of characteristics of its pure components.

Another interesting way for investigating the actual viscoelastic properties of the interphase component is the use of a reverse mechanical modeling. In the reverse mode, such a new approach for mechanical modeling appeared4) to be well-suited for separating the viscoelastic characteristics of one phase among others in multiphased systems. Thus, according to the thermal history of samples and with the knowledge of the viscoelastic properties of the blend, pure matrix and pure particle, we propose to use such a reverse mechanical modeling to study (1) the actual viscoelastic characteristics of the interphase in a *in-situ* compatibilized thermoset/thermoplastic blend (2) their evolution as a function of the thermal history of samples, and (3) their frequency dependence.

Mechanical Modeling Section

The mechanical model used in this work is based on the (n+1) phase self-consistent scheme5,6) and it is here applied for a three-layered phase-concentric sphere. Such a modeling is based on the following assumptions : (1) the inclusions are randomly dispersed in the matrix, (2) each phase is homogeneous and isotropic, and (3) bonding between neighboring phases are perfect.

For self-consistent schemes, it is required to define a Representative Volume Element (RVE). The RVE (depicted in Figure 1) is constituted by three concentric spheres embedded in an homogeneous medium. Here, the central core (Phase 1) is constituted by the thermoplastic inclusion with the radius r_1. Phase 1 is surrounded by a shell of interphase (Phase 2) which is limited by the spheres with the radii r_1 and r_2. Phase 2 is covered by a shell of thermoset matrix (Phase 3) which is limited by the spheres with the radii r_2 and r_3. The radii of the shells are expressed as functions of the volume fractions of the dispersed phase (V_p), interphase (V_i), and matrix (V_m) :

$$\begin{cases} V_p = \dfrac{r_1^3}{r_3^3} \\ V_m = 1 - \dfrac{r_2^3}{r_3^3} \\ V_i = 1 - (V_p + V_m) = \dfrac{r_2^3 - r_1^3}{r_3^3} \end{cases}$$

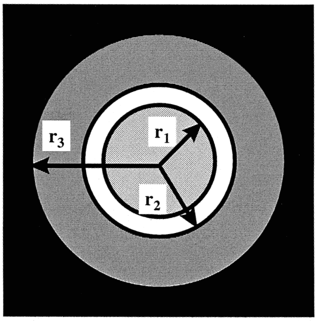

Figure 1:

Illustration of the Representative Volume Element

▨ thermoplastic inclusion
☐ interphase
▨ thermoset matrix
■ equivalent homogeneous medium

Then, as for usual self-consistent schemes, prediction of elastic and the linear viscoelastic properties of the ternary polymer blend is based on the derivation of the elastic strain or stress field in an infinite medium constituted by a three layered inclusion embedded in a matrix submitted to uniform stress or strain at the infinity. All details of the mechanical model were given by Herve and Zaoui$^{5)}$ and Alberola and Mele$^{6)}$. We precise that experimental shear or Young's moduli as well as Poisson's ratios and volume fractions of the various phases are required to carry out such a mechanical modeling.

Results and Discussion

Reverse mechanical modeling was performed by considering as input data the viscoelastic characteristics for pure matrix, pure inclusion, and both "unrefreshed" and "refreshed" blends at three frequencies (0.01, 0.1 and 1Hz) in order to investigate the frequency dependence of the interphase relaxation. To perform the accurate separating of the characteristics of the interphase in a reasonable computer-time, we chose to consider the temperature range from 10°C to 140°C, *i.e.* the temperature range where the interphase relaxation was revealed1). In this temperature range, both thermoset matrix and thermoplastic inclusions are in the glassy state. That is why, Poisson's ratios for vitreous matrix and inclusions were chosen equal to 0.33 and that of the interphase component was chosen equal to 0.50. In so far as Maurer's simulations3) predicted that the location of a "micromechanical transition" depends on the Poisson's ratio of the interphase, we also tested various values for the Poisson's ratio of the interphase ranging from 0.33 to 0.50. No significant change was detected in predicted data which were derived from the reverse mechanical modeling. The last input which is required for the reverse mechanical modeling is the composition of the blend. All numerical results in this work were performed for a volume fraction equal to 0.10 for the thermoplastic inclusions. The effective volume fraction of the interphase component being unknown, the reverse mechanical modeling were performed for volume fractions of interphase equal to 0.015, 0.020, 0.030, 0.050 and 0.070. The volume fraction of the thermoset matrix was then chosen by considering the sum of the volume fractions be equal to 1.

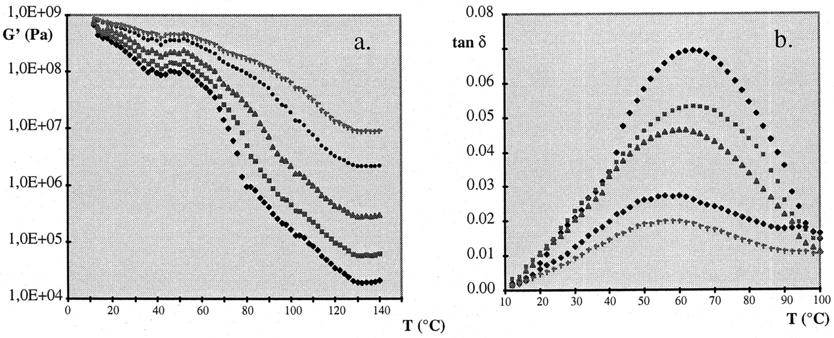

Figure 2: Theoretical viscoelastic characteristics at 1Hz for the *in-situ* synthesized interphase as a function of the effectively considered amount of interphase in the unrefreshed blend. (◆) 1.5% interphase in the blend, (■) 2%, (▲) 3%, (◆) 5% or (+) 7%
a. Storage modulus *versus* temperature **b.** Loss factor tan δ *versus* temperature

Theoretical issues from the reverse mechanical modeling performed at 1Hz for the unrefreshed blend are given in Figure 2. Figures 2a and 2b show the evolution of both predicted storage modulus and predicted loss factor tan δ *versus* temperature for the various contents of interphase. It can be seen in Figure 2a that the storage modulus depends on the value chosen for the volume fraction of the interphase. The higher is the volume fraction of the interphase, the higher are the predicted values of the storage modulus. Nevertheless, whatever the volume fraction of the interphase can be, predicted storage modulus curves follow the same tendency. First, a significant decrease of these values is shown from 10°C to about 130°C. Then, the predicted storage modulus appears constant on average with a slight tendency to increase with temperature. Such a viscoelastic behavior corresponds to that of a rubbery material, which is consistent with chemical composition of the interphase component mainly containing poly(ethylene-co-butene). Figure 2b reveals that the predicted loss factor tan δ shows a maximum and depends on the assumed volume fraction of the interphase. Thus, it can be seen that the magnitude of the peak significantly decreases when the effectively considered volume fraction of interphase increases. Subsequently, the temperature location of the maximum is slightly decreased from 65°C to 58°C for volume fraction ranging from 0.01 to 0.07.

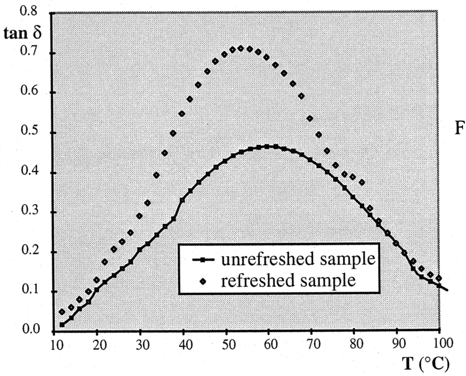

Figure 3: Predicted loss factor tan δ at 1Hz *versus* temperature for the *in-situ* synthesized interphase component in both unrefreshed and refreshed samples.

Figure 3 gives the theoretical loss factor tan δ predicted for both unrefreshed and refreshed blends by considering 5 vol.% of interphase in the reverse mechanical modeling. It can be seen that the magnitude of the relaxation is predicted to be more important from the refreshed blend and its maximum appears at about 5°C below the temperature location of the maximum obtained from the unrefreshed blend. At a constant blend composition, these results suggest a significant increase of the molecular mobility in the interphase area after the refreshing treatment. These theoretical issues from the reverse mechanical modeling are in agreement with our first experimental conclusions(1) while such an increase of the molecular mobility could result from a less dense interphase area.

Lastly, the reverse mechanical modeling was performed at three different frequencies. Subsequently, considering an Arrhenius dependence of the relaxation process, the apparent activation energies (E_a) of the relaxation of the interphase component were estimated at about

114kJ/mol for unrefreshed sample and at 108kJ/mol for the refreshed sample. Accordingly, because of such values are close, it could confirm the self-consistency of the reverse approach.

Conclusion

In this work, a reverse mechanical modeling based on the (n+1) phase self-consistent scheme[5,6)] was successfully applied to investigate the actual viscoelastic characteristics of the interphase in an *in-situ* compatibilized thermoset/thermoplastic blend.

The thermal history of the samples was taken into account and the evolution of the predicted viscoelastic issues revealed a significant increase of the molecular mobility in the interphase area of the refreshed sample.

The reverse mechanical modeling was also performed at different frequencies to investigate the frequency dependence of the predicted relaxation of the interphase component as a function of the thermal history of the samples.

Acknowledgments

The authors would like to thank Dr E. Girard-Reydet from Laboratoire Matériaux Macromoléculaires U.M.R.-C.N.R.S. 5627 - Institut National Sciences Appliquées - LYON - FRANCE - for preparing the samples used in the present work.

References

[1] D. Colombini, G. Merle, J.J. Martinez-Vega, E. Girard-Reydet, J.P. Pascault and J.F. Gerard, *Polymer*, **40**, 4, 935-943 (1999)

[2] H. Eklind, S. Schantz, F.H.J. Maurer, P. Jannasch and B. Wesslen, *Macromolecules,* **29**, 984-992 (1996)

[3] H. Eklind and F.H.J. Maurer, *Polymer*, **37**, 13, 2641-2651 (1996)

[4] D. Colombini, G. Merle, and N.D. Alberola, *J. Macromol. Sci., Phys.,* **B38**, 5 & 6, 957-970 (1999)

[5] E. Herve, and A. Zaoui, *Int. J. Eng. Sci.*, **31**, 1-10 (1993)

[6] N.D. Alberola, and P. Mele, *Polymer Composites*, **17**, 751-760 (1996)