Solid-State Structure and Properties of Poly(ethyl methacrylate)/Phenoxy Blends

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ABSTRACT: Poly(ethyl methacrylate)/poly(hydroxy ether of bisphenol A) (PEMA/phenoxy or PEMA/Ph) blends were obtained by melt mixing to investigate their solid-state characteristics and mechanical properties. The slight structural change from poly(methyl methacrylate) (PMMA) to PEMA spoiled the miscibility of PMMA/Ph blends leading to biphasic PEMA/Ph blends. It is proposed that an antiplasticizer in the case of PEMA, and a low molecular weight component in the case of Ph, as well as minor amounts of each component, migrated to the other phase during melt mixing. The mechanical properties of the blends were good, given that they were biphasic. The modulus of elasticity and yield stress values were found to be additive. Despite the below-additivity ductility values, ductile behavior was observed. The minor amount of the other component in each phase, and the migration of the antiplasticizer of PEMA, are proposed as the main causes of the observed mechanical properties. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 74: 1539–1546, 1999

Key words: poly(ethyl methacrylate); phenoxy; blends; mechanical properties; migration of low molecular weight components

INTRODUCTION

Polymer blending has became the most common way to develop new polymeric materials. With a few exceptions, the majority of the studied and commercialized polymer blends are immiscible, even though complete immiscibility usually gives rise to poor mechanical properties, i.e., incompatibility, unless steps are taken to avoid incompatibility. However, compatibility usually improves in partially miscible blends, and obviously in miscible blends, thus rendering them more commercially blends.

The pendant hydroxyl group of the poly(hydroxy ether of bisphenol A) (phenoxy) (Ph) can interact chemically with groups of other polymers. This gives rise to interactions that have yielded miscible phenoxy blends with, for example, poly(butylene terephthalate),[1–4] poly(ether sulphone),[5,6] polycaprolactone,[7–9] poly(methyl methacrylate) (PMMA),[10–15] Hytrel,[16,17] aliphatic polyesters,[18] water-soluble polyethers,[19] and phenolphthalein-poly(ether ether ketone).[20,21] Partially miscible blends, such as those with polysulphone[22] have also been studied.

With respect to the poly(methacrylate)/phenoxy blends, in a preliminary work[12] on several poly(methacrylate)/Ph blends obtained by solution casting, poly(ethyl methacrylate) (PEMA)/Ph blends appeared with two T_gs close to those of the pure polymers. However, the (PMMA)/Ph blends[10–15] were miscible whatever composition, as observed by the transparency and the existence of a single T_g by DMTA. In these PMMA/Ph blends, although clear decreases in impact

strength were found due to the notch sensitivity of Ph, the modulus of elasticity, the yield stress and the ductility of the blends agreed with the observed miscibility.

The possibility of interactions like those in PMMA/Ph blends also exists in the case of the blends of phenoxy with other methacrylates such as PEMA. This would indicate a tendency to miscibility in these blends, and suggest that the solid-state structure of PEMA/Ph blends warrants further study. Moreover, the study of these blends will show the effect that a slight change in the nature of a component has, both on the miscibility state and on the physical properties of the blends. For these reasons, in this work, PEMA/Ph blends were obtained by melt blending throughout the composition range. The phase structure and the solid-state characteristics of the blends were studied by differential scanning calorimetry (DSC), dynamic mechanical thermal analysis (DMTA), infrared spectroscopy (FTIR), and specific volume measurements. The mechanical properties of the blends were measured by means of the tensile test.

EXPERIMENTAL

PEMA was Elvacite 2042 (DuPont) (inherent viscosity in solution 0.5% weight/volume in methylene chloride at 20°C is 0.83, as declared by the supplier.[23] Phenoxy resin was PKHH (Union Carbide), with a weight average molecular weight of 50,700.[24]

Melt blending was carried out for 12 min (at which time a steady torque was reached) at 30 rpm and 180°C in a Brabender Plasticorder bowl mixer after drying both polymers for at least 12 h at 80°C under vacuum. Rectangular sheets (200 $\times$ 200 $\times$ 1.5 mm) were obtained by compression molding at 150°C using a Schwabenthan Polystat 200 T press, which provided a maximum pressure of 400 bars. The sheets were cooled in air after removing from the press.

Density measurements were carried out by the displacement method in butanol at 23°C. Infrared spectrometry analysis was carried out with a Nicolet Magna-IR 560 equipment. The DSC scans were carried out in a Perkin-Elmer DSC 7 at a heating rate of 20°C/min after quenching. The samples were tested 1 week after specimen preparation.

The samples for dynamic-mechanical analysis were obtained from the central part of the dumb-
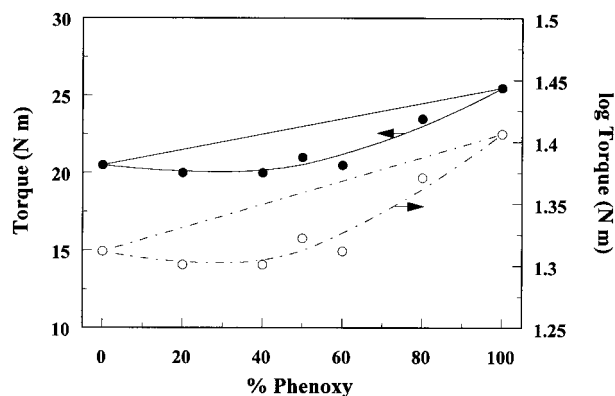

Figure 1 Torque ($\bullet$) (left scale) and log torque ($\circ$) (right scale) needed to mix the blends into the Brabender vs. composition.

bell tensile specimens. The analysis was carried out in a DMTA (Polymer Laboratories) at 1 Hz on samples aged for at least 1 month at room temperature (to study the phase structure under typical conditions of use). The scans were carried out at a constant heating rate of 4°C/min in bending mode from -100°C until the sample became too soft to be tested.

The samples for the tensile tests (ASTM D-638 Type IV) were milled from the compression sheets. The tests were performed at 23°C in an Instron model 4310. A nominal strain rate of 1.3 $\times$ 10^{-3} s^{-1} and an initial length between grips of 64 mm were used. The Young's modulus, yield stress, and break stress and strain were computed from the force-displacement curves.

RESULTS AND DISCUSSION

Solid-State Features

All the melt-processed blends were opaque, both in the melt and solid states. Given the amorphous nature of both components, this suggests the presence of two phases. The torque to mix the blends in the Brabender (which is an indication of viscosity), and the log torque are shown in Figure 1 as a function of blend composition. The torque values of the blends were similar to that of PEMA, with the exception of the 20/80 blend. Thus, the processability of the blends was better than that which might have been expected from the torque behavior of the pure components. With respect to the logarithmic plot, the abrupt change of the log torque values in the 40/60 blend suggests the presence of a PEMA matrix up to the
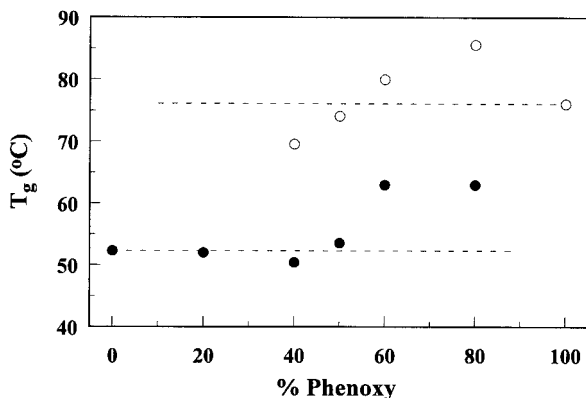
Figure 2 T_gs of the blends by DSC: (○) T_g of the Ph phase, (●) T_g of the PEMA phase.

40/60 blend. This was probably due to the lower viscosity of PEMA that facilitates the encapsulation of the Ph. Moreover, the values of the blends are also well below the linear values. Although the existence of a relationship between the miscibility state and deviations with respect to the linearity of the log viscosity-composition plot has been discussed,[25,26] this torque behavior may be an indication of a lack of interaction between the blend components, which should lead to immiscibility, or at least of an interaction smaller than that which exists between molecules of the pure polymer.

The phase structure of the blends was first studied by DSC. In the DSC plots of the first scan of the blends, the T_g was occluded by the enthalpy relaxation of PEMA. This enthalpy relaxation presence was due to the proximity of the T_g of PEMA (57°C) to room temperature. This enthalpy relaxation appeared, not only in pure PEMA but also in PEMA-rich and intermediate composition blends. Therefore, the phase structure of the blends was studied by DMTA.

The miscibility level of the blends was clearly observed in the second DSC scan. The T_g values by DSC as a function of blend composition are shown in Figure 2. Two T_gs were seen, indicating the presence of two phases at all compositions. The lack of a second T_g value in the case of the 80/20 blend was due to the fact that the position of the second T_g was difficult to determine. The presence of two phases was additionally supported by the lack of change of the low temperature T_g with respect to that of pure PEMA, that would move to higher temperatures if the blend were miscible.

With respect to the T_g values, the high-temperature T_g of the blends, which corresponds to the Ph phase, was higher than that of pure Ph in the Ph-rich compositions. This is unexpected, and cannot be due to presence of PEMA. As in other blends, this T_g behavior is probably due to the migration of low molecular weight component[27–29] from the Ph-rich to the PEMA-rich phase. This was the reason given for the increase in the T_g of Ph-rich phase in other immiscible blends of Ph with a component of lower T_g than that of Ph.[27,28] As might be expected, the increase in the T_g of Ph in its blends was not seen in the case of miscible Ph blends,[4,11,16] and was masked by the presence of the second component when its T_g was higher than that of Ph.[30,31] The values of the high-temperature T_g of the rest of the blends were smaller than that of pure Ph. This indicated the presence of PEMA in the Ph-rich phase.

With respect to the low-temperature T_g of the blends, it increased with Ph content only at the highest levels. This T_g behavior indicates the probable presence in the PEMA-rich phase of the Ph-rich blends of some miscibilized Ph. The structure of this low T_g phase can be better explained using the DMTA results.

The DMTA scans of the blends are shown in Figure 3. As can be seen, the T_gs of PEMA and Ph appear respectively at 86 and 91°C. The relative small difference in the T_gs compared with that
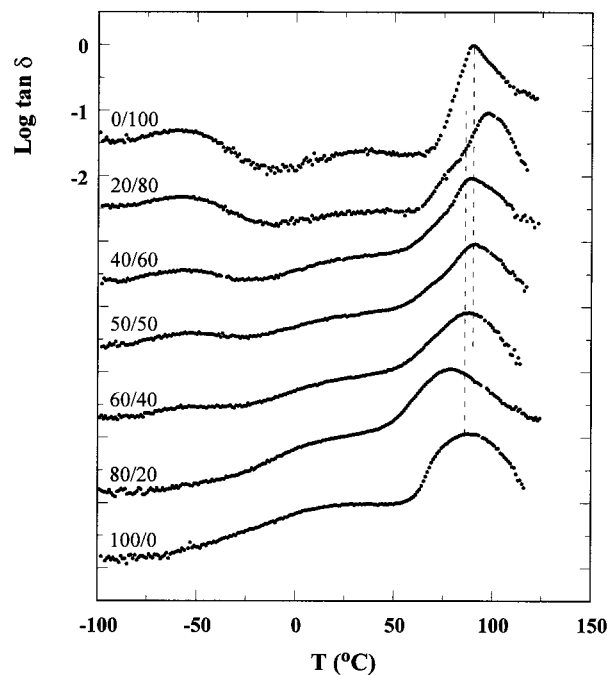

Figure 3 DMTA tan δ plot of the blends and of the pure polymers against temperature. To aid clarity, the curves are shifted on the vertical axis.

which was seen by DSC (52 and 76°C, respectively) is due to the very wide nature of the T_g of PEMA and to the fact that the T_gs by DSC were measured at the maximum slope of transition region. As can be seen, DMTA was not able to discern the miscibility level of the blends due to the proximity of the tan δ peak of the two components. However, the shapes of the peaks and their position can give some information about the phase structure, and were helpful in the discussion of the mechanical properties that were measured under the same solid state conditions.

As can be seen, the high-temperature T_g peak appeared in the 20/80 blend at a temperature higher than that of pure Ph, in agreement with the DSC results. With respect to the T_g peak of pure PEMA, it appeared unusually wide for a pure polymer. This also took place in the blends rich in PEMA. More significantly, this T_g peak appeared at a lower temperature in the case of the 80/20 blend than in the case of pure PEMA. This was a very weak feature in the DSC scans of the blends quenched in the calorimeter (Fig. 2), but in the DMTA results it was much clearer. This shift in the T_g cannot be due to the presence of Ph. It could be due to a change, moisture absorption, for example, during the time elapsed from molding to testing. Alternatively, as in the case of Ph, this shift in the T_g could be due to the migration of a low molecular weight component of PEMA to the Ph during melt mixing.

The possibility of moisture absorption was checked by DMTA scans of the pure PEMA and of the 80/20 blend after drying in vacuum for 5 days. The DMTA scans were the same as those of Figure 3, showing the same peak width in the case of pure PEMA, and the same slip to lower temperatures of the low temperature T_g of the 80/20 blend. This rules out the possibility of moisture absorption as a reason for the observed DMTA behavior.

The presence of a low molecular weight component in the PEMA, which could migrate to the minority Ph-rich phase and would be responsible for the T_g behavior, was studied by dissolving the PEMA in acetone and then precipitating it with methanol to isolate any soluble component of PEMA after solvent evaporation. The nature of the isolated fraction was studied by FTIR, and its spectrum is shown in the upper part of Figure 4. The presence of absorption peaks typical of phthalates points to the presence of an additive or other low molecular weight component in the PEMA. This supports the above-mentioned mi-
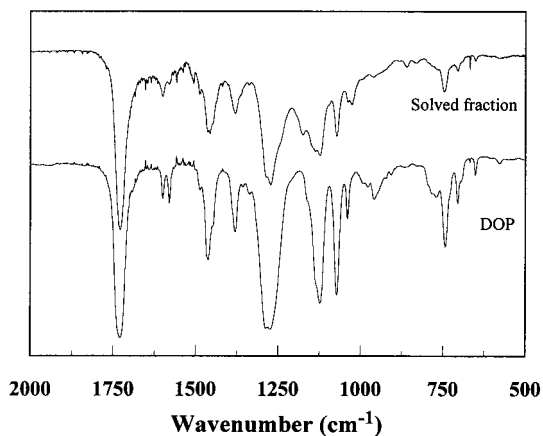

Figure 4 FTIR spectra of the soluble fraction of PEMA and of DOP.

gration of the PEMA additive. The FTIR spectrum is compared in Figure 4 with that of di(2-ethylhexyl) phthalate (DOP), which is a plasticizer often used in thermoplastics. The probable presence of DOP can be inferred because of the similarity of the two spectra.

Finally, the characterization of the solid state of the blends was accomplished by studying the strength of the low temperature secondary transitions. The presence of a miscibilized component can affect, although not always,[7] the strength of these transitions in a different way to the linear change that would appear as an effect of simple dilution.[32–35] In the case of PEMA, a β transition was observed at approximately 20°C. However, this is of little concern due to the proximity of the T_g to room temperature. Therefore, its possible strength variation was not studied. In the case of Ph, its secondary transition (γ) is found by DMTA at roughly −65°C, a temperature at which PEMA did not show any transition. A change in the transition strength should affect the mobility in the solid state, and as a consequence, influence the mechanical properties of the blends.[36] For example, the presence of a polar diluent in amounts as low as 5% can give rise to clear decreases in the strength of the secondary transitions of polymers,[32] including Ph.[37] Moreover, it is known that the presence of a strong γ transition is the reason for the toughness of some glassy amorphous polymers such as PC or Ph.[38] Thus, a change in the γ secondary transition of Ph, which may occur[39] due to the presence in the Ph-rich phase of the additive of PEMA, may affect the mechanical properties of the Ph-rich phase. The γ transition strength of Ph is shown in Figure 5 as
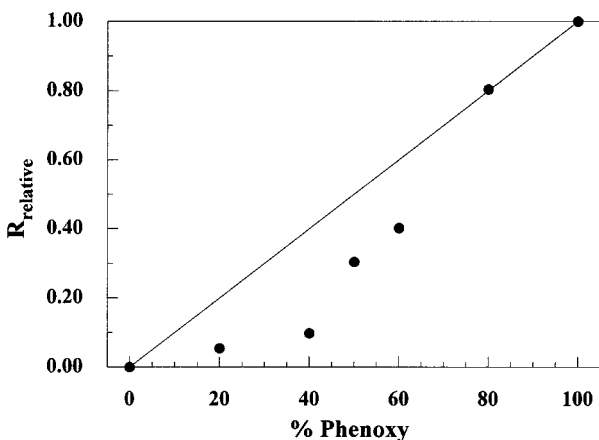
Figure 5 Strength of the secondary transition of Ph in the blends relative to that of pure Ph vs. composition of the blends.

a function of composition. It was calculated by means of[40]

$$R \approx \int_{\text{peak}} \tan \delta \, d\left(\frac{1}{T}\right)$$

and plotted relative to the strength of the γ transition of pure Ph.

As can be seen, the clear deviation from the additivity predicted by the linear rule of mixtures, mainly in blends with high PEMA content, indicates a reduction in the strength of the transition. This must be due to the presence of a miscibilized component in the Ph-rich phase, for example, pure PEMA or the PEMA additive. The low molecular volume of the additive makes the suppression of the γ transition easier than in the case of PEMA. Moreover, as can be seen, the strength of the γ transition of Ph in the 20/80 blend remains unchanged. This points to the additive as the component that produces the γ suppression, because 20% PEMA should be enough to at least slightly modify the γ strength; this being likely in the case of the additive that must be present at a much lower level. This decrease in the γ transition strength will probably influence the deformation ability of the blends as will be seen in the next section.

Thus, the slight chemical structure change from PMMA to PEMA clearly hinders the miscibility with Ph, giving rise to PEMA/Ph blends composed by two amorphous phases. However, taking into account the observed T_g changes, the

presence in each amorphous phase of the another component of the blend, i.e., partial miscibility is inferred. Low molecular weight components are present in both pure polymers. Both of them are able to migrate to the another phase during melt mixing. Their presence in the other phase is relatively most important at low levels of the other component, i.e., in the 80/20 and 20/80 blends. There is a decrease in the γ transition strength of Ph, which is attributed to the migration of the PEMA additive to the Ph-rich phase.

Mechanical Properties

When the tensile tests were carried out on the blends, deformation took place by nonlocalized shear. This was the opposite to that which took place in both the more rigid PMMA and in the PMMA-rich blends with Ph, which deformed by crazing.[10] Necking was only slightly seen in the blends, and was less important in the blends than in the Ph.

The Young's moduli of the blends are shown vs. composition in Figure 6. As can be seen, the moduli of the blends follow the additivity rule between the values of the two pure components. This was with the exception of the 80/20 blend that showed a significant reduced modulus of elasticity and yield stress. This plot of the modulus against composition, as well as that of the yield stress that will be shown later, are very similar to those of PMMA/Ph blends[10] and indicate the lack of influence of the miscibility level on small strain properties.

With respect to the low modulus value of the 80/20 blend, it cannot be due to the γ suppression effect that should give rise to a modulus increase,
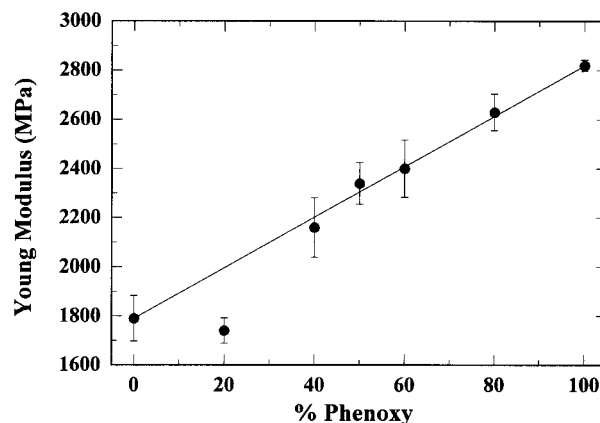

Figure 6 Young's modulus of the blends vs. composition.

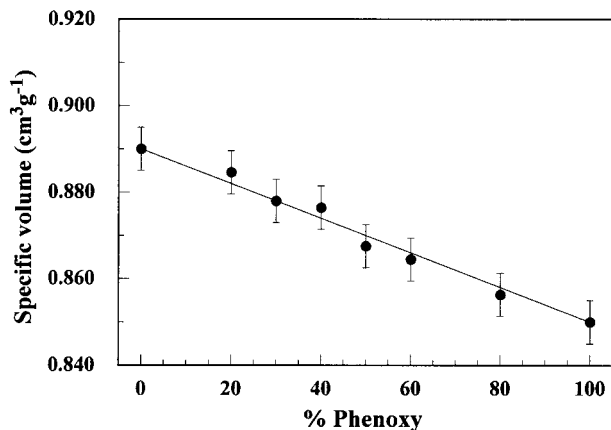**Figure 7** Specific volume of the blends vs. composition.

Figure 8 Yield stress of the blends vs. composition.

so this behavior may be due to (a) change in the specific volume, or (b) migration of the PEMA additive.

With respect to the first possibility, although occasionally it does not take place,[36] the relation between specific volume and modulus is known.[17,41–43] For this reason the specific volume of the blends were measured and are plotted in Figure 7 as a function of composition. As can be seen, the experimental specific volume behavior was additive. This took place, both in the PEMA-rich and Ph-rich sides. No positive deviation was seen in the 80/20 blend, so a change in the specific volume is not the main reason that accounts for the observed modulus behavior. This lack of change in the specific volume values of the blends,[40,44] indicates either that the migration of the two low molecular weight components had not influence on the specific volume, or that it was counteracted by the presence of small amounts of the other blend component. The accuracy of the experimental values of ± 0.003 cm^3 g^{-1} means that these data are significant, because specific volume changes of 0.007 cm^3 g^{-1} have been observed in Ph with plasticizer amounts as low as 2.5%.[32]

Finally, rejecting the possibilities discussed above, the decrease in the modulus of elasticity of the 80/20 blend has to be related with the T_g decrease shown in Figure 3, and with migration of the PEMA additive to the Ph-rich phase. Taking into account that the migration gave rise to a modulus decrease, the additive was acting in PEMA as an antiplasticizer.

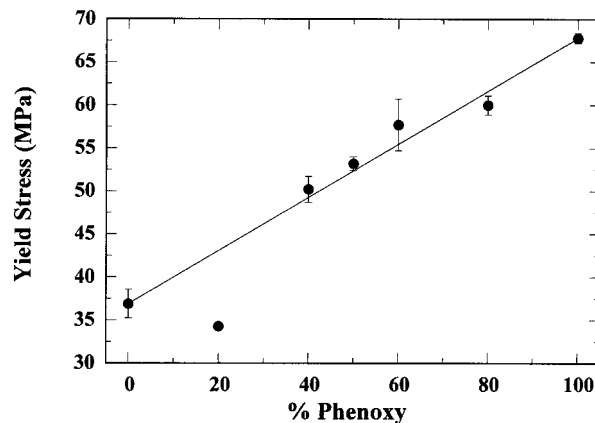The yield stress of the blends is plotted against composition in Figure 8. The plot of the break

stress against composition showed the same features. As can be seen, and as often takes place in polymers[11,45–48] the behavior of the yield stress was very similar to that of the modulus of elasticity. The observed overall additive behavior indicates[49] that the adhesion level is at least enough to withstand the stress and strain associated with yielding. The value of the yield stress of the 80/20 blend agrees with that observed for the modulus of elasticity and will be due to the same structural reasons.

Finally, the ductility values of the blends are shown in Figure 9. As can be seen, with the exception of the 20/80 composition, the values are rather typical of an immiscible blend with below linear break properties. However, all the blends yielded, thus maintaining the ductile nature of the two components. This is not usual in completely immiscible blends because complete immiscibility and γ suppression should yield brittle-
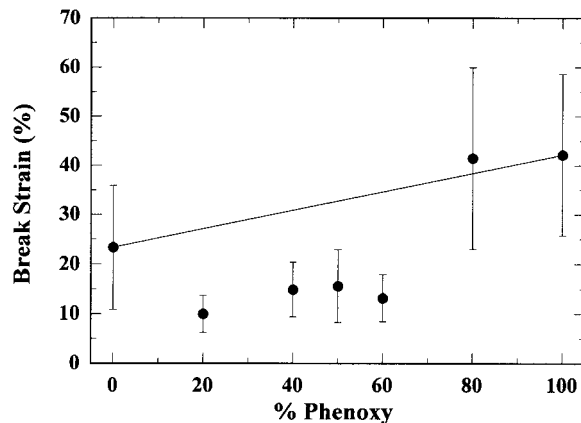

Figure 9 Break strain of the blends vs. composition.

ness. This agrees, however, with the presence, although slight, of the other component in each phase of the blends, that was inferred from the DSC results. This overall behavior of the ductility, although better than average for biphasic blends, contrasts with that observed in PMMA/Ph blends[10] where additive ductility values were seen. Although the additive also plays a role, this ductility behavior shows the effect that the small structural change from PMMA to PEMA has on the ductility of the blends with Ph.

The high ductility value of the 20/80 blend points to the γ suppression of Ph as an additional parameter that influences the ductility behavior. This is because γ suppression (Fig. 5) did not take place in the 20/80 blend, but did take place in the rest of the blends when ductility was less than additive. The negative effect of the suppression of secondary transitions on ductility has been seen in other blends.[17,32,50] In the rest of the blends, the presence of the other main component in each phase has a positive effect on the ductility of the blends. This may not be sufficient to counteract the more important combined negative effects of both the biphasic structure and γ suppression caused by PEMA migration, which overall, yield the below additivity ductility values observed in Figure 9.

CONCLUSIONS

PEMA/Ph blends are composed of a PEMA-rich and a Ph-rich phase, with minor amounts of Ph and PEMA, respectively, in each phase. Moreover, both the antiplasticizer of PEMA, probably DOP, and the low molecular weight component of the Ph, migrate to the other phase during melt mixing, giving rise in the case of the antiplasticizer of PEMA, to a partial suppression of the γ transition of Ph.

Both the modulus of elasticity and the yield stress follow an overall additive behavior, with the exception of the slightly negative value of the 80/20 blend. This is attributed to the migration of the antiplasticizer from the PEMA matrix. The biphasic structure and the suppression effect of the γ transition of Ph by the antiplasticizer of PEMA, appear to be the main reasons for the behavior of the ductility, which is below additivity. However, the blends remained ductile throughout the composition range, probably due to the presence of the other component in the each phase of the blends.

REFERENCES

1. Martínez, J. M.; Eguiazabal, J. I.; Nazabal, J. J Macromol Sci Phys 1991, B30, 345.
2. Robeson, L. M.; Furtek, A. B. J Appl Polym Sci 1979, 23, 645.
3. Eguiazábal, J. I.; Nazábal, J. J Mater Sci 1990, 25, 1522.
4. Martínez, J. M.; Eguiazábal, J. I.; Nazábal, J. J Macromol Sci Phys 1991, B30, 345.
5. Singh, V. B.; Walsh, D. J. J Macromol Sci Phys 1986, B25, 65.
6. Reimers, M. J.; Barbari, T. A. J Polym Sci Part B Polym Phys 1994, 32, 131.
7. de Juana, R.; Hernández, R.; Peña, J. J.; Santamaria, A.; Cortázar, M. Macromolecules 1994, 27, 6980.
8. de Juana, R.; Cortázar, M. Macromolecules 1993, 26, 1170.
9. Defieuw, G.; Groeninckx, G.; Reynaers, H. Polymer 1989, 30, 2164.
10. Erro, R.; Gaztelumendi, M.; Nazábal, J. New Polym Mater 1992, 3, 87.
11. Erro, R.; Gaztelumendi, M.; Nazábal, J. J Appl Polym Sci 1992, 45, 339.
12. Goh, S. H.; Lee, S. Y.; Siow, K. S.; Hong, J. Polym Bull 1993, 30, 691.
13. Kim, B. K.; Choi, C. H. Polymer 1996, 37, 807.
14. Chiou, J. S.; Paul, D. R. J Appl Polym Sci 1991, 42, 279.
15. Soh, Y. S. J Appl Polym Sci 1992, 45, 1831.
16. Gaztelumendi, M.; Nazábal, J. J Appl Polym Sci 1998, 70, 185.
17. Gaztelumendi, M.; Nazábal, J. J Appl Polym Sci, to appear.
18. Harris, J. E.; Goh, J. H.; Paul, D. R.; Barlow, J. W. J Appl Polym Sci 1982, 27, 839.
19. Robeson, L. M.; Hade, W. F.; Merriam, C. N. Macromolecules 1981, 14, 1644.
20. Qipeng, G.; Jinyu, H.; Tianlu, C. Polym Bull 1988, 20, 517.
21. Qipeng, G.; Jinyu, H.; Binyao, L.; Tianlu, C.; Honfang, Z.; Zhiliu, F. Polymer 1991, 32, 58.
22. An, L.; He, D.; Jing, J.; Ma, R.; Jiang, Z.; Kou, X. J Appl Polym Sci 1996, 59, 1843.
23. Elvacite Acrylic Resins, Properties and Uses. DuPont Co. Specialty Resins Division, Wilmington, DE, 1987.
24. Iribarren, J. I.; Iriarte, M.; Uriarte, C.; Iruin, J. J. J Appl Polym Sci 1989, 37, 3459.
25. Utracki, L. A. In Polymer Alloys and Blends. Thermodynamics and Rheology; Hanser: Munich, 1990.
26. Utracki, L. A. In Current Topics in Polymer Science, Volume II, Rheology and Polymer Processing/

Multiphase Systems; Ottembrite, R. M.; Utracki, L. A.; Inoue, S., Eds.; Hanser: Munich, 1987.

27. Choi, C. H.; Kim, B. K. Eur Polym J 1995, 31, 705.

28. Choi, C. H.; Yoon, L. K.; Kim, B. K. J Appl Polym Sci 1996, 60, 779.

29. Greco, R.; Mancarella, C.; Martuscelli, E.; Ragosta, G.; Jinghua, Y. Polymer 1987, 28, 1922.

30. Mondragón, I.; Gaztelumendi, M.; Nazábal, J. Polym Eng Sci 1988, 28, 1126.

31. Mondragón, I.; Remiro, P. M.; Nazábal, J. Eur Polym J 1987, 23, 125.

32. Robeson, L. M. Polym Eng Sci 1969, 9, 277.

33. Butzbach, G. D.; Wendorff, J. H. Polymer 1991, 32, 1155.

34. Butzbach, G.; Wendorff, J. H. Polym Adv Technol 1992, 3, 23.

35. Landry, C.; Henrichs, P. M. Macromolecules 1989, 22, 2157.

36. Maeda, Y.; Paul, D. R. J Polym Sci Part B Polym Phys 1987, 25, 957.

37. Stevenson, W. T. K.; Garton, A.; Wiles, D. M. J Polym Sci Part B Polym Phys 1986, 24, 717.

38. Boyer, R. F. Polym Eng Sci 1968, 8, 161.

39. Jurado, M. J.; Gaztelumendi, M.; Mondragón, I.; Nazábal, J. J Polym Sci Part B Polym Phys 1990, 28, 1015.

40. Kim, C. K.; Aguilar-Vega, M.; Paul, D. R. J Polym Sci Part B Polym Phys 1992, 30, 1131.

41. Barlow, J. W.; Paul, D. R. Polym Eng Sci 1981, 21, 985.

42. Yee, A. F.; Maxwell, M. A. J Macromol Sci Phys 1980, B17, 543.

43. Sánchez, P.; Remiro, P. M.; Nazábal, J. J Appl Polym Sci 1993, 50, 995.

44. Maeda, Y.; Paul, D. R. J Polym Sci Part B Polym Phys 1987, 25, 981.

45. Seitz, J. T. J Appl Polym Sci 1993, 49, 1331.

46. Brow, N. In Failure of Plastics; Breston, W.; Corneliussen, R. D., Eds.; Hanser: Munich, 1986, p. 106.

47. Choi, C. H.; Lee, S. M.; Kim, B. K. Polym Adv Technol 1994, 5, 327.

48. Turek, D. E.; Simon, G. P. Polym Int 1992, 27, 165.

49. Kolarik, J. Polymer 1994, 17, 3631.

50. Robeson, L. M.; Faucher, J. A. J Polym Sci Polym Lett 1969, 7, 35.