

# Effects of the Chemical Structure on the Miscibility Level and Properties of Phenoxy/Polymethacrylate Blends

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**ABSTRACT:** The important effect that even a small change in the nature of the side chain of a component of a blend has in its miscibility level was observed in a series of blends of phenoxy (Ph) with poly(methacrylates). Thus, while the Ph/poly(methyl methacrylate) blends are miscible and the Ph/poly(ethyl methacrylate) blends partially miscible, Ph/poly(butyl methacrylate) blends were almost fully immiscible. The observed miscibility of Ph/poly(butylmethyl methacrylate) indicates that the change in a component of a miscible blend of some pendant units that give rise to miscibility, by those from a different second component, which give rise to immiscibility is less important. The observed decrease in the strength of the  $\beta$  secondary transition of Ph was clearly related to the miscibility level of the blends. The negative effects on properties of a very low molecular weight material can be overcome by blending with a miscible second component, rendering the overall molecular weight of the blend above the critical value. The change in the nature of the side chain, apart from the negative effect on fracture properties such as ductility, also had considerable effect on the short-term mechanical properties such as modulus of elasticity and yield stress. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 77: 2978–2986, 2000

**Key words:** phenoxy; poly(methacrylates); mechanical properties; miscibility; effects of the chemical structure

## INTRODUCTION

The phase structure and properties of polymer blends is an active research field both in the academic and in the industrial worlds.<sup>1,2</sup> Among the polymer blends, those composed by a thermoplastic matrix and a dispersed phase, either rubbery or thermoplastic, are the most common. Of the thermoplastic matrices, phenoxy (Ph) has been widely studied due to the possibility of interac-

tions with the second component that its pendant hydroxyl offers. Thus, the phase structure,<sup>3–14</sup> the reactions<sup>15–23</sup> and the mechanical properties<sup>24–32</sup> of Ph-based blends have been studied.

Of the blends with a Ph matrix, Ph/poly(methacrylate) (PMA) blends have particular interest because Ph is widely used in many kinds of coatings, and the applications of PMA include some barrier and also scuff-resistant coatings that complement those of Ph. Thus, the miscibility of Ph/poly(methyl methacrylate) (PMMA) blends<sup>3,4,33,34</sup> and their mechanical properties have been studied.<sup>34</sup> The miscibility is due<sup>3</sup> to the interactions between the pendant hydroxyl of Ph and the carbonyl groups of the PMMA. The nature of the PMA was slightly changed by means of a longer side chain in blends of

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Ph with poly(ethyl methacrylate) (PEMA).<sup>35</sup> In this case, the presence of plasticizers and of partial miscibility was deduced by dynamic-mechanical analysis (DMTA), and the mechanical properties of the blends measured. It is known that small variations in the molecular structure of one component may cause significant changes in the phase behavior of a polymer blend.<sup>36-44</sup> Thus, it appears interesting to extend the study of the effects of small changes in the molecular structure of the second component with other blends of Ph with PMA. Given that poly(propyl methacrylate) has not been commercialized, the next in the series is poly(butyl methacrylate) (PBMA), which has an ester chain with four carbon units.

The immiscibility of Ph/PBMA was predicted,<sup>45</sup> but only observed at three compositions by DSC<sup>46</sup> along with many other blends. The largest commercially available PMA is that composed by an 82/18 copolymer of methyl methacrylate and butyl methacrylate (PBMMA) whose blends with Ph have not been, to our knowledge, studied previously. Thus, additional work on the phase structure in the full composition range of Ph/PBMA blends and in Ph/PBMMA blends as well as on their mechanical properties is necessary. This would allow the effects that a slight change in the chemical nature of the side group of a component of a miscible blend, has both on the miscibility level of the blend, and also on the mechanical properties to be elucidated.

In this work, Ph/PBMA and Ph/PBMMA blends were mixed in the melt state and then compression molded. The melt behavior of the blends was compared with that of previous Ph/PMA blends and related to their degree of miscibility. The structure of the blends was studied by DMTA and density measurements. The mechanical properties of the blends were measured by means of tensile tests. Both the structure and the properties are discussed with respect to those of the other Ph/PMA blends.

## EXPERIMENTAL

The phenoxy (Ph) resin used was PKHH (Union Carbide). The PBMA and the PBMMA copolymer were Elvacite 2044 and 2013 (DuPont), respectively. The PBMMA had 82% MMA and 18% BMA units. The molecular weight of PBMMA and, as references, those of both the PMMA and the PBMA, were measured in a GPC/SEC chromatograph (Waters ALC/GPC 150C) using THF as

**Table I** Molecular Weights of the Used Polymers

Material	$\bar{M}_n$	$\bar{M}_w$
Phenoxy <sup>a</sup>	18,000	50,800
PBMMA	15,000	30,000
PMMA	63,000	119,000
PBMA	91,000	190,000

<sup>a</sup> From ref. 47.

eluent, relative to polystyrene standards. The calculated molecular weights are shown in Table I.

Prior to mixing, the pellets were dried at 80°C under vacuum for at least for 12 h. The blends were melt mixed in a Brabender Plasticorder during 12 min at 30 rpm. The mixing temperature was 180°C in the case of the Ph/PBMMA blends, and, in the case of the Ph/PBMA blends, it was interpolated in function of composition from 80°C for pure PBMA to 150°C for pure Ph. Compression molding was carried out in a Schwabenthan Polystat 200T press at 150°C in the case of Ph/PBMMA blends, and at the mixing temperature in the case of the Ph/PBMA blends. The sheets obtained were cooled in air.

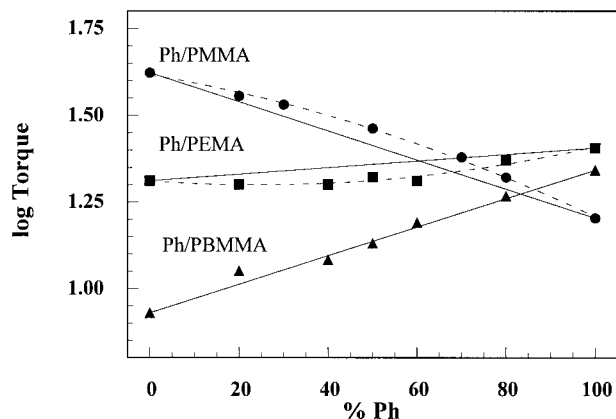
The dynamic-mechanical tests (DMTA) (Polymer Labs.) were carried out in single cantilever mode at 4°C/min and 1 Hz on specimens (15 × 6 × 1.5 mm) obtained from the compression sheets. With the aim of comparison of the DMTA results of the full PMA series, DMTA tests were also carried out under the conditions of Reference 33 on Ph/PMMA specimens.

The tensile tests were carried out on ASTM D-638 type IV specimens obtained by cutting from compression-molded sheets at 23 ± 2°C. The tensile rate was 5 mm/min and 1 mm/min in the case of PBMA and PBMMA, respectively. The Young's modulus, yield stress, and the break stress and strain were obtained from the tensile curve. A minimum of five specimens was tested for each reported value, with the exception of the yield stress value of the 50/50 Ph/PBMMA blends, which corresponds to the single specimen that yielded.

## RESULTS AND DISCUSSION

### Melt State

The Ph/PBMA blends were opaque both in the melt and in the solid state, whatever the compo-



**Figure 1** Log-blending torque against composition: (●) Ph/PMMA, (■) Ph/PEMA, and (▲) Ph/PBMMA.

sition. This proved the presence of two phases in the blends. The Ph/PBMMA blends were transparent in the mixing chamber at 180°C and also in the solid state when fast cooled. However, they became opaque when they were cooled slowly. Taking into account the amorphous nature of both components, this miscibility behavior may be a result of either an entropic contribution or the presence of an UCST. The first possibility can be excluded because of the large molecular weights (Table I) of the components.<sup>1</sup> The determination of the cloud point temperatures associated with the presence of an UCST was attempted both by light microscopy and by visual observations of the blends in the mixing chamber at decreasing temperatures. The determination of the phase separation by light microscopy could not be performed probably as in other works<sup>48</sup> for kinetic reasons. The visual observations of the blends showed that the blends were transparent even at 140°C. The UCST is, therefore, likely to be at lower temperatures. Mixing at temperatures lower than 140°C could not be carried out because of the too high viscosity of the components of the blends.

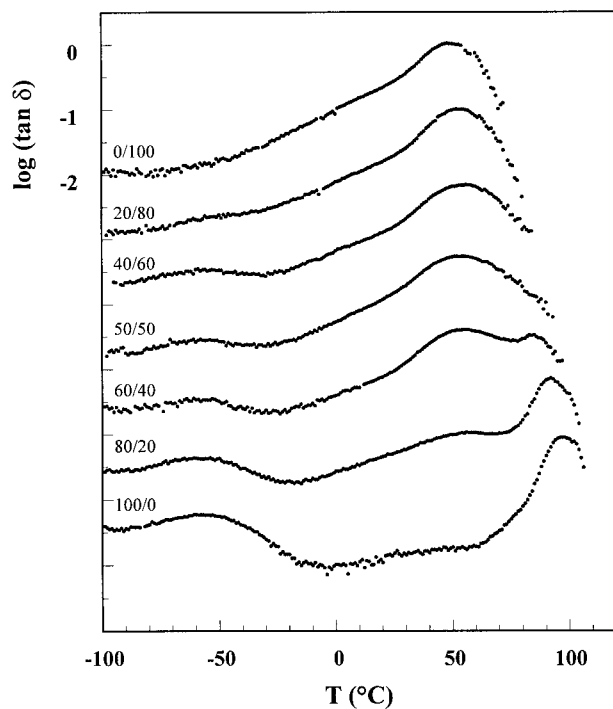
In Figure 1 the semilogarithmic plot of the torque of blending of the Ph/PBMMA blends against composition is shown together with those corresponding to the PMMA and PEMA blends collected from previous works.<sup>33,35</sup> That of the Ph/PBMA blends does not appear because different blending temperatures had to be used to mix the different blend compositions, due to the large  $T_g$  difference between the Ph and the rubbery PBMA. This meant that a torque-composition plot could not be drawn. The small torque difference

between the Ph of the Ph/PEMA blend and that of the Ph/PBMMA blend was due to the slightly different experimental conditions of both works. The large torque difference between the Ph of the Ph/PMMA blend and that of the Ph/PBMMA blend was due to the different blending temperatures used.

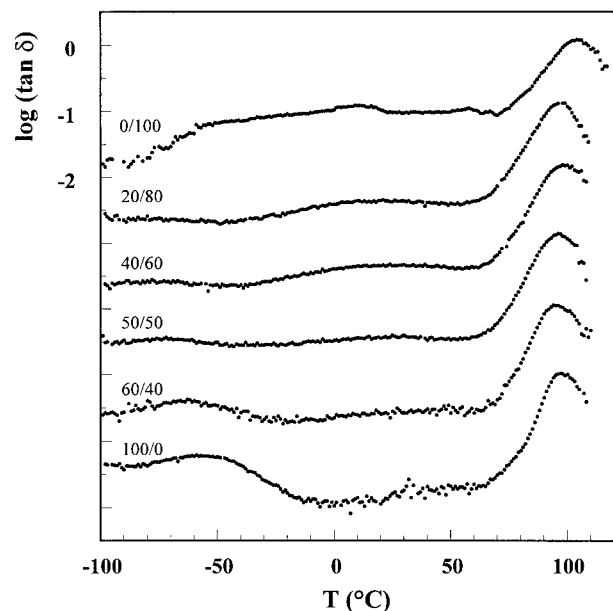
As can be seen in Figure 1, the log torque values of the PBMMA blends of Figure 1 are very close to the additivity tie line. As can also be seen, a clear relation exists in Figure 1 between miscibility level and the position of the blending torque with respect to the additivity tie line. Thus, positive deviations were seen in the case of the miscible Ph/PMMA blends. Values close to the additivity will be seen in the Ph/PBMMA blends, which will appear as less miscible in the next section. Finally, negative deviations were seen in the case of the partially miscible Ph/PEMA blends. This indicates that the interactions between the groups of the two components of the blend that in the solid state gave rise to miscibility, gave rise in the melt state to a higher viscosity for the miscible polymer blend than that predicted by additivity. The existence of a relation between miscibility level and deviation of torque or viscosity from additivity has been discussed.<sup>2,49,50</sup> However, it clearly takes place in these Ph/PMA blends, where the chemical nature of the compared blends are very similar, and most of the processing parameters are the same.

### Miscibility Level

The structure of the blends was studied by DMTA. The  $\tan \delta$  results are shown in Figure 2(a) and 2(b), and the  $T_g$  values from the  $\tan \delta$  peak are collected in Figure 3(a) and 3(b) for the PBMA and PBMMA, respectively. As can be seen in the Ph/PBMA blends of Figures 2(a) and 3(a), the low temperature  $T_g$  was located close to the  $T_g$  of PBMA (55°C), and was independent of the blend composition. This proved the presence of a practically pure PBMA phase. The second  $T_g$  at high temperature was determined only in the blends with a Ph content of at least 50%. This was due to the fact that the PBMA-rich blends become too soft to be analyzed at the likely temperature of the second  $T_g$ . As can be seen, this high temperature  $T_g$  decreased as the PBMA content of the blends increased, reaching an apparent constant value of 85°C in the blends with 50 and 60% Ph content. This is 13°C below the  $T_g$  of pure Ph, thus indicating that some PBMA was present in



(a)



(b)

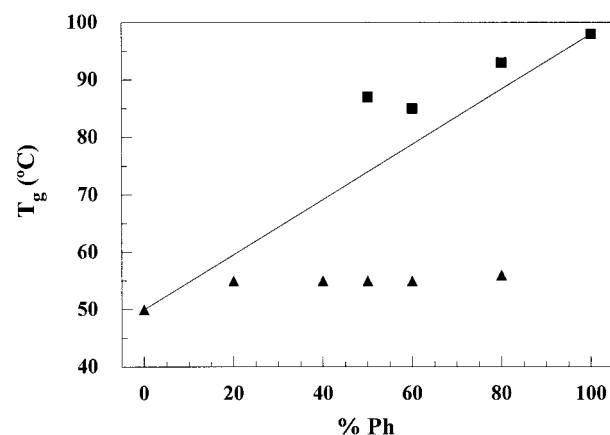
**Figure 2** DMTA  $\log \tan \delta$  vs. temperature of the (a) Ph/PBMA and (b) Ph/PBMMMA blends. To aid clarity, the curves are shifted on the vertical axis.

the Ph-rich phase. Supposing that the Fox equation<sup>51</sup>

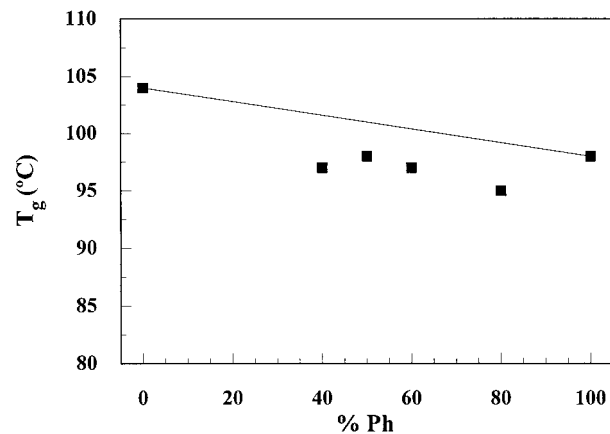
$$\frac{1}{T_g} = \frac{w_1}{T_{g1}} + \frac{w_2}{T_{g2}}$$

held for the Ph-rich phase, an approximate PBMA content of 24% in the Ph-rich phase was calculated.

As can be seen in both Figures 2(b) and 3(b), a single  $\tan \delta$  peak appeared whatever the composition in the Ph/PBMMMA. The 20/80 composition could not be tested due to the extreme fragility of the blend that broke upon testing. The observance of only a  $T_g$ , however, is not indicative of the presence of a single amorphous phase when the  $T_g$ 's of both components are close together. However, as mentioned earlier, all the blend compositions were transparent in the solid state after the fast cooling procedure used. Taking into account that the refraction indices of Ph (1.598)<sup>52</sup> and PBMMMA (1.487)<sup>53</sup> are rather different, the transparency of the blends proved that there is a single amorphous phase, although this might be metastable. Alternatively, there might be a second



(a)



(b)

**Figure 3**  $T_g$  of the (a) Ph/PBMA blends [(●) high temperature  $T_g$ , (▲) low temperature  $T_g$ ] and of the (b) Ph/PBMMMA blends (■).

phase, smaller than the wavelength of visible light, i.e., approximately  $0.1 \mu\text{m}$ .<sup>54</sup>

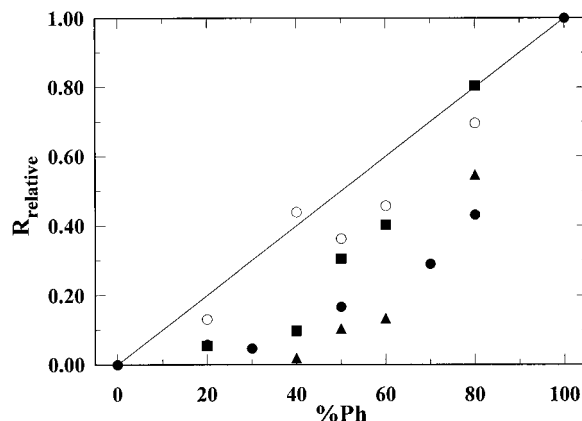
Thus, there is a clear influence on the miscibility level of the Ph/PMA blends of the length of the side chain close to the carbonyl group of the PMA's. This is because Ph/PMMA blends are miscible.<sup>33</sup> Ph/PEMA blends are biphasic,<sup>35</sup> but both components are present in the two amorphous phases. Only three additional methylene groups in the side chain of the PMMA make the Ph/PBMA blends almost immiscible, giving two almost pure amorphous phases. The presence as a copolymer of some pendant side chains of an immiscible second component, however, has a minor influence, as Ph/PBMA blends are miscible in the melt state and give a metastable but monophasic structure upon fast cooling.

### Secondary Transitions

As can be seen in Figures 2(a) and 2(b), and as proper to Ph, a strong  $\beta$  secondary transition, well known in pure Ph, appeared at roughly  $-50^\circ\text{C}$ . It also appeared in the case of the blends in Figure 2(a) and 2(b). In the case of the Ph/PBMA blends of Figure 2(a), the  $\beta$  transition strength was rather proportional to the Ph content of the blends, so the transition strength decrease was due to the dilution effect, and there was no suppression induced by the presence of the second component. However, in the case of Ph/PBMA blends, the  $\beta$  transition disappeared rapidly when the Ph content of the blends decreased.

As is well known,<sup>55-58</sup> the presence of a miscibilized component in one phase of a polymer blend may give rise to a decrease in the strength of the low temperature  $\beta$  transition of the component when it exists and is important enough. A miscibilized component does not always decrease the  $\beta$  transition strength,<sup>55</sup> but provided it takes place, and supposing that other parameters such as thermal treatment do not change, the presence of a miscibilized component would be proved.

In the case of Ph, as in PC, it is known that the  $\beta$  transition strength decrease takes place both in the case of miscible,<sup>58</sup> and also in the case of partially miscible blends.<sup>35</sup> In the case of Ph/PMMA blends [as in the Ph/PBMA blends of Fig. 2(b)], the DMTA results obtained under the same conditions of reference 33 but from  $-100^\circ\text{C}$ , showed that a clear decrease in the  $\beta$  transition strength took place. Although the plasticizer presence may also have an influence, this secondary transition strength decrease also took place in



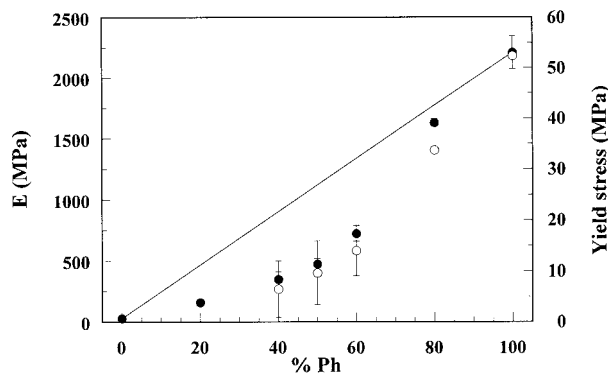
**Figure 4** Strength of the secondary transition of Ph in the blends relative to that of the pure Ph against composition of the blends. (●) Ph/PMMA, (■) Ph/PEMA, (▲) Ph/PBMA, and (○) Ph/PBMA.

the case of partially miscible Ph/PEMA blends.<sup>35</sup> However, it was very weak in the immiscible Ph/PBMA blends. This clearly suggests a relationship between the importance of the presence of a miscibilized second component and that of the  $\beta$  transition strength decrease. For these reasons, in Figure 4 the quantitative values of the strength of the  $\beta$  transition of Ph in the blends relative to that of pure Ph are plotted against the composition for the Ph/PBMA, Ph/PBMA, and Ph/PEMA blends, together with those of the Ph/PEMA blends taken from ref. 35. As can be seen, in the fully immiscible Ph/PBMA (empty circles) of Figure 4, the trend is rather close to the additivity tie line, so no decrease in the  $\beta$  transition strength decrease took place. In the partially miscible Ph/PEMA blends (squares) the suppression was seen only in PEMA-rich blends. However, in the case of the miscible Ph/PBMA blends (triangles), the  $\beta$  transition of Ph almost disappears at a PBMA content of only 40%. In the most miscible Ph/PMMA this transition was not seen in PMMA-rich blends, and was very weak at the other compositions.

As can also be seen, the strength decrease was maximum when the Ph content of the blend was minimum corresponding to the maximum possibility for the Ph to be saturated in PMMA. Such a decrease in the maximum strength also took place in the case of the blends with PEMA, but could not be observed at all in the cases of these immiscible Ph/PBMA blends.

Thus, there is a clear relation between the presence of a miscibilized component and the reduction in strength of the  $\beta$  transition. This de-





**Figure 5** Mechanical properties of the Ph/PBMA blends: (●) modulus of elasticity, (○) yield stress.

crease in the transition strength may inform about the composition of a blend phase when the  $T_g$  cannot be observed, for example, due to the crystallization or to the superposition of the  $T_g$  of another component.

### Mechanical Properties

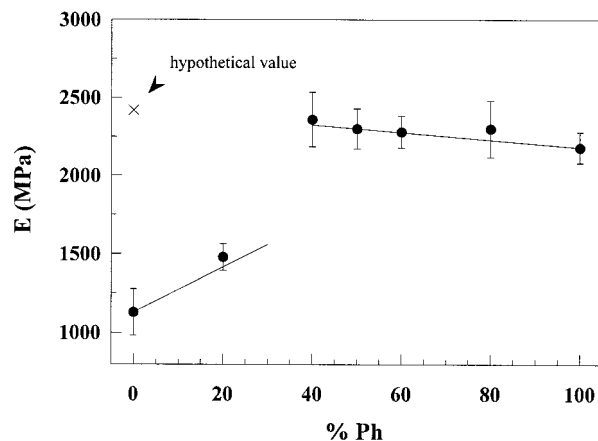
The modulus of elasticity and the yield stress of the immiscible Ph/PBMA blends are shown against composition in Figure 5. As can be seen, both plots show clear negative deviations from the additivity tie line. This is not usual in polymer blends, more so in the case of the modulus of elasticity, because values close to additivity are often seen even in fully immiscible blends.<sup>43,59,60</sup> However, additivity is not as usual in blends with a soft component<sup>57,58</sup> as in PBMA, where the large difference between the modulus of both phases leads to deformation to concentrate in the more deformable rubbery phase. This would give rise to clear negative deviations from the additivity tie line.

With respect to the Ph/PBMMA blends, their moduli of elasticity are collected in Figure 6. As can be seen, it showed an unexpected behavior. Most of the values increased when the Ph content decreased, instead of decreasing towards the values of the PBMMA. The fact that this behavior did not take place only in the case of the 20/80 blend, very rich in PBMMA, suggests that PBMMA is responsible for the observed behavior. As stated in the Experimental section, the molecular weight of the PBMMA was low, below the critical molecular weight of PMMA (31,000)<sup>61</sup> for the entanglements to be effective. This may be the reason for the behavior of Figure 6 because the negative effect of a low molecular weight in the

mechanical properties is well known.<sup>62</sup> Moreover, if a hypothetical value of the modulus of elasticity of a high molecular weight PBMMA were calculated as a linear combination of those of PMMA (2940 MPa, ref. 34), and PBMA (29 MPa, this work), and the composition of the copolymer (82% PMMA and 18% PBMA), it would be approximately 2420 MPa. When this value was plotted in Figure 6 (cross in the vertical axis), we realized that the modulus of elasticity of the blends followed the expected additivity tie line, but between the values of Ph and that of the calculated of PBMMA. This indicated that the low modulus of the 20/80 blend was due to the fact that the Ph content was not large enough to be able to increase the overall molecular weight of the miscible blend to a value above the critical value.

In the case of the yield stress of the blends, the PBMMA-rich compositions did not yield due to the extreme fragility (break stress = 0.3 MPa, break strain = 0.6%) of the PBMMA. The yield stress of the Ph-rich and 50/50 compositions followed, and were slightly above the yield stress values, calculated in a way similar to that of modulus of elasticity.

The ductility of the Ph/PBMA blends was clearly below the tie line connecting the values of the two pure components due to the almost total immiscibility of the blends. It was very low in the case of the Ph/PBMMA blends where ductility decreased from 52% in Ph to below 5% at most compositions. This was due to the important effect of low molecular weight on fracture properties such as ductility. The differences in ductility



**Figure 6** Modulus of elasticity of the Ph/PBMMA blends. (X) Hypothetical value corresponds to the pure PBMMA taking into account its composition and the properties of the pure PMMA and PBMA.

**Table II** Deviation from the Additive Values of the  $\beta$ -Transition Strength Decrease and of the Ductility of the PMA Blend

	Composition	Ductility Deviation (%)	Deviation in the Transition Strength Decrease (%)
Ph/PMMA	100/0	0	0
	80/20	+6	46
	70/30	+6	59
	50/50	+18	67
	30/70	-6	81
	20/80	-5	71
	0/100	0	0
Ph/PBMA	100/0	0	0
	80/20		32
	60/40		78
	50/50		79
	40/60		95
	0/100		0
	Ph/PEMA	100/0	0
	80/20	+32	0
	60/40	-74	33
	50/50	-57	39
	40/60	-54	75
	20/80	-85	73
	0/100	0	0
Ph/PBMA	100/0	0	0
	80/20	-71	13
	60/40	-92	24
	50/50	-86	27
	40/60	-84	-9
	20/80	-25	34
	0/100	0	0

The deviation values are relative to those of the correspondent additive values.

between the measured values and those based on the linear contribution of each pure component are collected in Table II for both the Ph/PBMA blends and the Ph/PMMA and Ph/PEMA blends. The values are given as a percentage of the corresponding additive value. Positive values indicate positive deviations from additivity. The ductility values of the Ph/PBMA blends have the additional influence of the low molecular weight of the copolymer, so they are not included. Besides the miscibility level, the decrease in the  $\beta$  transition strength also gives rise usually to a decrease in ductility, due to the smaller flexibility of the polymer chain. Hence, the relative reduction in strength is also collected in Table II.

The quantitative effect of the miscibility level on the ductility values is clear. An overall slight positive deviation appears in Ph/PMMA blends, an overall clear negative deviation in Ph/PEMA

blends, and a very negative deviation is found in the immiscible Ph/PBMA blends. The correlation between miscibility and the decrease in the  $\beta$  transition strength was seen in Figure 4, and is also clear in Table II. Moreover, the negative influence of this decrease on ductility is also seen in Table II. This is because, for each blend, leaving out the miscibility level, the relationship between important decreases in the  $\beta$  transition strength and low ductility values is clear. Finally, when the three Ph/PMA blends are compared, the highest ductility values take place when the decrease in strength is maximum, i.e., in the Ph/PMMA blends, and the lowest ductility values when this decrease is minimum, i.e., in Ph/PBMA blends. This clearly shows the larger effect of miscibility level on ductility compared with that of the decrease in the strength of the  $\beta$  transition.

## CONCLUSIONS

A chemical modification in the molecule of a component responsible for miscibility is very relevant for miscibility, even if this modification occurs at the end of a side chain where the steric hindrance should be lower. Thus, the chemical changes associated to a varying number of methylene units drastically change the miscibility level of Ph/PMA blends. However, when the chemical structure of PMMA is changed by means of the presence of up to roughly a 18 wt % of the lateral units of PBMA, which are responsible for immiscibility, the blends remain miscible.

There is a clear correlation between the miscibility level, i.e., maximum amount of PMA miscible in Ph and the importance of the decrease in the  $\beta$  transition strength. This gives rise to the disappearance of the  $\beta$  transition in some of the miscible Ph/PMMA compositions, whereas it is proportional to the Ph content at most of the compositions of the almost fully immiscible Ph/PBMA blends.

The mechanical properties showed important decreases as miscibility decreased, even in the case of short-term properties such as the modulus of elasticity or the yield stress. Finally, the negative effect on mechanical properties of a molecular weight below the critical value can be nullified by means of the addition of a miscible second component, due to the increase of the mean molecular weight of the miscible blend above the critical value.

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## REFERENCES

- Paul, D. R.; Newman, S. *Polymer Blends*; Academic Press: Orlando, FL, 1978.
- Utracki, L. A. *Polymer Alloys and Blends*; Hanser: Munich, 1989.
- Soh, Y. S. *J Appl Polym Sci* 1992, 45, 1831.
- Chiou, J. S.; Paul, D. R. *J Appl Polym Sci* 1991, 42, 279.
- Robeson, L. M.; Furtak, A. B. *J Appl Polym Sci* 1979, 23, 645.
- Robeson, L. M.; Hale, W. F.; Merriam, C. N. *Macromolecules* 1981, 14, 1644.
- Chong, Y. F.; Goh, S. H. *J Appl Polym Sci* 1992, 44, 633.
- Seymour, R. W.; Zehner, B. E. *J Polym Sci Part B Polym Phys* 1980, 18, 2299.
- Qipeng, G.; Keshi, S.; Tianru, F.; Yuchen, Q.; Zhiliu, F. *J Appl Polym Sci* 1993, 48, 547.
- Jo, W. H.; Kim, J. Y.; Lee, M. S. *J Polym Sci Part B Polym Phys* 1994, 32, 1321.
- Etzeberria, A.; Uriarte, C.; Fdz-Berridi, M. J.; Iruin, J. J. *Polymer* 1994, 35, 2128.
- Coleman, M. M.; Yang, X.; Painter, P. C. *Macromolecules* 1994, 25, 4414.
- Espí, E.; Alberdi, M.; Fdz-Berridi, M. J.; Iruin, J. J. *Polymer* 1994, 35, 3712.
- Alberdi, M.; Espí, E.; Fdz-Berridi, M. J.; Iruin, J. J. *Polym J* 1994, 9, 1037.
- Chen, S.; Chang, F. *J Appl Polym Sci* 1994, 51, 955.
- Woo, E. M.; Yau, S. N. *J Polym Sci Part A Polym Chem* 1997, 35, 97.
- Gaztelumendi, M.; Nazábal, J. *J Appl Polym Sci* 1998, 70, 185.
- Mondragón, I.; Gaztelumendi, M.; Nazábal, J. *Polym Eng Sci* 1988, 28, 1126.
- Mondragón, I.; Remiro, P. M.; Nazábal, J. *Eur Polym J* 1987, 23, 125.
- Mondragón, I.; Gaztelumendi, M.; Nazábal, J. *Polym Eng Sci* 1986, 26, 1478.
- Mondragón, I.; Nazábal, J. *J Mater Sci Lett* 1987, 6, 698.
- Eguiazábal, J. I.; Cortázar, M.; Iruin, J. J.; Guzmán, G. M. *J Macromol Sci-Phys* 1988, B27, 19.
- Yuan, Y.; Ruckenstein, E. *Polymer* 1998, 39, 1893.
- Choi, C. H.; Lee, S. M.; Kim, B. K. *J Macromol Sci-Phys* 1994, B33, 317.
- Martínez, J. M.; Eguiazábal, J. I.; Nazábal, J. *J Macromol Sci-Phys* 1991, B30, 345.
- Qipeng, G.; Jinyu, H.; Binyao, L.; Tianlu, C.; Hongfang, Z.; Zhiliu, F. *Polymer* 1991, 32, 58.
- An, L.; He, D.; Jing, J.; Ma, R.; Jiang, Z.; Kou, X. *J Appl Polym Sci* 1996, 59, 1843.
- Choi, C. H.; Yoon, L. K.; Kim, B. K. *J Appl Polym Sci* 1996, 60, 779.
- Kim, B. K.; Choi, C. H. *J Macromol Sci-Phys* 1996, B35, 129.
- Kim, B. K.; Choi, C. H. *Polymer* 1996, 37, 807.
- Choi, C. H.; Kim, B. K. *Eur Polym J* 1995, 31, 705.
- Lee, S. M.; Choi, C. H.; Kim, B. K. *Eur Polym J* 1994, 30, 993.
- Erro, R.; Gaztelumendi, M.; Nazábal, J. *New Polym Mater* 1992, 3, 87.
- Erro, R.; Gaztelumendi, M.; Nazábal, J. *J Appl Polym Sci* 1992, 45, 339.
- Erro, R.; Gaztelumendi, M.; Nazábal, J. *J Appl Polym Sci* 1999, 74, 1539.
- Fernandes, A. C.; Barlow, J. W.; Paul, D. R. *Polymer* 1986, 27, 1799.
- Cruz, C. A.; Barlow, J. W.; Paul, D. R. *J Appl Polym Sci* 1979, 23, 589.
- Cruz, C. A.; Barlow, J. W.; Paul, D. R. *J Appl Polym Sci* 1979, 24, 2101.



39. Shaw, M. T. *J Appl Polym Sci* 1974, 18, 449.
40. Fernandes, A. C.; Barlow, J. W.; Paul, D. R. *Polymer* 1986, 27, 1788.
41. Kunori, T.; Geil, P. H. *J Macromol Sci-Phys* 1980, B18, 93.
42. Keitz, J. D.; Barlow, J. W.; Paul, D. R. *J Appl Polym Sci* 1984, 29, 3131.
43. Fowler, M. E.; Barlow, J. W.; Paul, D. R. *Polymer* 1987, 28, 1177.
44. Ahn, T. O.; Lee, M.; Jeong, H. M.; Cho, K. *J Polym Sci Part B Polym Phys* 1998, 36, 201.
45. Coleman, M. M.; Graf, J. F.; Painter, P. C. In *Specific Interactions and the Miscibility of Polymer Blends*; Technomic Publishing Inc.: Lancaster, PA, 1991.
46. Goh, S. H.; Lee, S. Y.; Siow, K. S.; Hong, J. *Polym Bull* 1993, 30, 691.
47. Uriarte, C.; Eguiazábal, J. I.; Llanos, M.; Iribarren, J. I.; Iruin, J. J. *Macromolecules* 1987, 20, 3038.
48. Kwei, T. K.; Wang, T. T. In *Polymer Blends*; Paul, D. R.; Newman, S., Eds.; Academic Press: Orlando, FL, 1978.
49. Utracki, L. A. *Polym Eng Sci* 1983, 23, 602.
50. Jurado, M. J.; Mondragón, I.; Nazábal, J. *Rev Plást Mod* 1987, 370, 487.
51. Fox, T. G. *Bull Am Phys Soc* 1956, 1, 123.
52. Singh, V. B.; Walsh, D. J. *J Macromol Sci-Phys* 1986, B25, 75.
53. Van Krevelen, D. W. In *Properties of Polymers*; Elsevier Sci. Pub.: Amsterdam, 1976.
54. MacKnight, W. J.; Karasz, F. E.; Fried, J. R. In *Polymer Blends*; Paul, D. R.; Newman, S., Eds.; Academic Press: Orlando, FL, 1978.
55. de Juana, R.; Hernández, R.; Peña, J. J.; Santamaria, A.; Cortázar, M. *Macromolecules* 1994, 27, 6980.
56. Kim, C. K.; Aguilar-Vega, M.; Paul, D. R. *J Polym Sci Part B Polym Phys* 1992, 30, 1131.
57. Gaztelumendi, M.; Nazábal, J. *Polym Eng Sci*, to appear.
58. Gaztelumendi, M.; Nazábal, J. *J Appl Polym Sci* 1999, 72, 85.
59. Eguiazábal, J. I.; Nazábal, J. *Plast Rubber Proces Appl* 1990, 14, 211.
60. Butzbach, G.; Wendorff, J. H. *Polym Adv Technol* 1992, 3, 23.
61. Graesley, W. W.; Edwards, S. T. *Polymer* 1981, 22, 1329.
62. Martínez, J. M.; Eguiazábal, J. I.; Nazábal, J. *J Macromol Sci-Phys* 1995, B34, 171.