

# Effects of Injection Temperature on the Mixing Level and Properties of Injection-Mixed PMMA–Phenoxy Blends

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## SYNOPSIS

Polymethyl methacrylate–phenoxy blends have been obtained in an injection machine at different injection temperatures in order to determine the possibility of direct blending in these processing machines and also the effect that different blending levels have in the mechanical properties of these miscible blends. High injection temperatures, but in the range used in production of the components, provided fairly well homogenized blends comparable both in transparency and mechanical properties to those obtained by kneading and subsequent compression molding. Very good mechanical properties, although less transparent, were obtained when processing at low injection temperatures.

## INTRODUCTION

Polymer blending is one of the most common techniques employed for developing new polymeric materials. Blending may be carried out by solution of both components in a common solvent and subsequent precipitation; but if the purpose of the work is not only scientific, it is usually carried out by mixing in the melt state. Different machines for blending in the melt state may be used depending on the nature and state of aggregation of the materials to be mixed. In the case of blends of thermoplastics, a two-roll mill may be used. But twin or single-screw extruders for continuous production, or kneading twin counterrotating batch mixers for discontinuous production, are also widely used.

Although blending provides a fast and inexpensive way to develop and produce new polymeric materials as compared to development of new formulations, it usually needs a premixing before molding by any of the different molding methods available today. This premixing, usually carried out by kneading or extrusion, makes the mixing process longer and more expensive than if it were done in a single step. Thus, it seems quite interesting to test

the blending level achieved if blending were directly made in the processing equipment and the effect that processing parameters, such as processing temperature, would have on the achieved blending level.

Injection molding is the method most widely used in the production of plastic products and is generally<sup>1,2</sup> used in combination with previous kneading or extrusion. For the reasons mentioned, in this work blending has been carried out directly in an injection machine at different injection temperatures in order to discover the obtained mixing level and the effect that injection temperature has on the mixing level and on the properties of the obtained products. With this aim in mind, injection temperature was changed from the lowest temperature available in the injection machine due to the viscosity increase of the blend to the maximum temperature compatible with an undegraded product.

With the aim of producing, if possible, the widest miscibility change, two miscible polymers should be chosen. Moreover, in order not to have too great a viscosity difference between the two components of the blend, both polymers should be amorphous and, if possible, there should not be too great a difference between the  $T_g$ 's of the components.

The polymethyl methacrylate–phenoxy (PMMA–phenoxy) blends, recently recognized as miscible,<sup>3,4</sup> fulfill the conditions mentioned. Thus PMMA–

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phenoxy blends have been obtained in this work at different injection temperatures. The mixing level obtained has been followed by means of the change in the  $T_g$ 's of the components, and the  $T_g$ 's were obtained by dynamic mechanical tests. The influence of injection temperature in the tensile and impact properties has also been measured. Finally, previously mixed compression-molded specimens, which are known<sup>5</sup> to give rise to a poorer mechanical compatibility due to processing than the injected specimens, have been also obtained in order to compare their behavior with that of injection-molded specimens.

## EXPERIMENTAL

The two polymer samples used in this work were both commercial grades. Polymethyl methacrylate was DIAKON CMH 454/L (I.C.I.), with a weight average molecular weight determined by gel permeation chromatography of about 120,000. Phenoxy resin was PKHH with a molecular weight of 50,700<sup>6</sup> manufactured by Union Carbide and kindly supplied by Quimidroga S.A. (Barcelona, Spain).

Most of the blends were prepared in a Battenfeld BA 230 E injection machine after drying for at least 14 h at 80°C under vacuum in order to blend the two polymers and also to obtain the desired specimens for mechanical tests. The screw of the plastification unit of the machine was a standard screw with diameter of 18 mm,  $L/D$  of 17.8, compression ratio of 4, helix angle 17.8°. No mixing devices were present. Five barrel temperatures were used to reach different levels of homogenization of the blends: 180, 200, 220, 240 and 260°C. The temperatures of the melt after plastification just ahead of the nozzle for the two pure materials, measured by means of a thermocouple inserted in the melt, are shown in Table I. High PMMA viscosity made it impossible to use plastification temperatures lower than 180°C

**Table I** Temperature of the Melt for Pure Polymers at Different Barrel Temperatures

Barrel Temp. (°C)	PMMA Melt Temp. (°C)	Phenoxy Melt Temp. (°C)
180	198	204
200	209	213
220	229	228
240	240	243
260	261	260

and degradation problems with PMMA gave us the upper bound temperature.

Blends were also prepared after drying, by melting the components in the desired composition in a Brabender bowl mixer at 200°C. Afterward, specimens 0.5 mm thick were obtained by compression molding using a Schwabenthan Polystat 200T press, which provided a maximum pressure of 400 bars that was maintained for 3 min. The sheets obtained were cooled by submerging them in water at about 12°C. A minimum of seven tensile test specimens were punched out from the sheets. The different geometry of the compression-molded specimens and the high pressure involved in compression molding makes full comparison of the data difficult.

The molded tensile test specimens were ASTM D638 Type IV. The tests were carried out at room temperature (23°C) by an Instron machine model 1190. A nominal strain rate of  $2.6 \times 10^{-4}$ /s and an initial length between grips of about 64 mm were used. Young's modulus, nominal yield stress, and break stress and strain were computed from the force-displacement curves. A minimum of ten specimens were tested for each reported value. The average standard deviation were 85 MPa, 1 MPa, 2 MPa, and 4%, respectively.

Izod impact testing was carried out in a CEAST 6545/00 pendulum with a 25 J hammer on ASTM D256 specimens prepared by injection molding and notched after processing. Plots of force versus time were obtained by means of an AFS/MK3 device and impact resistance was calculated from them. A minimum of eight specimens were tested for each reported value.

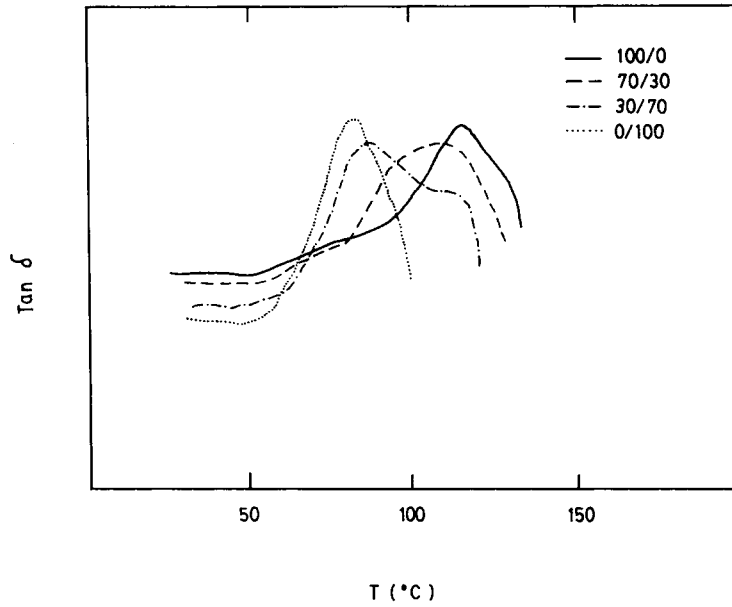
Dynamic mechanical analysis was carried out in a dynamic mechanical thermal analyzer (DMTA) from Polymer Laboratories at 1 Hz. The scans were carried out at a constant heating rate of 4°C/min in bending mode from -130°C until the sample became too soft to be tested.

Scanning electron microscopy was carried out on the gold-coated fracture surface of tensile specimens with a Jeol JSM-35C scanning microscope at 25 kV.

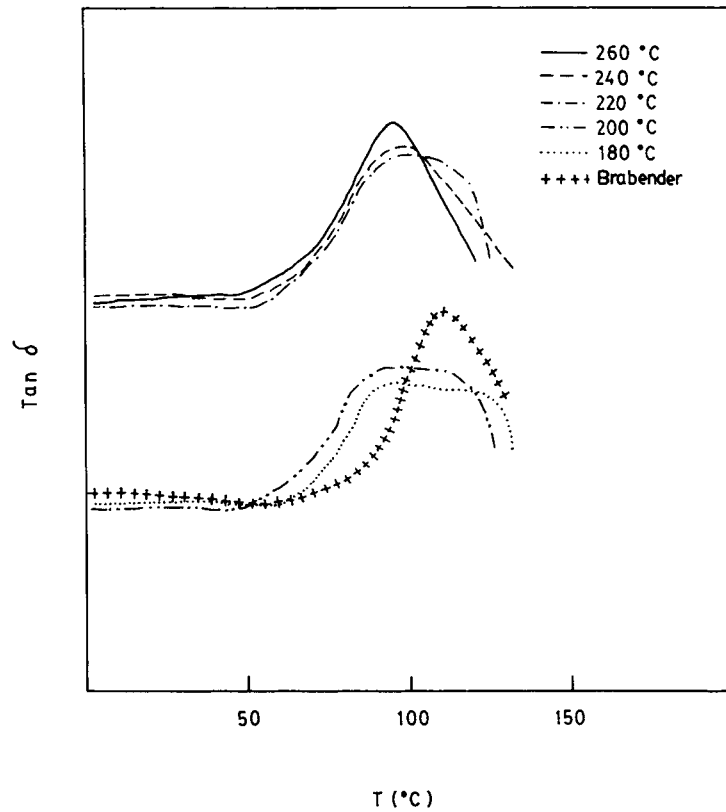
## ATTAINED LEVEL OF MIXING

The attained level of mixing was followed by  $T_g$  measurements of the blends obtained by dynamic mechanical testing and also by the observance of the transparency of the blends.

In Figure 1 the  $T_g$  region of the pure materials and that of the 70/30 and 30/70 PMMA-phenoxy blends obtained at 180°C, that is, at the lowest tem-



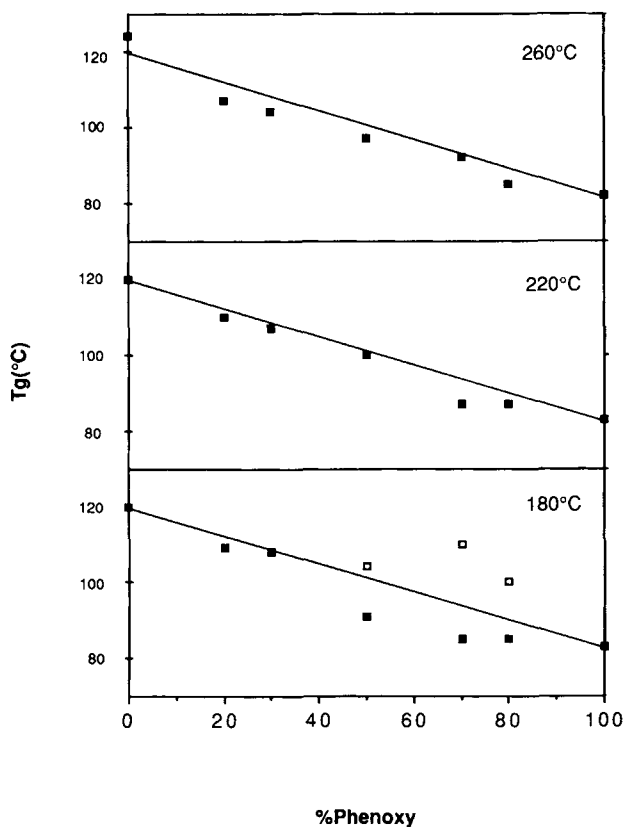
**Figure 1** Log tan  $\delta$  versus temperature for 100/0 (—), 70/30 (— —), 30/70 (- · -), and 0/100 (· · · · ·) PMMA-phenoxy blends injected at 180°C.



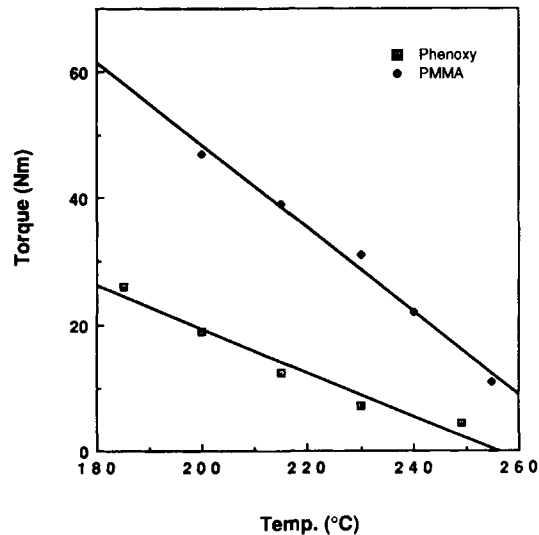
**Figure 2** Log tan  $\delta$  versus temperature for 50/50 PMMA-phenoxy blends injected at 260 (—), 240 (— —), 220 (- · -), 200 - · · -), 180 (· · · · ·), and kneading-compression molded (+++).

perature used, is shown. The other compositions showed intermediate behaviors, which are not presented for the purpose of clarity. As can be seen, the existence of two transitions as a consequence of two phases is clearly seen because of the observed peak and clear shoulder in the 30/70 and the wide transition of the 70/30 PMMA-phenoxy blends. These blends have been recently recognized<sup>3,4</sup> and will also appear in this work as miscible, so lack of mixing is due to unsuitable blending only by injection molding at an injection temperature of at least 180°C. The shoulder caused by PMMA in phenoxy-rich blends, which does not appear in the case of PMMA-rich blends, is due to the low mixing level attained in a blend of well-plasticized less viscous majoritary phenoxy with a not so plasticized much more viscous PMMA.

In Figure 2 the effect of injection temperature in homogeneity, represented by the  $T_g$  behavior, of the 50/50 blend is shown together with the  $T_g$  behavior of the reference Brabender-mixed 50/50 blend. Al-



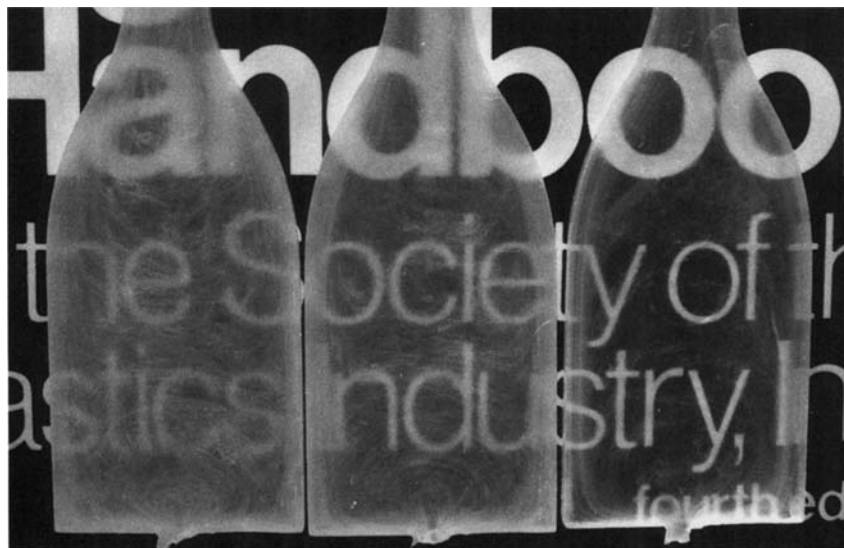
**Figure 3**  $T_g$  versus composition plots for 180°C, 220°C, and 260°C PMMA-phenoxy injected blends. Main peak (■), peak shoulder (□).



**Figure 4** Torque (N·m) measured in the Brabender versus temperature for phenoxy (■) and PMMA (□).

though similar changes exist, in the other compositions they are less evident due to the low presence, and consequently small peak, of one of the two components. As can be seen, the  $T_g$  behavior changes from a very broad transition indicative of two  $T_g$ 's at an injection temperature of 180°C to only one transition at 260°C. Because of its great similarity to that of the Brabender-mixed blend, this transition of the 50/50 blend injected at 260°C is a single one and consequently may be reasonably attributed to a single  $T_g$ . The different geometry that had to be used because of the different thickness of the specimens avoids a direct comparison between the two  $T_g$  regions of both the Brabender-mixed and the 260°C injection-molded 50/50 blends. However, although a direct comparison cannot be made, no widening of the transition is observed at the peak for the injection molded 50/50 blend, and there is only a slight widening in the surrounding temperatures. This widening indicates that the homogeneity of the blend, although quite good, as might be supposed, is not total.

Apart from its influence on the number of transitions, injection temperature also changes the position of the transitions, as is seen in Figure 3 where the  $T_g$  versus composition plots of PMMA-phenoxy blends obtained by injection molding at 180, 220, and 260°C are shown. The  $T_g$  of PMMA appeared at 124°C after processing at 260°C instead of at 120°C after processing at all the other temperatures. This may be due, if we allow for an experimental error in the technique of approximately one or two



**Figure 5** Tensile test specimens obtained from 30/70 PMMA-phenoxy blends injected at (from left) 180, 200, and 240°C.

degrees, to polymer degradation at this temperature, a degradation that does not often take place to the same extent in the blends,<sup>7-9</sup> so in Figure 3 the plotted value of the  $T_g$  of PMMA was 120°C instead of 124°C. The  $T_g$ 's of the blends, which were clearly caused by a superimposition of two  $T_g$ 's, such as that of the 30/70 PMMA-phenoxy blend of Figure 1, were decomposed in two  $T_g$ 's following the method proposed by Rusling.<sup>10</sup>

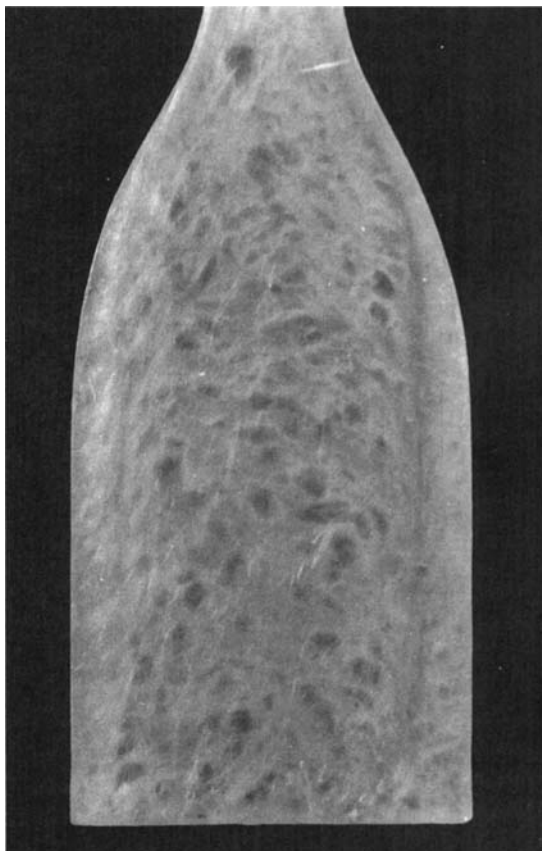
As can be seen, in the case of phenoxy-rich blends injected at 180°C in Figure 3, two clear transitions appeared, but these two  $T_g$ 's were not so clear in the case of PMMA-rich blends. Moreover, in these PMMA-rich blends, the higher the injection temperature the clearer the presence of a single  $T_g$ . The influence of injection temperature is even clearer in the case of phenoxy-rich blends, because the two  $T_g$ 's, which appear in blends injected at 180°C, approach each other at increasing injection temperatures until a clear single  $T_g$  is produced after an injection temperature of 260°C or even 240°C. This single  $T_g$  is very similar to that obtained in compression-molded blends.<sup>4</sup> This behavior of the  $T_g$  proves the increasing presence of the other component in each phase of the blend when injection temperature increases. This increasing presence produces the miscibilization of the blend.

Thus, these results demonstrate first the beneficial effect of increasing injection temperatures on the obtained level of mixing and, second, the possibility of blending directly in an injection machine.

Moreover, the mixing level may reach a fairly good level at injection temperatures that are compatible with those used in the processing of the two components of the blend. This improvement in the level of mixing must be due to the lower viscosity difference between the two components of the blends as temperature increases. This has been shown in Figure 4 where torque measurements at different temperatures in the Brabender plasticorder bowl mixer are shown.

The beneficial effect of increasing injection temperature in the attained homogeneity level was also followed by observance of transparency of the blends, which depended both on injection temperature and on composition of the blends. In Figure 5 several 30/70 tensile specimens obtained at injection temperatures of 180, 200, and 240°C are shown. As can be seen, at low injection temperatures, such as 180°C, in several cases even the shape of the not completely plasticized grains can be seen (detailed picture of a 70/30 specimen in Fig. 6), but at high temperatures such as 240 or 260°C although several flow lines appeared, the specimens may be considered to be totally transparent.

Transparency also increased when the PMMA content of the blend increased as is seen in Figure 7 for 30/70, 50/50, and 70/30 PMMA-phenoxy blends injected at 180°C. As can be seen, even in the case of the lowest injection temperature used, the PMMA-rich blends appear to be somewhat transparent. In the case of middle or low PMMA



**Figure 6** Detail from a 70/30 PMMA-phenoxy blend tensile specimen.

contents, however, the unplasticized remains of grains are visible. This is in accordance with the shoulder caused by PMMA observed in Figure 1 in PMMA-poor blends. Finally, the observed homogeneity gradient among the specimens of Figure 7 is in accordance with the miscibility level of the blends commented on previously.

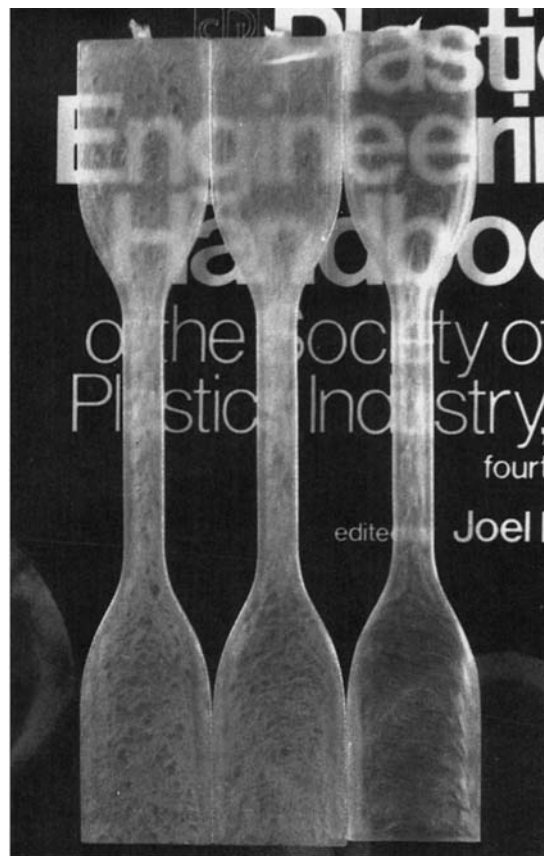
### MECHANICAL PROPERTIES

The mechanical properties of the blends obtained both by kneading-compression molding and by injection molding versus injection temperature are shown in Figures 8, 9, 10, and 11, respectively, for Young's modulus, nominal yield stress, and ductility as measured by elongation at break and impact strength. The values of the kneading-compression molded blends are plotted on the right abscissa. For clarity only the 100/0, 70/30, 50/50, 30/70, and 0/100 compositions are shown. The plots of these properties, and also those of the density of the blends

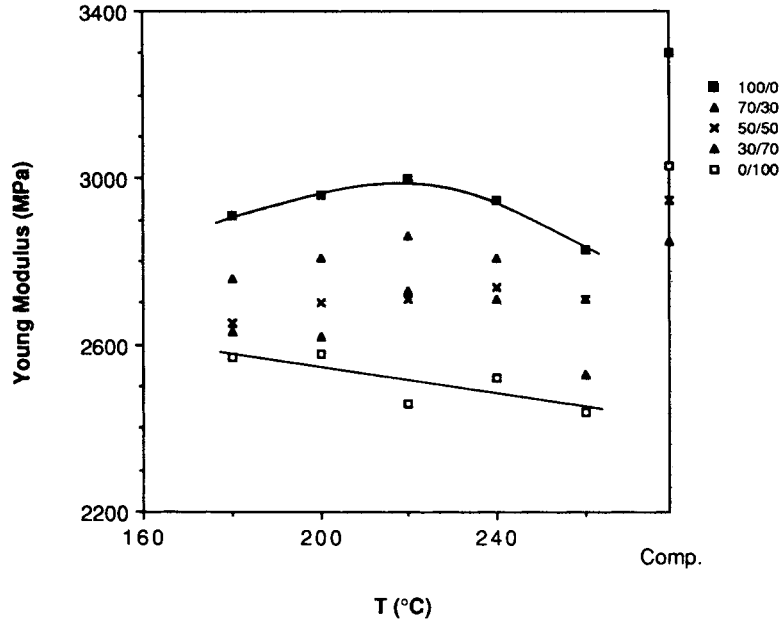
that are not plotted, versus composition of the blends and not versus injection temperature, provided in most of the properties and molding conditions behaviors linear or almost linear behaviors. However, impact strength did not follow linearity since clear negative deviations were obtained.

If we look again at Figures 8 to 11 we can see that the influence, if any, of injection temperature in the measured properties is very slight whatever the composition of the blend. This is a very surprising result since, although such behavior could be expected in the case of well-homogenized, monophasic amorphous blends molded at different high injection temperatures, it is not an intuitive fact that injection-molded specimens at 180°C, where even the grains could be observed with the naked eye as was shown in Figure 6, may behave almost like the well-homogenized specimens molded at 260°C.

It may be supposed that compatibilization by processing,<sup>5,11,12</sup> which is known to take place in injection molding, was the cause of such behavior. However, the fibrillar structure obtained in that case



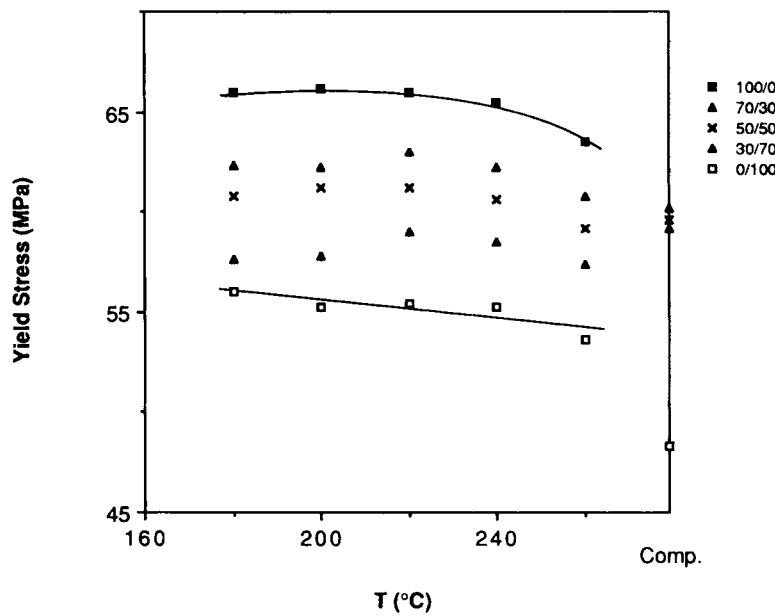
**Figure 7** Different blend compositions, (from left) 30/70, 50/50, and 70/30 injected at 180°C.



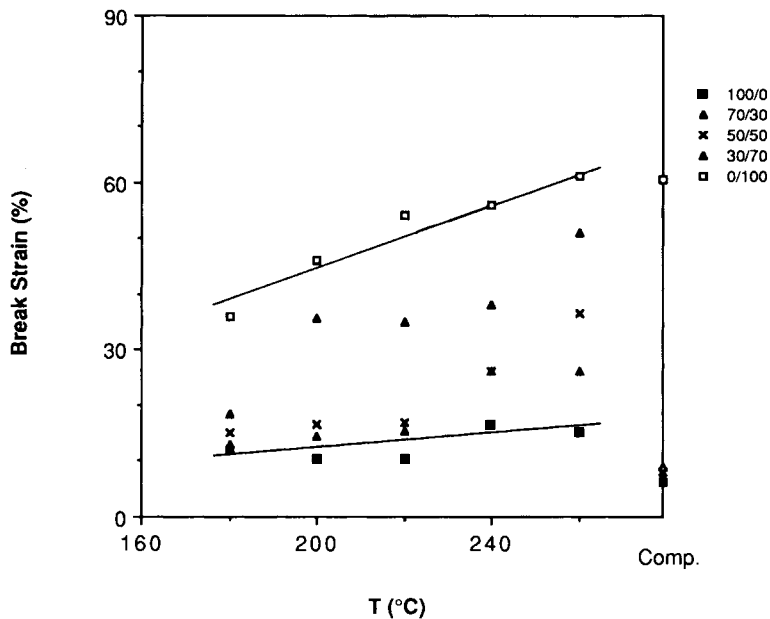
**Figure 8** Young's moduli versus injection temperature for 100/0 (■), 70/30 (▲), 50/50 (X), 30/70 (△), and 0/100 (□) PMMA/phenoxy blends. Kneading-compression molding data are shown on the ordinate axis.

is not, as will be shown further on, observed in this case. Thus, this indicates that a good adhesion level, obtained by the probable interdiffusion of the two components of the blend due to the inherent mis-

cibility of the components, is responsible for the observed mechanical behavior.<sup>13,14</sup> This interdiffusion takes place even at the lowest injection temperature of 180°C probably because, although the pellets are



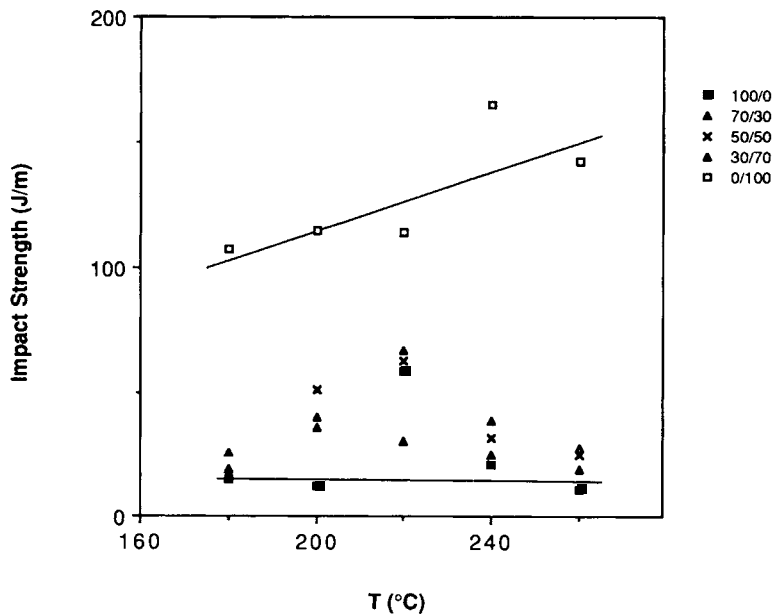
**Figure 9** Nominal yield stress versus injection temperature for 100/0 (■), 70/30 (▲), 50/50 (X), 30/70 (△), and 0/100 (□) PMMA-phenoxy blends. Kneading-compression molding data are shown on the ordinate axis.



**Figure 10** Break strain versus injection temperature for 100/0 (■), 70/30 (▲), 50/50 (X), 30/70 (△), and 0/100 (□) PMMA-phenoxy blends. Kneading-compression molding data are shown on the ordinate axis.

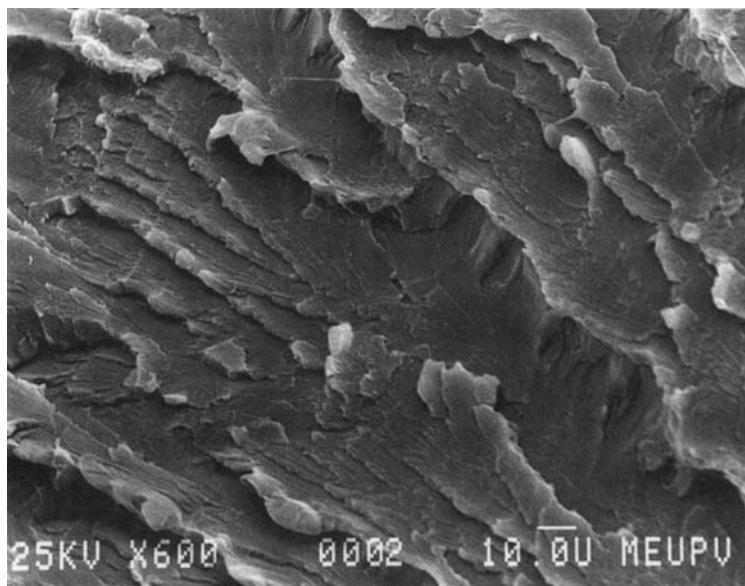
not fully plasticized at this temperature, plastification will clearly take place on the surface of the pellets. This plastification on the surface will pro-

duce an interdiffusion among the pellets that will be active enough to give rise to the observed good mechanical properties.



**Figure 11** Impact strength versus injection temperature for 100/0 (■), 70/30 (▲), 50/50 (X), 30/70 (△), and 0/100 (□) PMMA-phenoxy blends.





**Figure 12** Scanning electron micrography from a 50/50 blend injected at 180°C.

The surprising mechanical properties of all the blends, mainly ductility and impact strength, which are intermediate to those of the pure polymers, obtained by injection molding at low temperatures are corroborated by the morphology of the fracture surface observed by scanning electron microscopy as shown in Figure 12. In this figure the typical morphology of a 50/50 blend obtained at the minimum injection temperature of 180°C is shown. As can be seen, in spite of the fact that the conditions for showing more than one phase were probably the best, there is no sign of multiphasic structure. No multiphasic structures were found even at X6000, and the morphology of the fracture surface, rather fragile in spite of fracture being produced after yielding, is consistent with what could be expected in a material with an elongation at break percentage of 16%.

## CONCLUSIONS

PMMA-phenoxy blends can be obtained directly in an injection machine with a fairly good homogeneity level at high injection temperatures. Homogeneity of the blends depends mainly on injection temperature and also on the miscibility level of the blend. Both increasing injection temperatures and miscibility of the blend improve the attained mixing level.

The measured mechanical properties of the blends studied were, surprisingly, very similar and good whatever the injection temperature. In the case of low injection temperatures this was probably due to the plastification and interdiffusion on the surface, which provided the good adhesion level shown to exist in these multiphasic blends of miscible polymers. Other properties, such as transparency, however, clearly increased with injection temperature to the point where it was clearly comparable to that obtained through other more extended mixing methods such as kneading.

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