

# Development of Interchange Reactions in Ternary PBT-PC/Phenoxy Blends

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## SYNOPSIS

Ternary PBT-PC/phenoxy blends were melt mixed for periods of time up to 110 min to determine the development of interchange reactions among the blend components. This development was evaluated by means of solvent extraction and DSC measurements on blends obtained after characteristic blending times shown in the torque vs. blending time curve. PBT reacts, after very short blending times and, probably due to residual catalyst, mainly with phenoxy. Although at high phenoxy contents a single torque peak is observed, at low phenoxy contents two peaks are observed that correspond to the two stages in which the reaction takes place: at the beginning in the phenoxy-rich phase and later in the overall blend.

## INTRODUCTION

Most technologically important polymer blends are blends of immiscible polymers. Incompatibility resulting from immiscibility, and as a consequence very poor mechanical properties, would be the usual response of blending polymers if different ways of improving compatibility could not be developed.

Among the different attempts to improve compatibility, a majority involve either addition or production of a third component which, due to its miscibility and its consequent presence in both of the components of the blend, should improve blend compatibility.

In the case of addition of a third component, it is usually either a polymer miscible<sup>1-3</sup> or partially miscible<sup>9-11</sup> in both components of the blend, or a copolymer of both of the components,<sup>12-16</sup> although the possible use of a plasticizer has also been tested.<sup>17</sup> The production of the third component may take place either during polymerization or during processing. In the latter case copolymers may be produced, mainly through interchange reactions between the components of the blend. These copolymers increase the compatibility of the blend and are

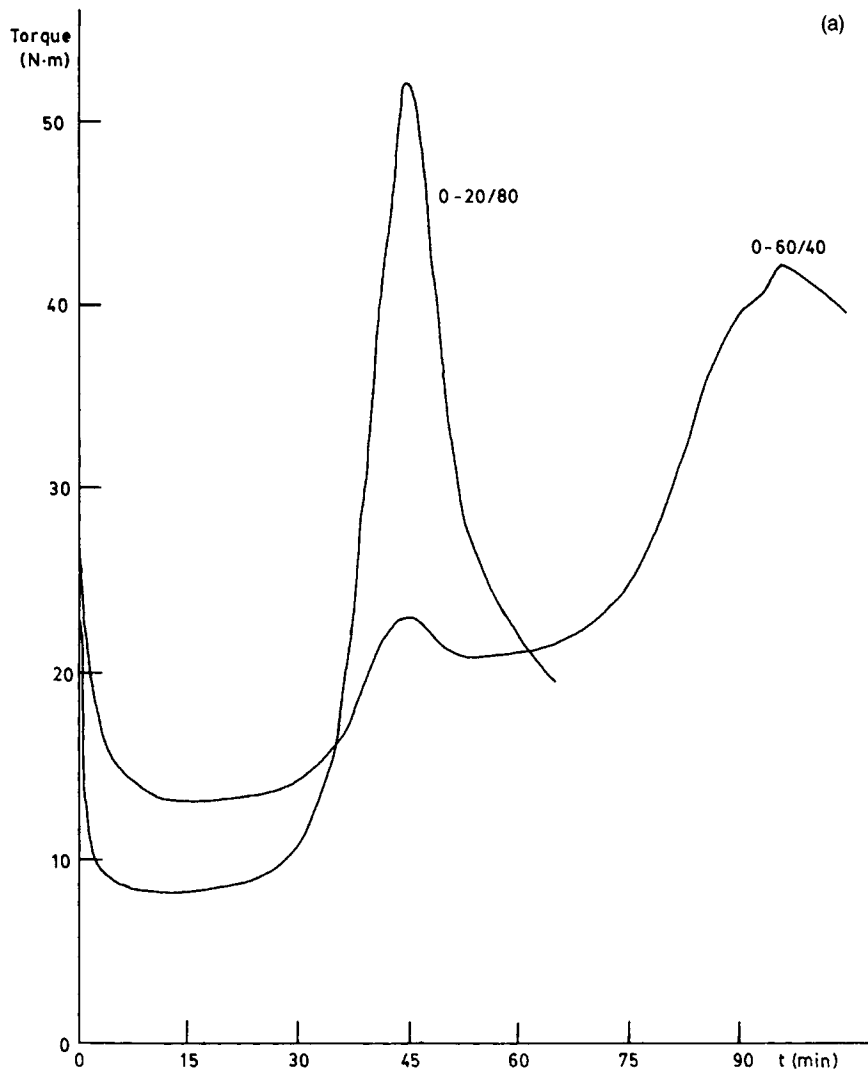
able to produce, in an extreme case, a single  $T_g$  monophasic material.<sup>18-22</sup>

Thus, it seems of interest to compare the effects of the two most common ways of compatibilizing polymer blends, i.e., addition of a third component miscible or partially miscible with the blend components and the production of copolymers by interchange reactions. The addition of PBT to the biphasic PC/phenoxy blends fulfills both of the above conditions. The phase behavior of PC/phenoxy blends with PBT as the third component to compatibilize the blend is the subject of a former work.<sup>23</sup> Therefore, this work will deal with the development of interchange reactions in these blends and with their effect on the miscibility state and phase behavior of PBT-PC/phenoxy blends.

## EXPERIMENTAL

The polymers used in this work, the compositions obtained, and the mixing method are described in a previous publication.<sup>23</sup> It must be pointed out that although the PBT content refers to that of the ternary blend, the PC and phenoxy contents refer to those of a binary blend; that is, a 10-80/20 blend has a real PBT/PC/phenoxy content of 10/72/18. High mixing times, in some cases of up to 110 min, were employed in both blends without PBT and

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**Figure 1** Torque versus time plots of (a) binary PC/phenoxy blends and (b) ternary PBT-PC/phenoxy blends containing 20% PBT.

those with a PBT content of 20% so as to observe the development of probable interchange reactions.

After mixing, the blends were processed by compression at 240°C and quenched in chilled water so as to provide the same thermal history to all the samples. DSC measurements of the compression molded materials were carried out in a Perkin-Elmer DSC-2 calorimeter equipped with a Perkin-Elmer TADS system at a scan rate of 20°/min.

Samples of about 2 g were obtained from the mixer at increasingly longer times. Determinations of solubility of these samples in dichloromethane were performed by measuring the weight loss after extracting the materials in a Soxhlet for a week and drying at 120°C for 1 day. Solubility in *o*-dichlorobenzene of blends containing PBT was also mea-

sured by immersing the samples previously extracted by dichloromethane in boiling *o*-dichlorobenzene for 8 h, washing with dichloromethane, and drying them at 120°C for 1 day.

## RESULTS AND DISCUSSION

Figure 1 collects the torque-time plots of PC/phenoxy blends [Fig. 1(a)] and of these same blends with a PBT content of 20% [Fig. 1(b)]. The torque-time plots of the 0-60/40 and 0-20/80 PC/phenoxy binary blends have been collected for the sake of comparison with those of blends with PBT and because they inform us about the behavior in the melt

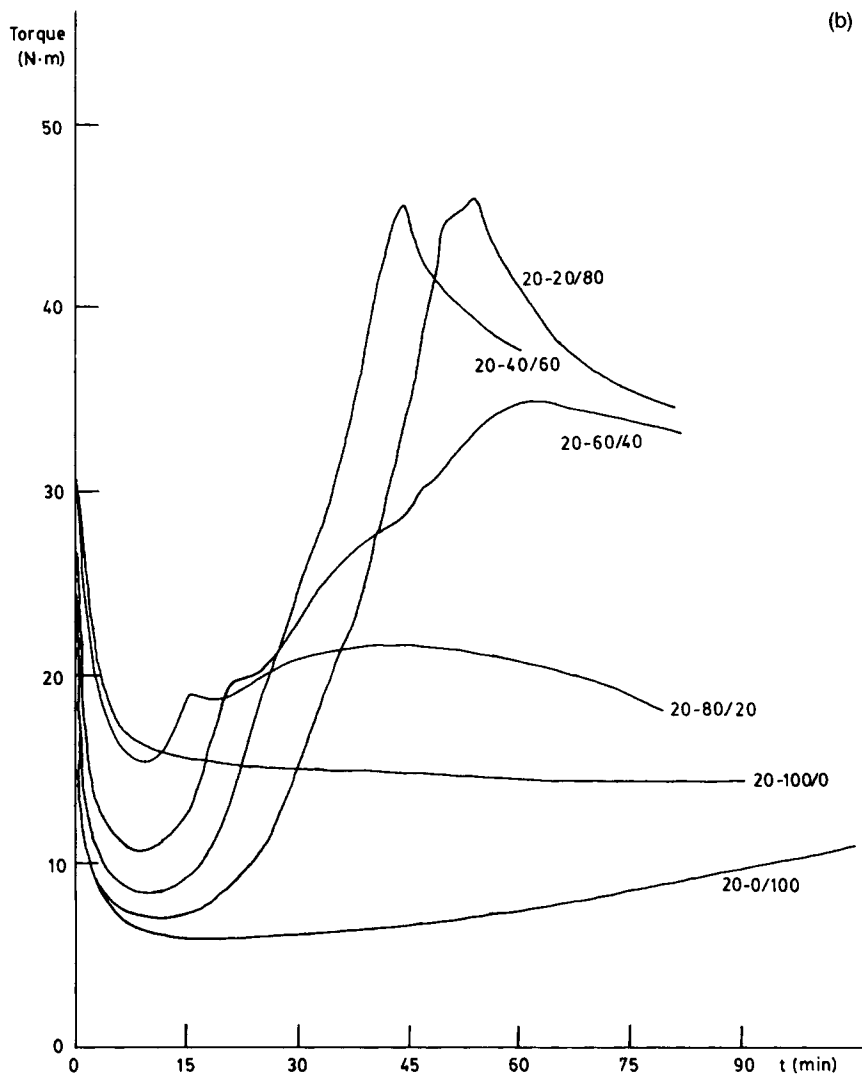


Figure 1 (Continued from previous page)

state of each of the phases of the blend in the absence of PBT.

As is known,<sup>21,22,24,25</sup> melt blending of PC/phenoxy and PBT/phenoxy produces branched copolymers that later develop high viscosity crosslinked products. Both branching and crosslinking give rise to torque increases in the torque of blending versus time plots. This is due to the decrease in mobility of the material as a result of the more complex branched and crosslinked molecules produced by the reaction. The torque increases are greater and sharper in PC/phenoxy blends and they also appear at shorter times than in the case of PBT/phenoxy blends. However, in the case of PBT/PC blends, the produced transesterification reactions<sup>26</sup> give rise to linear copolymers of a similar viscosity to that of the individual components; in this case of transe-

terification reactions, torque increases, provided that they appear, are much smaller than those taking place in phenoxy blends. This different behavior of the torque of blending in the three different binary blends offers a way of identifying which reaction is taking place.

As can be seen in Figures 1(a) and 1(b), most of the curves show one or two peaks, while no peak in the 20-100/0 and a continuous increase in the 20-0/100 blends are seen. This accords with the results of earlier studies because, although linear copolymers are produced in the case of PBT/PC blends (so that neither peak nor torque increase appears), branched copolymers and later crosslinked materials are produced in the case of blends with phenoxy. Moreover, the expected low reaction speed of PBT/phenoxy blends, as compared to that of PC/

phenoxy blends, gives rise to the appearance of a small slope in the torque–time plot instead of a peak.

### PC/Phenoxy Blends

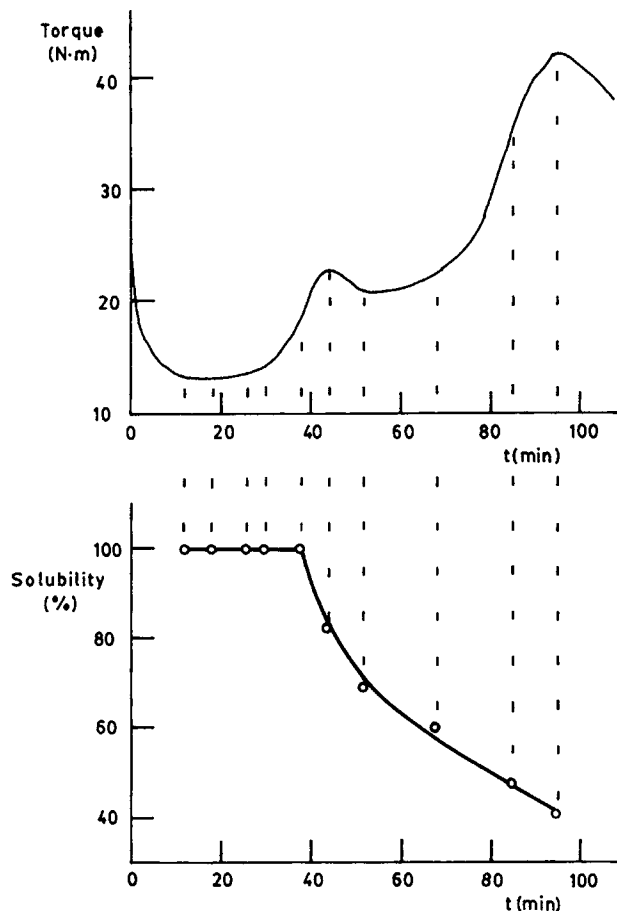
If we look at the curves without PBT in Figure 1(a), we realize that two peaks of torque appear in the case of the 0–60/40 blend and only one in the case of the 0–20/80 blend, though at the same time as that of the first peak of the 0–60/40 blend. The first small peak that appears at low phenoxy contents in blends both with and without PBT is highly reproducible; a similar peak has also been observed previously in PBT/phenoxy blends,<sup>21,24</sup> although it has not been commented upon.

As can also be seen in Figures 1(a) and 1(b), the phenoxy content is the main determinant of the height of the curves. In fact, the greater the phenoxy content of the blend is, the higher the peak of torque appears. This is probably due to the great accessibility of the hydroxyl groups of phenoxy as related to that of the carbonate groups of PC<sup>25</sup>; this different accessibility renders the phenoxy-rich blends more reactive.

In order to determine the origin of these torque maxima, the 0–60/40 PBT-PC/phenoxy blend was put into dichloromethane where both PC and phenoxy are dissolved; thus, a decrease in solubility will prove the presence of crosslinked polymers. In Figure 2 the obtained solubility versus blending time plot is shown together with the corresponding torque curve. As can be seen in Figure 2, the production of crosslinked structures arising from the solubility decrease begins at the first peak. At processing times shorter than that of the first peak, torque increases come together with full solubility; this clearly indicates that the appearance of this first torque jump is due only to branching between PC and phenoxy.

If we look at Figure 3, where the  $T_g$ 's corresponding to the two phases of the blend and to different blending times are collected, we realize that branching between PC and phenoxy must take place mainly in the phenoxy-rich phase. This is because the small  $T_g$  increase, which is due to the lower mobility of the branched molecule as compared to that of the linear molecule, and which corresponds to branching reactions, appears in two points and only in the phenoxy-rich phase. This production of the reaction mainly in the phenoxy-rich phase after short blending times accords with the observance of a high peak at the same processing time in the phenoxy-rich 0–20/80 blend where the reactions in the phenoxy-rich phase must govern the torque.

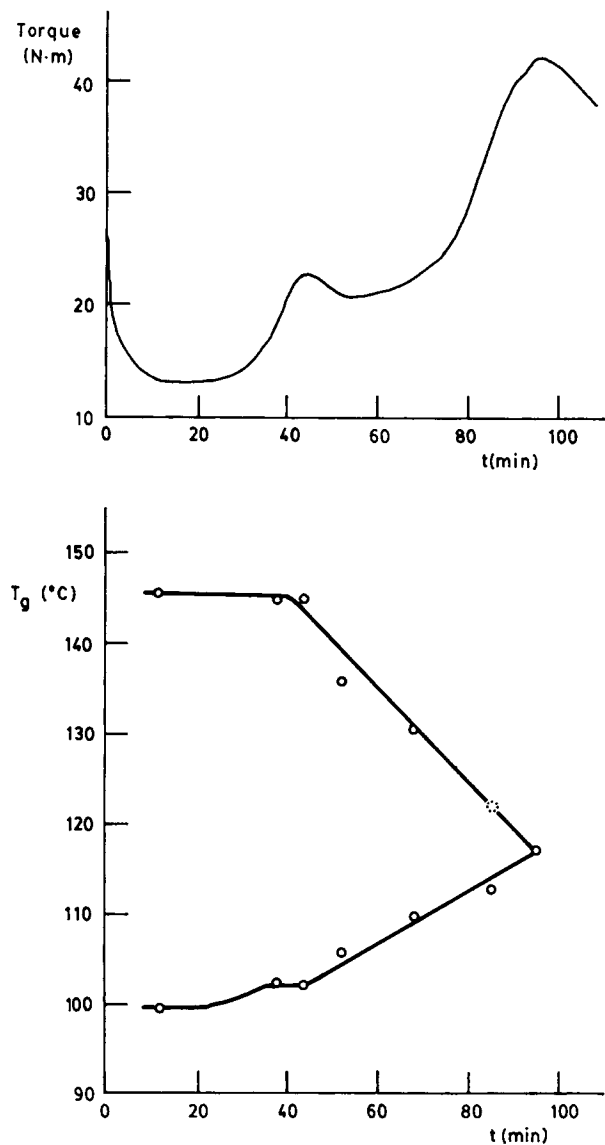
At processing times longer than those of the first



**Figure 2** Solubility versus blending time plot of a 60/40 PC/phenoxy blend. To indicate the position in the torque curve where the materials were collected, the corresponding torque–time curve is also shown.

maximum, the  $T_g$ 's of both of the phases shift very rapidly towards each other. This indicates an increase of the presence of the minority component in the two phases of the blend and must produce a compatibility increase. This increasing presence must take place through reactions since no other parameter changes with reaction time. The increased amount of minority component in each phase continues until the production, at high processing times, of a single- $T_g$  monophasic material. The compatibility increase and the increasing production of crosslinked structures must produce the observed torque behavior of Figure 1(a). After the second maximum a powderlike material appeared. This is definitive proof of the crosslinked nature of the produced materials.

In the case of the 0–20/80 blends, the torque maximum is very high, as corresponds to the high phenoxy content of the blend, and a single rapid



**Figure 3**  $T_g$ 's versus blending time of a 60/40 PC/phenoxy blend. The correspondent torque-time curve is also shown for the same reason as in Figure 2. The broken circle corresponding to a mixing time of 85 min indicates that the transition was not clearly seen.

maximum appears. This is due to the majority presence of phenoxy in the blend; this majority presence, as seen above, produces branching at very short processing times. This branching quickly develops crosslinking, because at the maximum a crosslinked powder appears. The contribution of the PC-rich phase to torque does not produce any peak due to the previous production of a powderlike material by the majority phenoxy-rich phase. The opposite behavior, that is, low torque maximum at long times, appeared in the case of 0-80/20 blends.

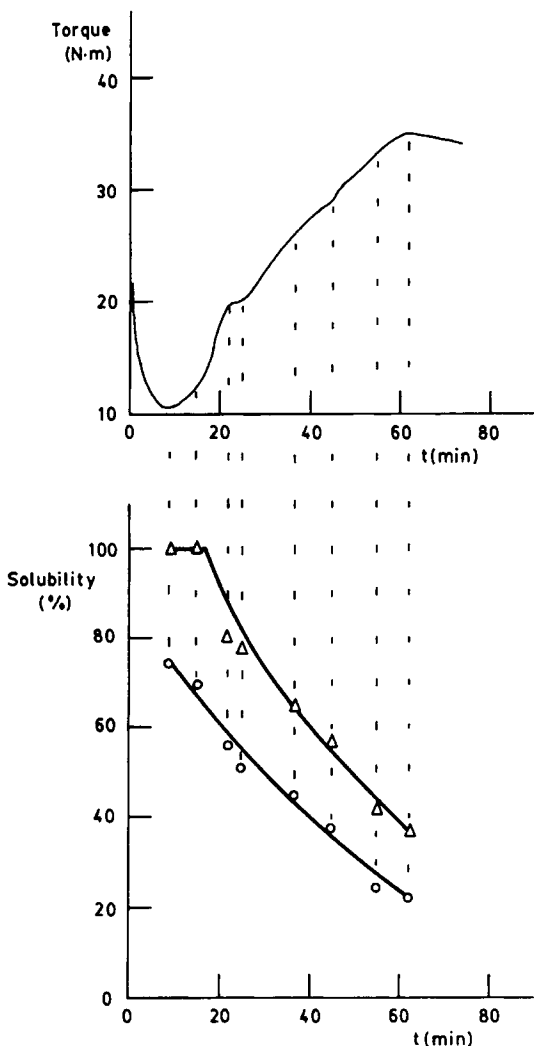
Thus, at intermediate PC/phenoxy compositions the reaction takes place in two stages. These two stages of the reaction correspond to the different development of the reaction in the two phases of the 0-60/40 blend. The first rapid peak corresponds to branching reactions in the phenoxy-rich phase; after that, additional branching, crosslinking, and compatibilization in both of the two phases of the blend occur. The combined effect of these processes gives rise to the observed torque behavior. However, in the case of phenoxy-rich blends, in spite of the probable occurrence of the reaction in two stages, a single, rapid, high peak appears as a consequence of the quick reactions in the phenoxy-rich phase; the high peak is a consequence of the high phenoxy content of the blend. The maximum that would correspond to the overall blend does not appear since it is produced after a processing time at which the majority phenoxy-rich phase has become a powderlike material.

#### PBT-PC/Phenoxy Blends

As can be seen in Figure 1(b), the torque curves of these blends are rather similar to those of PC/phenoxy blends. Phenoxy content is again the main determinant of the shape and of the height of the curves; that is, they show two peaks in the case of low phenoxy content blends and a single peak in the case of phenoxy-rich blends; moreover, the greater the phenoxy content of the blends is, the higher the maxima of the torque appear. However, the jump of the torque begins at shorter times and the maxima of the torque are always lower in the case of blends with PBT as compared with blends without PBT. The overall sharp shape and great height of the peaks indicates that the reaction of phenoxy with PC is produced because either PBT/phenoxy or PBT/PC blends give rise to flatter peaks, if any, than those observed in Figure 1(b).

In order to explain the behavior observed in Figure 1(b) and to determine what reaction takes place during blending of this ternary blend, solubility tests were carried out by extraction of the ternary blend with dichloromethane (where both PC and phenoxy are dissolved) and with *o*-dichlorobenzene (where the three components are dissolved).

In Figure 4, percent solubility in both solvents is plotted versus time together with the position of the torque-time curve where the specimens were taken out. The measurements were done for the 20-60/40 blend, that is, with the same PC/phenoxy composition as in the PC/phenoxy case but with a PBT content of 20%. As can be seen, when the blend is



**Figure 4** Solubility versus blending time plot of a 20-60/40 PBT-PC/phenoxy blend in dichloromethane (○) and in *o*-dichlorobenzene (△). The corresponding torque-time curve is also shown for the same reason as in Figure 2.

extracted with dichloromethane, even after such a very short processing time as 9 min (i.e., a bit less than the minimum time to reach a homogeneous blend), the extracted amount of PC plus phenoxy (74%) is lower than that of the composition of the blend. This indicates, even taking into account that a small amount of either PC or phenoxy may be occluded in the crystalline PBT, that PBT has already reacted with either PC or phenoxy, because the process produces no crosslinking reaction between PC and phenoxy which might give rise to an insoluble product, after short processing times like 9 min, as will be seen following the next paragraph.

In order to find out if PBT reacts after this short

blending time with either PC or phenoxy or both, two additional solubility tests were carried out. The test results revealed that the main reaction of PBT after a blending time of 9 min is with phenoxy (provided that the reaction of PBT with either PC or phenoxy is similar in either the presence or absence of the third component of the blend). This is because if we blend the 20/80 PBT/PC and PBT/phenoxy blends for 9 min and after that put them into dichloromethane (where both PC and phenoxy were soluble), only 78.6% of the PBT/PC blend and 70.8% of the PBT/phenoxy blends are dissolved. This indicates that, although a small amount of PC (1.4%) is reacted after this short blending time, the reaction of PBT is mainly with phenoxy (9.2% of phenoxy reacts).

Moreover, if we look at the solubility in *o*-dichlorobenzene in Figure 4, we realize that crosslinking reactions between PC and phenoxy are unexpectedly produced after a very short blending time, as compared with the blending time to produce crosslinking in PC/phenoxy blends: more than 40 min. This is because solubility clearly decreases after a blending time of 15 min, that is, a bit after the reactions with PBT begin. This is in accord with the behavior of the torque of blending observed in Figure 1 (b), because torque begins to increase at all the blend contents earlier in the PBT blends (after a blending time of  $\approx 10$  min) than in the correspondent blends without PBT (after a blending time of  $\approx 25$  min). At processing times between 10 min, when the jump of the torque appears, and 15 min, when solubility begins to decrease, branching reactions must be produced between PC and phenoxy.

The reason that reactions appear after a shorter reaction time in blends with PBT than in blends without PBT cannot be due to reactions of PBT with phenoxy and still less to reactions with PC. This is because either the branched copolymers of phenoxy with PBT or the block copolymers of PC with PBT have the same or less ability to react with either PC or phenoxy than with single phenoxy. Thus, the shown<sup>27</sup> presence of residues of catalysts, such as titanium compounds, in PBT, which catalyze interchange reactions, must be the origin of the observed speeding up. For this reason, the high slope increases of torque, characteristic of PC/phenoxy blends, appear in the ternary blend at shorter blending times than in the case of the binary PC/phenoxy blends; later, as seen in the solubility test in *o*-dichlorobenzene, they continue to take place until producing, as in PC/phenoxy blends, a powderlike material characteristic of a crosslinked product.

The attained reaction level, i.e., the maximum height of the torque-time plot, is lower in blends with PBT than in blends without PBT. This is due to the dilution effect of PBT, since blends of PBT with either PC or phenoxy give rise to either low torque increase or lack thereof. The appearance of more than one peak in these ternary blends is due, as mentioned regarding PC/phenoxy blends, to the two stages of the reaction and to the beginning of the reaction in the phenoxy-rich phase.

Thus, PBT reacts mainly with phenoxy after a very short blending time. This speeding up of the reactions is probably due to the presence in PBT of residues of catalysts. In this ternary blend the reaction between PC and phenoxy is the main reaction; it produces great torque increases in the torque-time plot after short blending times.

## CONCLUSIONS

In both PBT-PC/phenoxy blends and PC/phenoxy blends, at low phenoxy contents the torque-time plot shows two torque peaks. These two peaks correspond to the two stages in which the reaction takes place. At the beginning the reaction takes place in the phenoxy-rich phase, and later in both phases of the blend. Long processing times give rise to a progressive miscibility of the blend which renders the blend monophasic and transparent.

In blends with high phenoxy content, the rapid production of a reacted monophasic material and thereafter of a powderlike material prevents the observance of any change of the torque due to reactions in the PC-rich phase. The result is a single very high torque peak.

PBT speeds up the reactions between PC and phenoxy, probably due to residues of catalyst in PBT, and decreases the amount of reacted product achieved in PC/phenoxy blends.

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