# Effects of Processing Conditions on the Phase Morphology of PC/ABS Polymer Blends 

B. I. CHAUDHRY, E. HAGE, L. A. PESSAN<br>Department of Materials Engineering (DEMa), Universidade Federal de São Carlos, São Carlos, SP, Brazil 13565-905

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#### Abstract

The phase morphology of PC/ABS blends can be significantly affected by its processing conditions. Blends prepared in a mixing chamber at different conditions show a strong influence of mixing time and temperature on its morphology. The blend morphology changes from a well-dispersed PC phase surrounded by the ABS matrix phase to a cocontinuous morphology with increase in the mixing time. Higher blending temperatures promote changes in the PC/ABS morphology, probably due to thermal degradation. The rotor speed has not shown much influence on the blend phase morphology. The cocontinuous phase morphology of the PC/ABS blends obtained after mixing for 10 min was shown to be unstable as detected by the heat treatment. A melt annealing for a few minutes showed a significant change in the morphology. © 1998 John Wiley \& Sons, Inc. J Appl Polym Sci 67: 1605-1613, 1998


Key words: polycarbonate; ABS; polymer blends; processing conditions

## INTRODUCTION

Multiphase polymer blends usually have their mechanical behavior strongly affected by the size and shape of the phases generated during its preparation. ${ }^{1,2}$ The overall phase morphology for these blends depends on the blend composition, the rheological behavior of each component, the interfacial energy, and the processing conditions. ${ }^{1-4}$ The combination of all these parameters during the blend preparation establishes the main aspects of the morphology, such as cocontinuous or disperse aspects of the phases, geometric arrangement, and dimension of each phase. ${ }^{5,6}$ In spite of a component having a higher content in the blend, one cannot be certain that it will form the matrix phase. ${ }^{6}$ The viscosity ratio between the

[^0]disperse and matrix phases is more decisive in determining which phase plays as a matrix or a disperse phase. ${ }^{7}$ Furthermore, a change in the interfacial surface energy is more effective in the establishment of the particle size of the dispersed phase than does a change in the viscosity ratio of the components. ${ }^{8}$ Therefore, processing conditions have a stronger effect on the phase morphology than do blend composition and rheological behavior of the individual components. ${ }^{2,6,9,10}$

The processing conditions, besides being decisive in establishing the morphology for multiphase polymer blends, are also responsible for the morphology stability during further processing steps. Quitens et al. ${ }^{11}$ showed that the PC/SAN blends' morphology is unstable and changes after heat treatment. Its morphology changes from a cocontinuous form to a well-defined disperse phase system, after the blend is heated under pressure. Cheng et al. ${ }^{12}$ used melt annealing on PC-based blends to show a lack of morphology stability. A coarsening of the disperse phase was observed for some compositions and cocontinuous

Table I Mixing Conditions Used to Study PC/ABS (55/45) Blends

| Blending <br> Temperature $\left({ }^{\circ} \mathrm{C}\right)$ | Rotor Speed <br> $(\mathrm{RPM})$ | Mixing Time <br> $(\mathrm{min})$ |
| :---: | :---: | :---: |
| $230^{\circ} \mathrm{C}$ | 50 | 1 |
| $250^{\circ} \mathrm{C}$ | 30 | 2 |
| $250^{\circ} \mathrm{C}$ | 50 | 5 |
| $250^{\circ} \mathrm{C}$ | 50 | 7 |
| $250^{\circ} \mathrm{C}$ | 50 | 10 |
| $250^{\circ} \mathrm{C}$ | 50 | 10 |
| $250^{\circ} \mathrm{C}$ | 50 | 10 |
| $250^{\circ} \mathrm{C}$ | 70 | 10 |
| $270^{\circ} \mathrm{C}$ | 50 | 10 |

morphologies were changed into a disperse-phase morphology type by increasing the annealing time. Similar behavior was observed in the literature for PC/SAN/MBS ternary blends. ${ }^{13}$

PC/ABS blends have been investigated with respect to compatibility and mechanical behavior aspects. ${ }^{14-19}$ In these studies, a bead-andstring structure was observed in the injectionmolding direction. In addition, a continuous change in morphology was noticed along the sample thickness. A different degree of orientation of the ABS phase was observed at the sample edges. ${ }^{20}$ However, studies about the effect of
processing conditions on the morphology of $\mathrm{PC} /$ ABS blends have not been extensively investigated. Furthermore, studies of the morphological stability have not been reported in the literature for PC/ABS blends. The aim of this work was to study the effects of blending conditions on the morphology of PC/ABS polymer blends and also to observe how the PC/ABS morphologies obtained behave under annealing treatment.

## EXPERIMENTAL

Bisphenol-A polycarbonate (PC) from General Electric Co., Lexan 4535, was used as one of the blend components. Its main characteristics are $\bar{M}_{n}=35,000 \mathrm{~g} / \mathrm{mol}, \bar{M}_{w}=65,000 \mathrm{~g} / \mathrm{mol}$, and an intrinsic viscosity of $0.62 \mathrm{~g} / \mathrm{dL}$. The acryloni-trile-butadiene-styrene copolymer (ABS), obtained from Nitriflex S.A. and having approximately 23,21 , and $56 \%$ by weight of acrylonitrile, butadiene, and styrene, respectively, was used to blend with PC. The ABS matrix is made of SAN with a styrene/acrylonitrile ratio of 75/ 25 by weight. It shows also a content of $30 \%$ by weight of grafted SAN in its microstructure. The rubber-phase concentration is around $25 \%$ by weight with a rubber particle size in the range of $0.20-0.35 \mu \mathrm{~m}$.

Table II Effect of Mixing Parameters on the Phase Morphology of the PC/ABS (55/45) Blend Prepared in the Torque Rheometer

| Mixing Conditions | Torque (Nm) PC | Torque (Nm) ABS | $\begin{gathered} \text { Torque } \\ (\mathrm{Nm}) \\ \text { PC/ABS Blend } \end{gathered}$ | Torque Ratio PC/ABS | Average ${ }^{\text {a }}$ Equivalent Diameter ( $\mu \mathrm{m}$ ) | Shape ${ }^{\text {b }}$ <br> Factor |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| Temperature ${ }^{\text {a }}\left({ }^{\circ} \mathrm{C}\right)$ |  |  |  |  |  |  |
| 230 | 19.5 | 4.7 | 8.6 | 4.1 | 1.6 | 0.5 |
| 250 | 14.7 | 2.7 | 4.6 | 5.4 | 4.7 | 0.3 |
| 270 | 9.7 | 2.2 | 3.3 | 4.4 | 4.8 | 0.3 |
| Rotor speed ${ }^{\text {b }}$ (rpm) |  |  |  |  |  |  |
| 30 | 12.2 | 2.3 | 4.1 | 5.3 | 3.2 | 0.4 |
| 50 | 14.8 | 2.7 | 4.6 | 5.4 | 4.7 | 0.3 |
| 70 | 14.7 | 3.4 | 5.5 | 4.3 | 5.6 | 0.3 |
| Time (min) |  |  |  |  |  |  |
| 1 | 29.5 | 8.2 | 14.9 | 3.6 | 1.4 | 0.5 |
| 2 | 19.2 | 4.2 | 8.7 | 4.6 | 1.9 | 0.5 |
| 5 | 13.7 | 3.1 | 5.9 | 4.4 | 2.7 | 0.3 |
| 7 | 14.9 | 2.9 | 4.9 | 5.1 | 5.8 | 0.4 |
| 10 | 14.7 | 2.7 | 4.6 | 5.4 | 4.7 | 0.3 |

[^1]
(a)

(c)

(b)

(d)

(e)

Figure 1 SEM micrographs of PC/ABS (55/45) blends mixed for different times at $250^{\circ} \mathrm{C}$ and 50 rpm : (a) 1 min ; (b) 2 min ; (c) 5 min ; (d) 7 min ; (e) 10 min .


Figure 2 Torque versus time curves of PC and ABS fluxed at $250^{\circ} \mathrm{C}$ and 50 rpm .

The PC/ABS blends were prepared by meltmixing at different temperatures in a torque rheometer (Haake, Model Rheomix 600) using a 55 mL chamber. Both components were premixed in powder form at $45 \%$ by weight of ABS. This composition was chosen on the basis of previous studies. ${ }^{21}$ All materials were predried for a minimum of 4 h at $80^{\circ} \mathrm{C}$ under a vacuum. Parameters such as blending temperature, rotor speed, and mixing time were varied as shown in Table I. The melted blend obtained from the mixer was hot-pressed into plates at $200^{\circ} \mathrm{C}$.

An annealing treatment under a nitrogen atmosphere at $250^{\circ} \mathrm{C}$ was used to study the phase morphology stability of the blends. The samples were heat-treated for different times.

The morphology of the blends was examined using a Zeiss DSM 90-A scanning electron microscope (SEM). All specimens were prepared by cryofracturing molded plates in liquid nitrogen. The parts to be observed in SEM were cut from the fractured pieces of the plates. The fractured surfaces were exposured to a $30 \%$ by weight KOH aqueous solution for 4 days at room temperature. The PC phase was etched away, leaving holes in the SEM images. All samples were previously coated with gold before being observed in the SEM.

The blend morphologies were analyzed by using an image analyzer software from Jandel Scientific Co. (Mocha Model 1.2). Parameters such as the average equivalent diameter and shape factor were quantitatively obtained from the image analysis.

(b)

(c)

Figure 3 SEM micrographs of PC/ABS blends mixed at different temperatures for 10 min at 50 rpm : (a) $230^{\circ} \mathrm{C}$; (b) $250^{\circ} \mathrm{C}$; (c) $270^{\circ} \mathrm{C}$.


Figure 4 Torque versus time curves for PC/ABS blends fluxed at different temperatures and 50 rpm : (a) $230^{\circ} \mathrm{C}$; (b) $250^{\circ} \mathrm{C}$; (c) $270^{\circ} \mathrm{C}$.

## RESULTS AND DISCUSSION

Effect of Mixing Conditions on Morphology
Three main mixing parameters such as temperature, rotor speed, and mixing time were used
to characterize the effect of blending conditions on the morphology of the PC/ABS blend. The morphological behavior of the blends was quantified by the average equivalent diameter and the shape factor of the phase. Table II shows how the blending conditions affect the morphology. Torque values for PC, ABS, and their blend are presented in Table II to show the rheological behavior of the components during the mixing process.

## Mixing Time

The PC/ABS blend was prepared at different mixing times in the Haake rheometer at $250^{\circ} \mathrm{C}$ and 50 rpm . The average particle size of the PC phase increases with the mixing time, as observed through the average equivalent diameter in Table II. The effect of the mixing time on the PC/ABS blend morphology can be visualized in Figure 1. The blend prepared at 1 min shows a well-defined morphology where the PC phase (dark) was dispersed in the ABS phase (light) [Fig. 1(a)]. Furthermore, a wide distribution for the PC particle size was observed. Jordhamo et al. ${ }^{22}$ already showed that blend components with a lower viscosity have a tendency to form the matrix which encapsulates the one with higher viscosity. This behavior was observed even when the lower-viscosity phase was the minor component. For the blend studies, ABS had lower viscosity, as estimated from the torque behavior (Fig. 2); therefore, it should encapsulate the PC phase in the initial stage of mixing as shown in Figure 1 (a).

The PC/ABS blend mixed for 2 min has a similar morphology to the one discussed above ( 1 min mixing time); however, the PC particles seem to be more elongated [Fig. 1(b)]. After 5 min of mixing, the PC disperse phase becomes so elongated that the blend morphology is similar to a cocontinuous type, where both phases are interpenetrated [Fig. 1(c)]. Scott and Macosko ${ }^{4}$ proposed a mechanism for the morphologies developed during the initial stages of poly-mer-polymer blending. The original matrix phase is deformed by the mixing shear reaching a well-stretched state. Simultaneously, the disperse phase is elongated along with the matrix deformation. As a result, both phases can be represented as a cocontinuous morphology. Further mixing leads to capillary instability of the stretched matrix phase which breaks up into small droplets. At this stage, there is a phase


Figure 5 SEM micrographs of PC/ABS blends mixed at different rotor speeds for 10 min at $250^{\circ} \mathrm{C}$ : (a) 30 rpm; (b) 50 rpm ; (c) 70 rpm .
inversion where the initial matrix phase becomes the disperse phase in the last stage of the blending process. As observed in Figure 1, this mechanism might be applied to explain the changes in the morphology of the PC/ABS blends only in the initial stages of mixing. For mixing times longer than 5 min , no phase inversion was observed as predicted by the above mechanism. At 7 min of mixing time, the PC phase becomes again a well-defined disperse phase with larger domains, as observed in Figure 1(d) and Table II. A reasonable explanation for this behavior is a lack of mixing shear energy to break up the stretched ABS matrix phase. On the other hand, the mixing energy is sufficient to promote a coalescence of the stretched PC particles, transforming them in larger domains, as can be observed in Figure 1(d).

Blends prepared for 10 min [Fig. 1(e)] do not show drastic changes in the morphology compared to the one in Fig. 1(d). Both phases became, once again, well stretched, reaching a "quasi" cocontinuous phase morphology. During the mixing process, both stretching and coalescence mechanisms occur simultaneously for long periods of time, ${ }^{6}$ reaching a dynamic equilibrium. Therefore, the final morphology for the studied PC/ABS blend would be similar to the one obtained with a mixing time between 7 and 10 min . In addition, the final morphology reaches a metastable state, which may be relaxed by further heating, leading to a well-defined PC disperse phase.

The shape factor shown in Table II represents the geometric aspect of the disperse phase. It ranges from 0 , for fiber shapes with a very high aspect ratio ( $1 / d$ ), to 1 , for a well-defined spherical shape. Therefore, shape factors close to 0 , observed in Table II, indicate fibrilar morphology such as the ones observed in Figure 1 for 5 and 10 min of mixing.

## Blending Temperature

The effect of the blending temperature was observed by using temperatures below and above $250^{\circ} \mathrm{C}$ at 50 rpm for 10 min . An increase in the mixing temperature up to $270^{\circ} \mathrm{C}$ led to an increase in the average equivalent diameter for the phase. The shape factor indicates that the disperse-phase shape becomes more elongated as the temperature is increased (Table II). Figure 3 illustrates the phase morphology for the $\mathrm{PC} / \mathrm{ABS}$ blend as the temperature is increased.

Table III Effect of Annealing Time on the PC Phase Morphology for Blends Mixed at $250^{\circ} \mathrm{C}$ and Annealed at $250^{\circ} \mathrm{C}$

|  | Average <br> Annealing <br> Time <br> $(\mathrm{min})$ | Equivalent <br> Diameter <br> $(\mu \mathrm{m})$ |
| :---: | :---: | :---: |

A well-defined PC disperse phase changes to a "quasi" cocontinuous phase morphology. For the $\mathrm{PC} / \mathrm{ABS}$ blend prepared at $230^{\circ} \mathrm{C}$, the mixing shear energy does not seem to be enough to deform significantly both phases, even after a mixing period of 10 min .

As previously mentioned, the shear viscosity of the components is a very effective rheological parameter to define the phase morphology in polymer blends. ${ }^{1-5,9,23}$ Torque measurements during the mixing process were taken after 7 min to estimate the viscosity for every component and their blends (Table II). The torque ratio was calculated to estimate the viscosity ratio among the PC/ABS components. This ratio is quite important in establishing the blend morphology during the mixing process. ${ }^{7,8}$

The torque values showed a decrease for each component and its blend with increase of temperature. As expected, the lower polymer melt viscosity at higher temperatures needs less torque to flux the polymer. The torque ratio has not shown a consistent trend with respect to the blending temperature. However, the PC/ABS blend showed torque values closer to the neat ABS at $270^{\circ} \mathrm{C}$, in spite of its high PC content. One possible reason for this behavior is a thermal degradation of the blend during the melt mixing. Lombardo et al. ${ }^{24,25}$ already showed that PC is rapidly degraded at high temperatures when blended with some ABS. PC reacts with the high alkaline electrolyte and catalyst residuals from the ABS emulsion synthesis, leading to PC chain scission.

Figure 4 shows curves of torque versus time obtained from torque rheometry for PC/ABS blends at several temperatures. As a general trend, the torque drops sharply with the fluxing time, then levels down to a constant value. For
the blend mixed at $270^{\circ} \mathrm{C}$, the curve does not level down in the range of measured time. The torque value for the blend approaches that of the ABS. This tendency shows evidence of thermal degradation for the blend. This degradation leads to a change in the viscosity ratio during mixing, leading to a similar morphology as obtained at $250^{\circ} \mathrm{C}$.

## Mixing Speed

The blend was mixed at $250^{\circ} \mathrm{C}$ using different rotor speeds in the bowl. The average equivalent diameter of the PC phase increases as the rotor speed is increased (Table II). The shape factor indicates that the PC phase became more elongated as the rpm was increased. Figure 5 shows the morphological behavior of the PC/ABS blend prepared at different rotor speeds. A "quasi" cocontinuous morphology was observed for all speeds used, leading to the conclusion that this processing parameter does not have a strong influence over the blend morphology.

The torque behavior showed a general trend, that is, the values obtained increase with the increase in the rotor speed (Table II). Favis ${ }^{6}$ previously showed that the torque increases with the rotor speed for PC blends. The torque values level off as the rpm of the rotors is increased further. However, the torque ratio has not shown any consistent trend, as mentioned earlier.

## Effect of Annealing on the PC/ABS Blend Morphology

The annealing treatment was performed to observe the state of the morphological stability for the $\mathrm{PC} / \mathrm{ABS}$ blend mixed at $250^{\circ} \mathrm{C}$ and 50 rpm . Table III shows the change in size and shape for the PC phase in the blend. The average equivalent diameter showed a consistent increase along with the annealing time. The shape factors showed a tendency of the PC phase to become less and less stretched, reaching a circular shape after 15 min . Figure 6 illustrates the morphological changes with the annealing time.

In the absence of shear flow, the elongated immiscible phases retract when heated above the $T_{g}$ of both components. The high interfacial energy for those systems is a strong driving force to promote coalescence among the particles of the PC disperse phase. ${ }^{12}$ According to Quitens et al., ${ }^{11}$ a change from cocontinuous to disperse morpholog-

(e)

Figure 6 SEM micrographs of $\mathrm{PC} / \mathrm{ABS}$ blends mixed $250^{\circ} \mathrm{C}$ for 10 min at 50 rpm annealed for different times: (a) 0 min ; (b) 7 min ; (c) 15 min ; (d) 30 min ; (e) 45 min .
ies is due to several mechanisms such as coalescence, shrinking of deformed phases, breaking up of fibrils through capillary instability, and other viscoelastic phenomena.

## CONCLUSIONS

The PC/ABS phase morphology depends strongly on some blending conditions. A dispersed PC phase surrounded by the ABS matrix is observed at short mixing times. As the blending proceeds, both phases become elongated, reaching a "quasi" cocontinuous morphology. At this mixing stage, the individual phases become interpenetrated, remaining in this condition for a long period of blending time.

An increase in the blending temperature leads to a morphology where both PC and ABS phases are significantly elongated. Torque measurements were used to show evidence of thermal degradation of the blend at higher blending temperatures. According to the literature, the PC phase is affected by the presence of residual chemicals from the emulsion synthesis of ABS, which promotes chain scissions in the PC molecules, thereby reducing the blend melt viscosity. Even though higher mixing speeds increase the torque values, no significant change in the morphology was observed for the PC/ABS blend.

The PC/ABS phase morphology obtained after the blending in the Haake rheometer is quite unstable. An annealing heat treatment at melt temperatures leads to a significant change in the morphology. PC and ABS phases shrink and coalesce under heating, generating a PC disperse-phase morphology. As the annealing time increases, the PC domains become larger.

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[^0]:    Correspondence to: E. Hage, (elias@power.ufscar.br).
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[^1]:    ${ }^{\text {a }}$ All the torque measurements at different temperatures and rotor speeds were taken after mixing and fluxing the components for 7 min . The average equivalent diameter was measured after mixing the PC/ABS blend for 10 min .
    ${ }^{\mathrm{b}}$ Average equivalent diameter was obtained by image analysis.

