## Blend Morphology Development During Melt Flow: Correlation of a Model Concept Based on Dynamic Phase Volume with Practical Observations

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ABSTRACT: An approach is first developed that can be used to identify the global morphology of an immiscible two-phase polymer–polymer blend under shear flow. The basis for the modeling is the concept of a dynamic phase volume; this is based on relative abilities of the respective phases to flow when under stress, and determined by the actual phase volume fraction and the viscosity ratio between phases. One result of the modeling is a schematic diagram providing guidelines for morphology development during melt processing in a nonuniform stress field. Bisphenol A polycarbonate(PC)/ABS blends were studied as an immiscible system, using variations of component ratio and viscosity ratio at constant composition. Blend morphology was characterized by scanning electron microscopy and solid-state dynamic mechanical spectroscopy. Model predictions correlate well with experimental observations of the frozen-in solid-state morphology following injection molding. Discussion also cover the utility of the model for blend design and limitations of the modeling approach. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 71: 311–318, 1999

**Key words:** thermoplastic blends; morphology; shear flow; modeling; polycarbonate/ABS

#### **INTRODUCTION**

Melt processing operations under shear flow conditions are often employed to blend polymers and manufacture solid parts from mixed polymer systems. For immiscible polymer–polymer blends, the final solid state properties are known to be dependent not only upon the selection of blend components and composition ratio, but are also determined by the solid-state morphology.<sup>1,2</sup> The underlying technology is one of morphology development for which the rheological behavior of the blend components, interfacial characteristics, and processing conditions are generally accepted as important.<sup>3</sup> Basic descriptors for the types of morphology include matrix-inclusion (or complex occlusion), cocontinuous, and fibrillar or lamellar structures. As discussed by Paul and Barlow,<sup>4</sup> cocontinuity of phases can give possibilities for unique load-bearing or failure properties in immiscible blend systems.

Reference can be made to a wide range of communications<sup>3,5–7</sup> that describe and quantify the dispersion process used to produce a blend of two immiscible materials. One of the important concepts in relation to morphology is the condition for phase inversion where the function of a polymer changes from dispersed phase to matrix, or alternatively, where cocontinuity of phases is observed. Utracki<sup>8</sup> and Elmendorp<sup>9</sup> have covered the subject of polymer blend morphologies in more detail, from which it is evident that one of

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the key controlling factors is the microrheology of systems, and specifically, the viscosity ratio between components, discussed later.

In this study, a model is first developed that can be used to assess the global state of flowinduced morphology that results for polymer blends of two immiscible components after melt processing under shear. Model predictions are compared to experimental observations of the morphology as frozen-in after injection molding for bisphenol A polycarbonate(PC)/acrylonitrile– butadiene–styrene(ABS) copolymer blends using microscopy and solid-state dynamic mechanical spectroscopy (DMS) techniques.

#### MORPHOLOGICAL MODEL: BACKGROUND AND DEVELOPMENT

Polymer-polymer blend engineering is clearly concerned with evolution of morphology during processing and fabrication because of the links to properties and, hence, performance in the final part. With regard to the flow of two phase systems, it is generally acknowledged<sup>4</sup> and observed<sup>10</sup> that a lower viscosity component tends to encapsulate a high viscosity component, with the effect of the lower viscosity component forming the continuous phase over wider component composition ranges than the higher viscosity component. This has evolved<sup>4,11</sup> into a practically useful relationship between the viscosities  $(\eta)$  and volume fractions ( $\theta$ ) of phases 1 and 2 in an immiscible polymer-polymer blend that describes the condition for phase inversion or dual phase continuity as:  $\eta_1/\eta_2 \approx \theta_1/\theta_2$ . It has been recognized<sup>12,13</sup> that care needs to be taken that the viscosity data relates to the actual shear conditions of the melt processing equipment, which is not always easy to approximate.

As identified by Elmendorp,<sup>9</sup> when two immiscible polymers are blended together that show distinct differences in phase viscosity/temperature or viscosity/shear rate characteristics, changes in either temperature or shear rate can cause morphological changes from matrix dispersion to cocontinuity or even induce phase inversion. The final processing operation is thus critical in determining blend morphology and, hence, material properties. Utracki<sup>8</sup> has presented a general stepped approach to designing a polymer blend, emphasizing the interrelationship between developed morphology and performance. Due to nonuniformity of the stress field during injection molding, a complex morphology is usually generated in a solid part.

The model rationalizes the above themes, providing a pragmatic tool for blend development. Based on past experience,<sup>10</sup> including the observed generation of new interface between phases during compounding, and on consideration of the energy input during typical shear flow conditions, the influence of interfacial tension is not considered to be important for this particular modeling approach, which utilizes the rheological properties of the components.

The underlying concept is based on the assumption that when a two-phase fluid system is subjected to a stress field, the difference in viscosity will cause a difference in the average velocity of each phase. This difference in velocities has been considered to be the origin of morphology development in a flow field. The difference in velocity will result in a difference in the volumetric flow rate of the individual phases, even when their actual volume fraction is identical. Based on this assumption, a concept of dynamic phase volume fraction, F, has been introduced:

$$F_2 = (1 - F_1) = V_2 / (V_1 + V_2) \tag{1}$$

where V is the volumetric flow rate of phases 1 and 2.

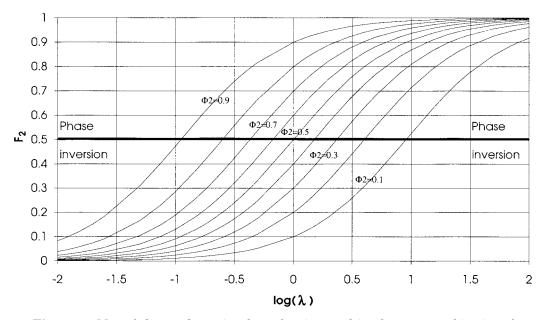
When stress is applied to the unit cross-sectional area of the blend, which consists of two phases of volume fractions  $\theta_1$  and  $\theta_2$ , the volumetric flow rate, *V*, for each phase is given by

$$V_1 = \theta_1 \times (u_1)$$
, and  $V_2 = \theta_2 \times (u_2)$ 

where (u) represents the average velocity of phases 1 and 2.

The ratio of velocities,  $u_2/u_1$  is equivalent to the viscosity ratio,  $\eta_1/\eta_2 (=\lambda)$ , between phases. As discussed by Utracki, and particularly relevant to higher shear conditions, the viscosity ratio should be determined at the same shear stress, although a number of reported studies often use viscosity ratio data generated at the same shear rate.

Equation (1) can then be expressed as  $F_2 = \theta_2 \lambda / (\theta_2 \lambda + \theta_1)$ . Figure 1 is constructed on the basis of this equation and, as can be seen, maps the different dynamic volume fractions that can result from any combination of actual volume fraction and viscosity ratio of two components. Considering that this flow-induced dynamic volume fraction and not the actual volume fraction



**Figure 1** Map of phase 2 dynamic volume fraction resulting from any combination of actual volume fraction and viscosity ratio of two immiscible components.

determines the morphology development, the condition of phase inversion or cocontinuity of phases will be achieved when  $F_1 = F_2 = 0.5$ . Under this condition, the above eq. (1) takes the form  $\theta_1/\theta_2 = \lambda$ .

# MODEL CORRELATION WITH PRACTICAL OBSERVATIONS

PC and ABS copolymer blends were studied as a model immiscible system. The two PC polymers used were Calibre®300-10(PC1) and Calibre®300-4(PC2), and are commercially available from the Dow Chemical Company. The ABS polymer was an experimental material produced via mass polymerization techniques and containing 16% acrylonitrile and 12% polybutadiene rubber. PC/ ABS blends as produced via melt processing operations described here are immiscible systems. Reported observations of shifts in glass transitions on blending of PC and styrene-co-acrylonitrile (SAN), which forms the matrix phase of the ABS copolymer, are not due to partial miscibility but can be attributed<sup>14,15</sup> to a redistribution or transfer of low molecular-weight species between phases.

#### **BLEND PREPARATION**

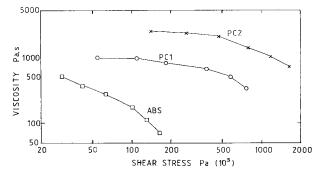
PC/ABS blend compositions containing 30, 60, and 70% PC1 and 60% PC2 were chosen to pro-

vide systems having variation of component ratio and variation of viscosity ratio at constant composition. PC polymers were dried in an air circulating oven at 90°C overnight prior to compounding. The blend components, available in pellet form, were weighted out in the desired weight ratios and tumble mixed for 10 min. The mixed pellet feedstock was melt compounded using a Buss MDK 46 Ko-Kneader machine with the following conditions: set temperatures 140°C screw, 230°C barrel, 240°C die; 15 kg/h; vacuum 0.8 bar. The resulting blends were pelletized after passing the strands through a water bath for subsequent injection molding.

All the blends and blend components were dried overnight at 90°C in an air circulating oven and injection molded with an Engle CC 90 ES 330/80 injection-molding machine into Izod test bars (ASTM D256; Fig. 4) with nominal dimensions of 63 by 12.5 by 3.2 mm, used for microscopy and dynamic mechanical spectroscopy analysis. Injection-molding machine settings were barrel temperature profile 260, 265, 270, 275, and 280°C, mold temperature 80°C, dosing speed 30%, holding pressure 50 bar, back pressure 5 bar, and filling speed 50 mm/s (unless stated).

#### **CHARACTERIZATION**

Melt rheological data were generated using a Gottfert capillary rheometer with die diameter of 1



**Figure 2** Viscosity versus shear stress for PC and ABS polymers; 280°C.

mm, length/diameter (L/D) ratio of 30, and entry angle of 180°. Data reported are on apparent wall shear rate and shear stress.

Estimates have been made using a Mold Flow software package to determine the apparent shear rates at different locations of the Izod mold, and used to help define the location of the respective blends on Figure 1 in the practical study.

Specimens were microtomed from the Izod test bars, and contrast achieved by etching away the PC phase with potassium hydroxide solution (2 h). Following sputtering with gold, scanning electron micrographs were obtained using a Phillips SEM 500 microscope.

Dynamic mechanical spectroscopy data were generated on as-molded test specimens using a Rheometrics Mechanical Spectrometer (RMS 800) having a forced constant amplitude fixed frequency mode of oscillation and for torsion rectangular test geometry. Measurements in the temperature (T) ramp mode with 2°/min heating rate were recorded for 0.1 shear strain and a test frequency of 10 rad/s.

#### **RESULTS AND DISCUSSION**

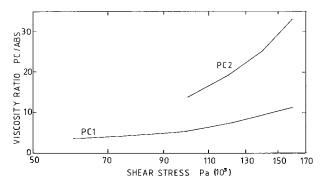
Figure 2 presents shear stress versus viscosity data for the PC and ABS blend components, and Figure 3 presents the viscosity ratio as a function of shear stress, derived from Figure 2. The viscosity ratio versus shear stress data confirm that significant differences can be found for the viscosity ratio between phases at different shear stresses, and this is an issue in the nonuniform stress fields associated with injection molding operations.

Figure 4 presents micrographs for the blends containing 30 and 70% PC1 taken at depths of 0

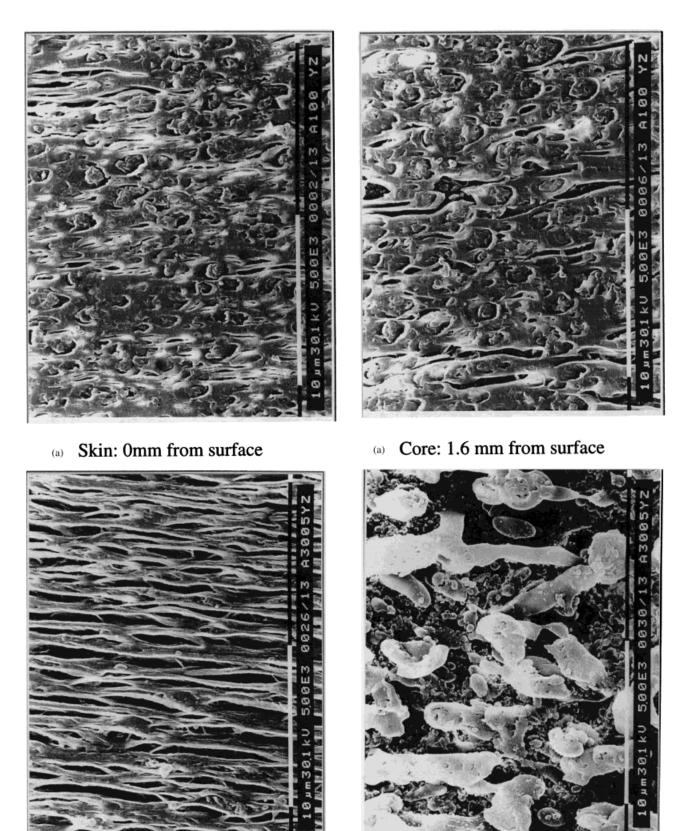
mm (skin) and 1.6 mm (core) from the surface of the Izod bar and in a plane parallel to the flow direction at the midpoint of the test bar. Considering ABS as the phase 2 material, Figure 5 includes a map of the morphology contours for the blends taken from Figure 1, and broadly locates the different micrographs. As is evident from Figure 2, the viscosity ratio  $\eta_{\rm PC}/\eta_{\rm ABS}$  is always greater than 1 within the stress range covered, and which is normally expected for practical processing, and increases as the shear stress increases. The applied shear stress is very low at the core of the part during injection molding, and is at its maximum close to the skin, with the consequence that the viscosity ratio  $\eta_{\rm PC}/\eta_{\rm ABS}$ grows on moving towards the skin region. Any changes on the rheological response of the PC and ABS phases in the blend compared to the unblended polymers due, for example, to a redistribution of low molecular weight species on blending is not taken into account.

The model correlates with the observation that the ABS phase forms the continuous phase for the blend with 30% PC1. The model also anticipates the major morphological differences observed for the 70% PC1/ABS blend, and corresponding with large differences in the dynamic volume fraction of the ABS phase for the relatively minor changes in shear stress that may be found in an injection molded part.

The DMS data of the 30 and 70% PC1/ABS blends and blend components is presented in Figure 6(a) for G' versus T and 6(b) for G'' versus T. By analogy with earlier reported studies,<sup>2,16</sup> the data give insight into the global state of blend morphology, with the particular test geometry used biasing the contribution of the skin region of the test bars. The data support the morphological observations made from the micrographs. The



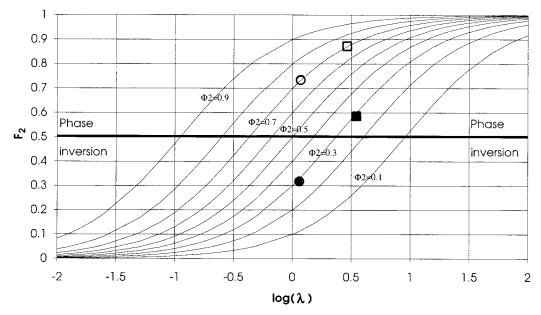
**Figure 3** Viscosity ratio versus shear stress for PC1/ABS and PC2/ABS.



### (b) Skin: 0 mm from surface

(b) Core: 1.6 mm from surface

**Figure 4** (a) SEM (0 and 1.6 mm from the surface of the Izod bar) for 30/70 PC1/ABS blend (scale: white line is 10 microns). (b) SEM (0 and 1.6 mm from the surface of the Izod bar) for 70/30 PC1/ABS blend (scale: white line is 10 microns).



**Figure 5** Model morphology predictions: 30/70 and 70/30 PC1/ABS blends [30/70 PC1/ABS: ( $\square$ ) skin, ( $\bigcirc$ ) core; 70/30 PC1/ABS: ( $\blacksquare$ ) skin, ( $\bigcirc$ ) core].

data give a measure of PC phase (co)continuity via the level of the G' plateau region between  $T_g(SAN)$  and  $T_g(PC)$ , and the amplitude of the  $T_g$  loss peaks. For the 30% PC1/ABS blend, the absence of a significant  $T_g(PC)$  peak or well-defined plateau region between  $T_g(SAN)$  and  $T_g(PC)$  provides additional evidence that ABS is the matrix phase. For the 70% PC1/ABS blend, the decreased, and unexpectedly low, amplitude of the  $T_g(PC)$  peak provides additional evidence that the PC fraction does not all lie in (co)continuous domains.

Figure 7 presents micrographs for the 60/40 blends containing PC1 and PC2 taken at the surface of the Izod bar and perpendicular to the flow direction at the midpoint of the test bar. The blend with PC1 was also molded using a slower filling speed of 25 mm/s, hence molding this material under different shear stress conditions. Considering ABS as the phase 2 material, Figure 8 includes a map of the morphology contours for the blends taken from Figure 1, and broadly locates the different micrographs. As is evident from Figure 2, the viscosity ratio  $\eta_{\rm PC}/\eta_{\rm ABS}$  is always greater than 1, and increases as the shear stress increases, in particular for the PC2 polymer. For these PC/ABS blends where the viscosity ratio between phases becomes very high at high shear rates, the created morphologies are more lamellar in form. The clear difference in the morphologies created at the two different filling

speeds is especially evident for the PC1/ABS blend, which shows the proportionally larger estimated change in dynamic volume fraction for the two molding conditions.

#### CONCLUSION

The rheological parameters of the respective phases in an immiscible blend clearly play a major role in determining blend morphology during flow. The model predictions, developed on the basis of a dynamic phase volume, correlate reasonably well to experimental observations of the frozen-in morphology for immiscible PC/ABS blends. DMS is effective in probing morphological differences and provides a clear link into morphology– property interrelationships.

There are some practical limitations in correlating the morphological structure to a model that only incorporates the viscosity ratio between components, rather than including other parameters such as melt elasticity. This latter parameter may contribute to the observed development of lamellar structures at high viscosity ratios between components. Additionally, it is not always possible to preserve the blend morphology developed during flow because of its nonequilibrium nature. Under low shear conditions, interfacial tension provides the driving force for morphological changes.

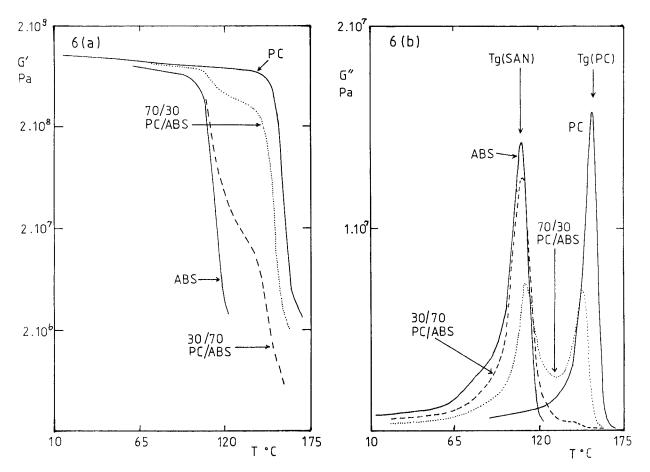


Figure 6 DMS data: 30 and 70% PC1/ABS blends and blend components. 6(a) G' versus T; 6(b) G'' versus T.

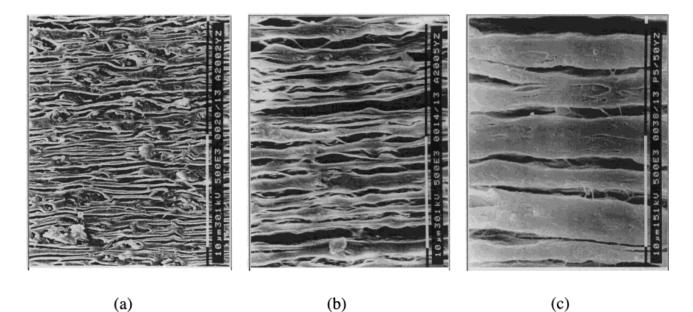
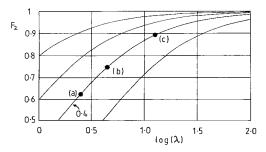


Figure 7 SEM (surface of Izod bar) for 60/40 PC/ABS blends having PC components of different viscosity. (a) PC1, 25 mm/min injection speed; (b) PC1, 50 mm/min injection speed; (c) PC2, 50 mm/min injection speed (scale: white line is 10 microns).

(c)

(a)



**Figure 8** Model morphology predictions: 60/40 PC/ABS. (a), (b), and (c) correspond to the Figure 7 caption.

In most molding operations the applied stress is nonuniform, and the flow is unlikely to involve pure shear. Nevertheless, the model has practical utility, and helps to identify the combination of components and processing conditions likely to result in mixed morphological structures, and possible unacceptable variation in part properties. As such, the model is a useful tool to assist in the design of a practical blend system.

The morphology map has also been linked with mold flow simulations that give shear stress distributions, and hence, anticipated blend morphology differences, on filling a final part during injection molding.

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