

# Phase inversion and dual-phase continuity in polymer blends: theoretical predictions and experimental results

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In this work, the point of phase inversion for several polymer blends is investigated experimentally. Four different blends were studied: polystyrene/polyethylene, poly(methyl methacrylate)/polyethylene, polystyrene/poly(methyl methacrylate) and polycarbonate/polystyrene. Blends were prepared at the compositions where phase inversion is expected to occur according to the predictions of the model of Avgeropoulos, equating the torque ratio with the volume-fraction ratio. The morphology of the prepared blends was examined using scanning electron microscopy. The results obtained were then compared to the values of the point of phase inversion calculated with various semi-empirical models. The results show that the model of Avgeropoulos predicts satisfactorily the point of phase inversion for torque ratios close to unity, whereas using the viscosity ratio the prediction is far away from the experimental values. The model of Metelkin and Blekht and that of Miles and Zurek were found to overestimate the composition at which phase inversion occurs, while the model of Utracki was found to agree with the experimental results for blends having a viscosity ratio far from unity. Moreover, no correlation was found between the torque ratio and the shear or complex viscosity ratio for the different blends, suggesting that the model of Avgeropoulos cannot be used by substituting the torque ratio by the viscosity ratio. Copyright © 1996 Elsevier Science Ltd.

**(Keywords: blend morphology; co-continuity; phase inversion)**

## INTRODUCTION

Blending two polymers usually results in the formation of an immiscible heterogeneous two-phase system due to thermodynamic reasons<sup>1,2</sup>. In general, the morphology of multiphase polymer blends depends on the composition, the viscoelastic properties of the individual components and the blending conditions<sup>14</sup>. Several morphologies can be obtained over the entire composition range. At low concentrations, a dispersed phase-matrix morphology is found, in which the shape of the dispersed phase can be spherical, fibrillar or lamellar<sup>58</sup>. Spherical domains are obtained for concentrations lower than 15% and they can be deformed into ellipsoids and/or fibres depending on the shear history during the processing step<sup>9,10</sup>. Above a threshold concentration of 15.6 vol%, the formation of a more continuous dispersed phase is obtained due to coalescence, in accordance with the percolation theory for spherical dispersions<sup>11,12</sup>. Above this concentration, the formation of a more continuous dispersed phase is obtained due to coalescence and coarsening. Further increase in the amount of the dispersed phase will lead to phase inversion at which a co-continuous structure is formed<sup>8,10,13,17</sup>.

The morphology of a two-phase polymer blend is usually a non-equilibrium structure, which may undergo severe changes during further processing. A practical way of stabilizing these morphologies is by modifying the interface between the two components. This can be achieved by adding block copolymers having end-groups partially compatible with the individual polymers<sup>1</sup>. Another method of modifying the interface is by reactive extrusion in which grafts are formed between the reactive sites of the blend components<sup>18</sup>.

Interpenetrating polymer blends (IPBs) or polymer blends exhibiting co-continuous structures are known to possess relatively stable morphologies, which seem to coarsen upon annealing without a change in the type of morphology<sup>16,17,19,21</sup>. This is obtained for compositions where almost total co-continuity is achieved. It has also been shown that reprocessing of this type of blend does not significantly affect the morphology<sup>22,23</sup>.

Co-continuity and phase inversion are still not fully described in the literature on polymer blends and alloys. One of the reasons is that, from a practical point of view, the formation of co-continuous structures in polymer blends requires relatively high amounts of both components. Another reason is that blends with such morphologies have not found a potential application. Although both components are continuous and can thus fully contribute to the properties of the blends, the materials usually possess weak mechanical properties. This is caused by weak interfacial interactions between the two

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polymers and a larger interfacial area. In the presence of interfacial modifiers, it is possible to obtain blends with co-continuous structures and improved mechanical properties simultaneously. The formation of co-continuous structures at low concentrations of one polymer in the other, in the presence of a compatibilizer, can be of significant importance for the design of novel materials. It is therefore necessary to control the parameters that alter these structures in their unmodified state in order to be able to consider the effect of compatibilization. The determination of the viscoelastic properties of the individual components (torque or viscosity ratio) to predict the composition of the blend where phase inversion occurs might represent the first step.

Co-continuous structures are usually observed in a range of compositions around the point of phase inversion. Several semi-empirical models are used throughout the literature to predict this point<sup>3,24,27</sup>. In the present work, the morphology of various immiscible blends and the validity of these theoretical models in their prediction of the point of phase inversion were investigated in the composition range where co-continuity is expected to occur.

## THEORETICAL ASPECTS

In general, the morphology of polymer blends is directly related to the viscoelastic properties of their individual components. The point of phase inversion at which co-continuity is observed is related to the rheology of the pure materials through semi-empirical models<sup>3,24,27</sup>. Avgeropoulos *et al.*<sup>25</sup> used a relationship between the torque ratio and the composition (volume fraction) expressed as:

$$\frac{T_1}{T_2} = \frac{\phi_1}{\phi_2} \quad (1)$$

where  $T_i$  is the torque of polymer  $i$  and  $\phi_i$  is the volume fraction of polymer  $i$ . By using the torque ratio as the viscoelastic characteristic of the materials, Avgeropoulos *et al.*<sup>25</sup> included all forces, such as shearing and elongational forces, that act on the polymers during blending in an internal mixer.

For blends prepared at low shear rates, Paul and Barlow<sup>3</sup> proposed a similar theoretical prediction of the point of phase inversion. This relationship was expressed in a semi-empirical equation by Jordhamo *et al.*<sup>24</sup> and Gergen *et al.*<sup>19</sup> and later generalized by Miles and Zurek<sup>27</sup> as:

$$\frac{\eta(\dot{\gamma})_1}{\eta(\dot{\gamma})_2} = \frac{\phi_1}{\phi_2} \quad (2)$$

where  $\eta(\dot{\gamma})_i$  is the viscosity of polymer  $i$  at the shear rate of blending. The validity of this equation was confirmed by several authors for blends with a viscosity ratio close to unity<sup>23,24,27,28</sup>.

Another model to predict the point of phase inversion was derived by Metelkin and Blekht based on the filament instability concept<sup>29</sup>. The critical volume fraction for phase inversion was calculated to be:

$$\phi_2 = \frac{1}{1 + \lambda F(\lambda)} \quad (3)$$

where

$$F(\lambda) = 1.25 \log \lambda + 1.81 (\log \lambda)^2 \quad (4)$$

with  $\lambda$  being the viscosity ratio of the blend components at the blending shear rate.

Utracki<sup>26</sup> suggested a model that can be used to predict the point of phase inversion for blends with a viscosity ratio away from unity:

$$\lambda = \left( \frac{(\phi_m - \phi_{2l})}{(\phi_m - \phi_{1l})} \right)^{[\eta] \phi_m} \quad (5)$$

where  $[\eta]$  is the intrinsic viscosity and  $\phi_m$  is the maximum packing volume fraction. This model is based on a dependence of the viscosity on the volume fraction of monodispersed hard spheres in the matrix, as proposed by Krieger and Daugherty<sup>30</sup>. For polymer blends, the maximum packing volume fraction in equation (5) can be taken as  $\phi_m = 1 - \phi_c$ , where  $\phi_c$  is the critical volume fraction for percolation<sup>11,12</sup>. The theoretical value of  $\phi_c$  for three-dimensional spherical dispersions is equal to 0.156<sup>31</sup>. Utracki<sup>26</sup> mentioned that the optimum value of the intrinsic viscosity  $[\eta]$  is 1.9, based on published data of the points of phase inversion of thermoplastics and rubbers.

## EXPERIMENTAL

### Materials

General-purpose polystyrene (PS 667) and high-density polyethylene (PE 04352N) in pellet form were supplied by Dow Chemical, Canada. Poly(methyl methacrylate) (PMMA, DWS 790-1) and polycarbonate (PC, Lexan HF1110) were provided by Rohm and Haas, USA, and General Electric, USA, respectively.

### Torque measurements

Torque measurements were carried out using a Haake Buchler system 90, equipped with a 60 cm<sup>3</sup> mixing chamber, to obtain the torque values of the individual polymers. A rotor speed of 50 rpm was used and a total mixing time of 10 min for each polymer. The equilibrium torque values, obtained after 10 min of mixing, and the densities of the polymers at the corresponding temperatures are reported in Table 1. These values were used to calculate the composition of the blends where phase inversion is expected to occur by using the model of Avgeropoulos<sup>25</sup>.

Table 1 Torque and density values of the raw materials

	$T$ (°C)	Torque (Nm)	Density <sup>a</sup> (g cm <sup>-3</sup> )
PS	180	7.4	0.980
	200	4.6	0.973
	220	2.1	0.960
	240	0.8	0.949
PE	180	5.8	0.758
	200	4.8	0.752
	220	4.2	0.741
PMMA	200	8.0	1.099
	220	3.7	1.089
PC	240	4.4	1.094

<sup>a</sup> Calculated from ref. 32

### Rheology

The materials were characterized using a Bohlin constant-stress rheometer CSM 25 under a constant nitrogen flow. Measurements were performed in the plate-plate configuration with a gap of approximately 1.50 mm in the frequency range of 0.01 to 40 Hz. Table 1 reports the temperatures at which the materials were characterized.

### Blending

The Haake Buchler system 90 was used to prepare different blends. Materials were mixed for 10 min in the melt state at 50 rpm and, after removal from the mixing chamber, air cooled without further shaping. Polycarbonate and poly(methyl methacrylate) were dried for 12 h at 120 and 90°C, respectively, before blending. The equation of Avgeropoulos *et al.*<sup>25</sup> was used to determine the theoretical compositions of phase inversion for the different blends prepared. The calculated volume fractions were converted to weight fractions by using the densities of the polymers at the respective temperatures (Table 1)<sup>32</sup>. Additional blends containing 5 wt% more or 5 wt% less of polymer *i* than the predicted composition were prepared, based on the estimation of experimental errors made in the preparation of the blends. For example, the theoretical point of phase inversion of the PS/PE blend prepared at 180°C is estimated at the 62/38 composition according to the model of Avgeropoulos *et al.*<sup>25</sup>. Therefore, blends having compositions 67/33, 62/38 and 57/43 were prepared. The calculated points of phase inversion for the different blends are underlined in Table 2.

### Morphology

The morphology of all blends was examined using a JEOL JSM 35 scanning electron microscope. All samples were cryofractured in liquid nitrogen and their surfaces were coated with a gold-palladium layer. Scanning of the whole sample, for the best representation, was done before the micrographs were taken.

## RESULTS AND DISCUSSION

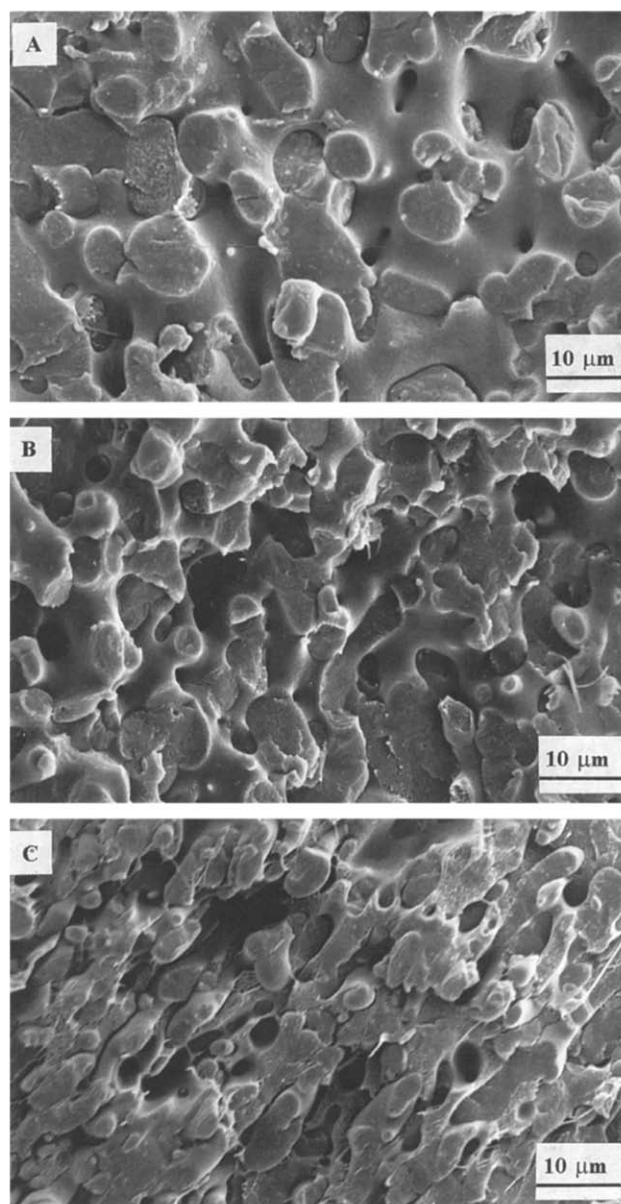
Morphological examination of the PS/PE blends prepared at 180°C showed that co-continuous morphologies were formed in all the compositions studied. This can be clearly seen in Figure 1, which shows the fracture surfaces of the respective blends. At 200°C, a lower torque ratio is obtained for the PS/PE blends, resulting in a shift of the theoretical point of phase inversion to a lower PS-containing composition (55/45). Figure 2 shows that at this composition and also at the other compositions prepared at 200°C co-continuous morphologies are obtained. Increasing the temperature to 220°C resulted in a torque ratio of 0.5, leading to a theoretical point of phase inversion at the 42/58 PS/PE composition. However, experimentally, a droplet-matrix morphology was obtained at this composition, while partial co-continuity was observed at 47/53 PS/PE (Figure 3). This indicates that full co-continuity can probably be obtained at a higher PS content.

For the PMMA/PE blends prepared at 200°C, having a torque ratio of 1.67, the theoretical point of phase inversion was estimated to be 70/30. Micrographs of the

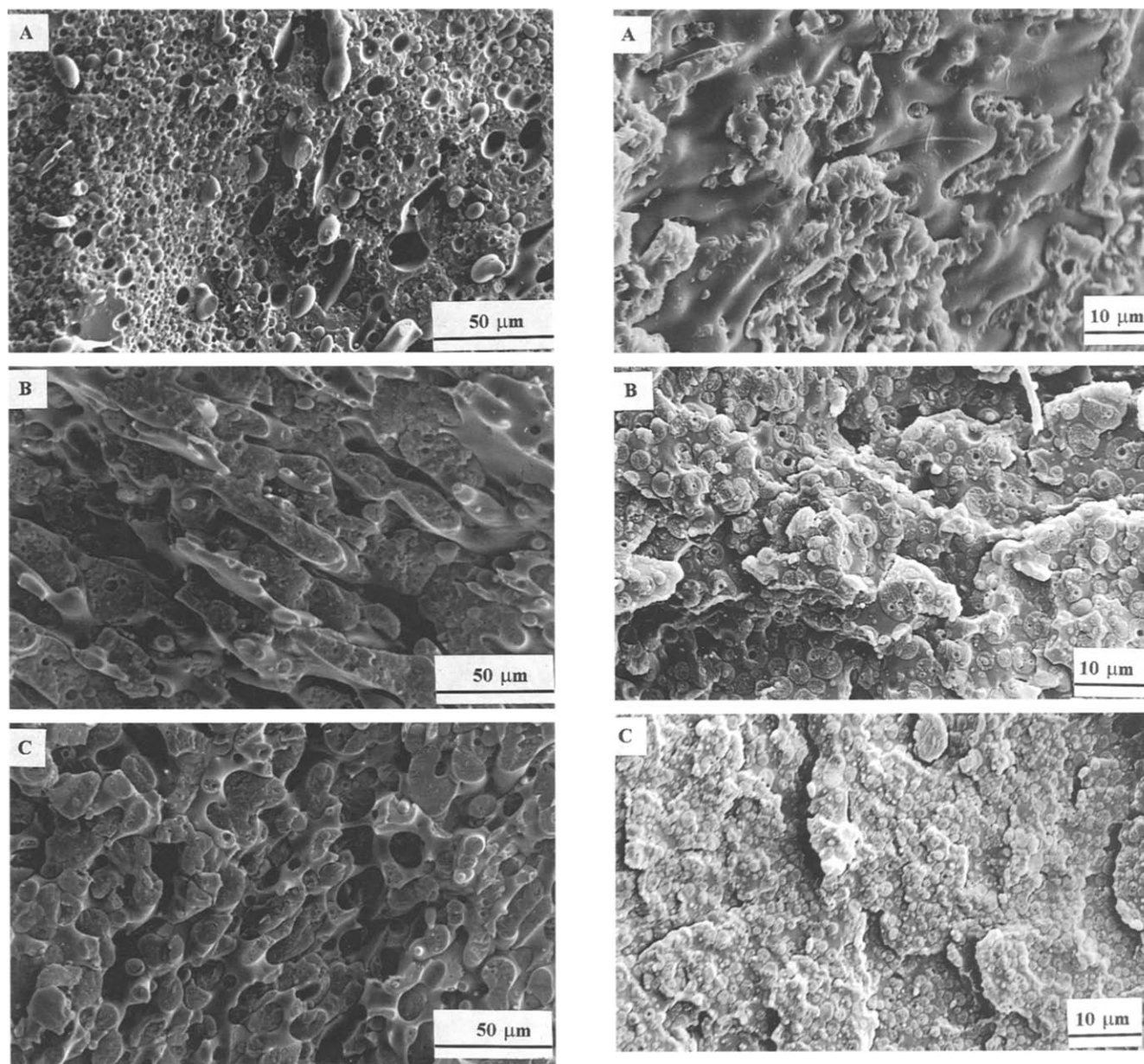
cryofractured blends show that co-continuity is obtained in blends containing 65 and 70 wt% PMMA, which is in agreement with the prediction of the model used (Figure 4). The 75/35 blend showed a transition morphology

**Table 2** Torque ratio and compositions of the prepared blends

	<i>T</i> (°C)	Torque ratio	Compositions (weight fractions)		
PS/PE	180	1.28	67/33	<u>62/38</u>	57/43
	200	0.96	60/40	<u>55/45</u>	50/50
	220	0.50	47/53	<u>42/58</u>	37/63
PMMA/PE	200	1.67	75/25	<u>70/30</u>	65/35
PS/PMMA	220	0.57	40/60	<u>35/65</u>	30/70
PC/PS	240	5.50	90/10	<u>85/15</u>	80/20
			75/25	<u>70/30</u>	65/35
			60/40	<u>55/45</u>	



**Figure 1** SEM micrographs for PS/PE blend prepared at 180°C: (A) 67/33, (B) 62/38, (C) 57/43



**Figure 2** SEM micrographs for PS/PE blend prepared at 200°C: (A) 60/40, (B) 55/45, (C) 50/50

consisting of droplets and elongated dispersed phases in a matrix of PMMA.

Figure 5 shows the morphologies of the PS/PMMA blends prepared at 220°C. Co-continuity is obtained at the 40/60 PS/PMMA composition, which is close to the theoretical point of phase inversion (35/65). As can be seen from Figure 5B, the morphology of the 35/65 composition consists of a tightly packed dispersed phase in a matrix. This might indicate that coalescence of PS has not yet occurred.

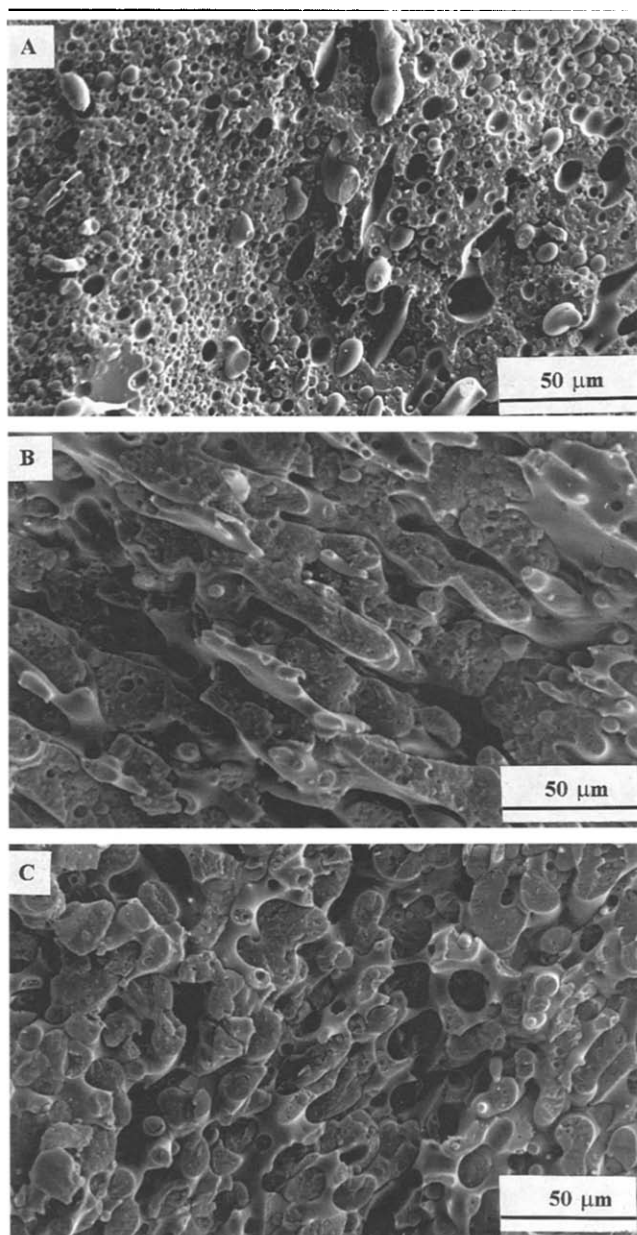
For the PC/PS blends prepared at 240°C, the torque ratio was found to be 5.50, indicating a theoretical point of phase inversion at a 85/15 PC/PS composition. However, the blends containing 80 to 90 wt% PC showed a droplet-matrix morphology (Figure 6). Therefore, additional blends containing lower amounts of PC were prepared to reach the experimental point of phase inversion. Co-continuity was obtained for blends with a PC content of 55 and 60 wt%.

47/53. (B)

A maximum error in the estimation of the values of the point of phase inversion is assumed to be within a range of  $\pm 5$  wt% from the experimental points. Based on this assumption, the morphological results indicate that the model of Avgeropoulos correctly predicts the point of phase inversion for the PS/PE (180 and 200°C) and PMMA/PE blends. The predicted values for PS/PE at 220°C and PS/PMMA are within 10% of the experimental results, whereas the model failed for the PC/PS blend. This might be explained by the fact that the torque ratio of this blend is much higher than that of the other blends and also far away from unity.

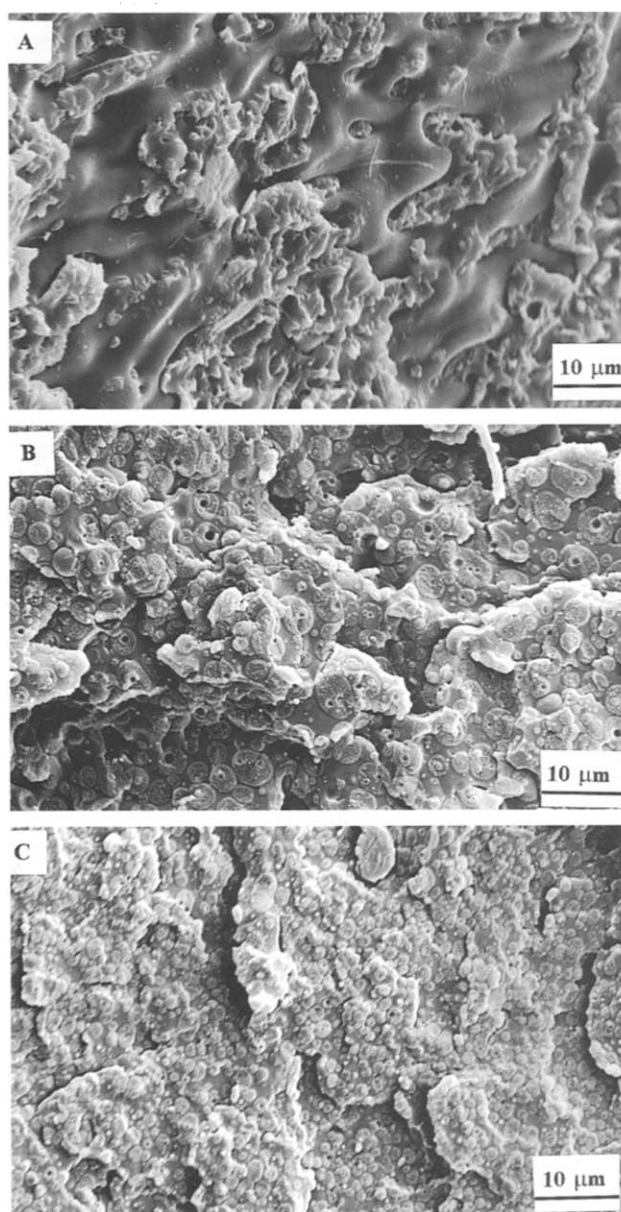
The points of phase inversion for the blends studied in this work were also calculated with the model of Miles and Zurek<sup>27</sup> described by equation (2). The required values of the viscosity of the individual blend components at the estimated shear rate of blending were obtained from rheological measurements. The maximum shear rate is estimated to be  $70 \text{ s}^{-1}$ , under the mixing conditions (50 rpm) and the type of mixing chamber used<sup>33,34</sup>.

The complex viscosity, the storage modulus and the



**Figure 4** SEM micrographs for PMMA/PE blend prepared at 200°C: (A) 75/25, (B) 70/30, (C) 65/35

loss modulus of the individual polymers at the specific temperatures are shown in *Figures 7–10*. In the low-frequency region, the complex viscosity seems to reach a plateau-like behaviour for all polymers. At higher frequencies, PE and PC exhibit almost a Newtonian behaviour, while PS and PMMA show a power-law behaviour. It is interesting to note that, in the low-frequency region, the viscosity of PS is largely influenced by the temperature, whereas only a slight decrease in viscosity is observed for PE with increasing temperature (*Figures 7 and 8*). The effect of temperature on the viscosity of PS is less pronounced at the shear rate of blending ( $70 \text{ s}^{-1}$ ). This suggests that the viscosity ratio of PS/PE blends at  $70 \text{ s}^{-1}$  is not significantly affected by the temperature. The viscosity ratios of the blends at the estimated shear rate of blending ( $70 \text{ s}^{-1}$ ) were used to calculate the point of phase inversion for each blend with the model described by equation (2).



**Figure 5** SEM micrographs for PS/PMMA blend prepared at 220°C: (A) 40/60, (B) 35/65, (C) 55/45

*Table 3* shows the torque ratios and the viscosity ratios at  $70 \text{ s}^{-1}$  for the different blends and the corresponding theoretical points of phase inversion calculated with equations (1) and (2), respectively. The values for the point of phase inversion as calculated with the viscosity ratio (equation (2)) differ largely from those based on the torque ratio (equation (1)) for PS/PE and PMMA/PE blends. For PS/PMMA and PC/PS blends, the difference is 8% and 4%, respectively. This is due to the smaller difference between the viscosity ratio and the torque ratio for the latter blends.

Morphological examination of the blends (*Figures 1–6*) showed that the values calculated with equation (2) differ largely from the experimental point of phase inversion for the PS/PE, PMMA/PE and PC/PS blends. Only the predicted value for the PS/PMMA blend is within 5% error of the experimental value. This indicates that equation (1) is more suitable for the prediction of the point of phase inversion.

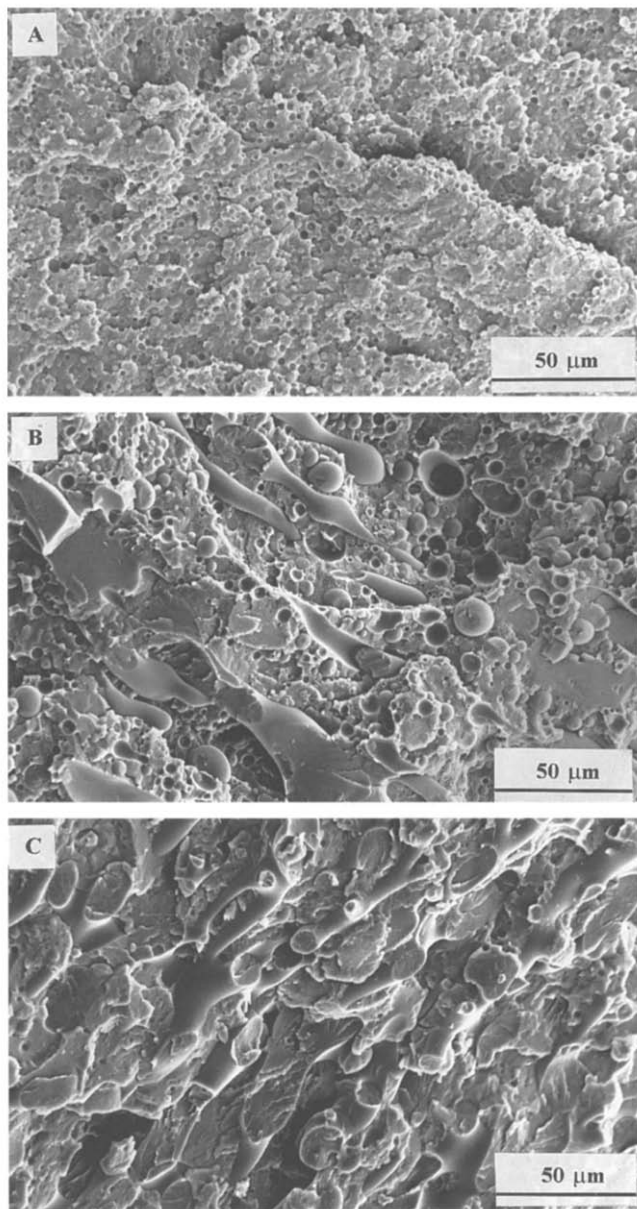


Figure 6 SEM micrographs for PC/PS blend prepared at 240°C: (A) 65/35, (B) 60/40, (C) 55/45

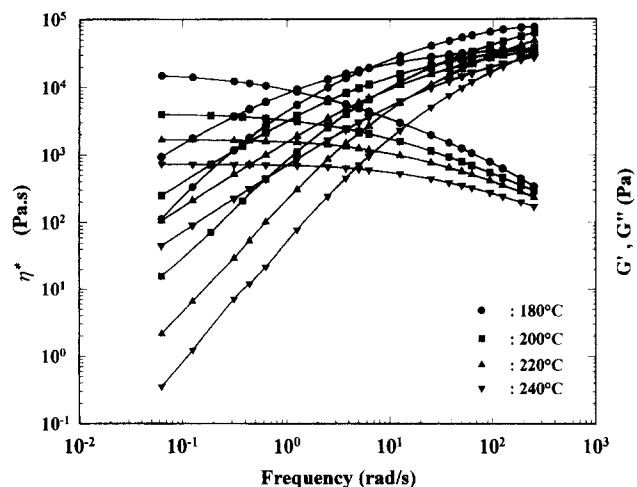


Figure 7 Complex viscosity  $\eta^*$ , storage modulus  $G'$  and loss modulus  $G''$  of PS at different temperatures

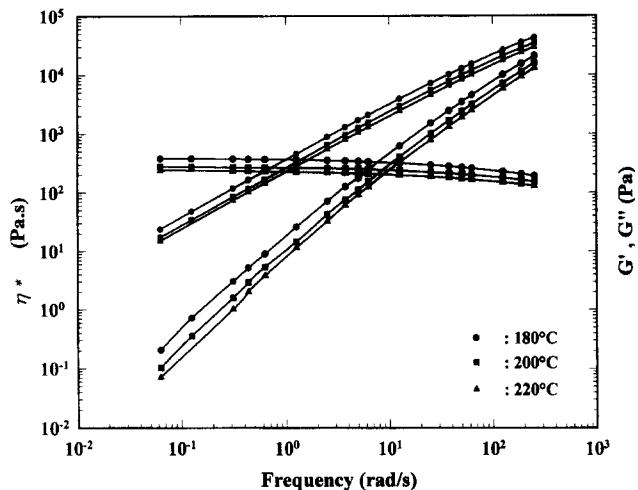


Figure 8 Complex viscosity  $\eta^*$ , storage modulus  $G'$  and loss modulus  $G''$  of PE at different temperatures

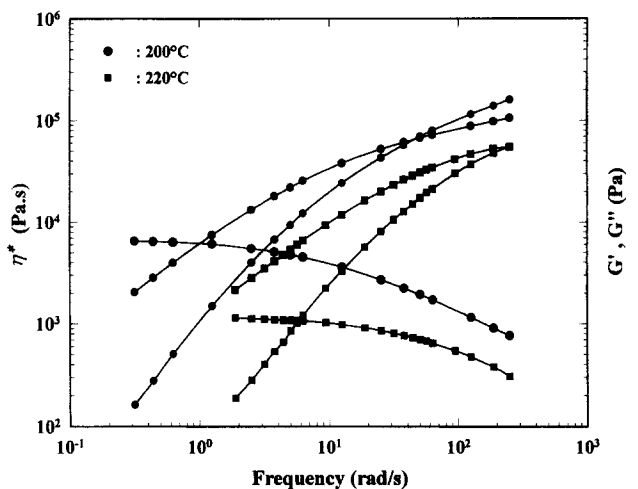


Figure 9 Complex viscosity  $\eta^*$ , storage modulus  $G'$  and loss modulus  $G''$  of PMMA at different temperatures

Several authors<sup>24,27,35</sup> have used the model of Avgeropoulos to predict the point of phase inversion for different blends. Some of them have equated the torque ratio with the composition ratio. Different approximations were used to convert the torque values to viscosity values, leading to the model proposed by Jordhamo *et al.*<sup>24</sup>. Other authors used the latter model and substituted the viscosity ratio by the torque ratio. In some cases, this procedure has led to a good agreement between the theoretical and experimental values of the point of phase inversion. Favis and Chalifoux<sup>36</sup> reported a direct correlation between the torque ratio and the shear viscosity ratio for nine blend combinations of three PC and three polypropylene (PP) resins. Later, Favis<sup>37</sup> described that, by substituting the shear viscosity ( $\eta'$ ) ratio by the complex viscosity ( $\eta^*$ ) ratio, the correlation between the two parameters goes to zero for these blends. Using this assumption, equations (1) and (2) lead to the same result. It should be noted that in this case the materials used were obtained from the same source and differ only in their molecular weights. This will have the same effect as if the temperature is varied for a unique set of polymers. Figure 11 shows that for the blends studied

in this work no correlation is found between the torque ratio and either shear or complex viscosity ratios. This is due to the fact that the rheological behaviours of the individual polymers differ significantly (almost Newtonian to power-law), especially in the region of shear rate of blending. The difference in their rheological behaviour is attributed to the random choice of the materials used in this study. Therefore, the torque ratio cannot be directly correlated with the viscosity ratio, since the shear history

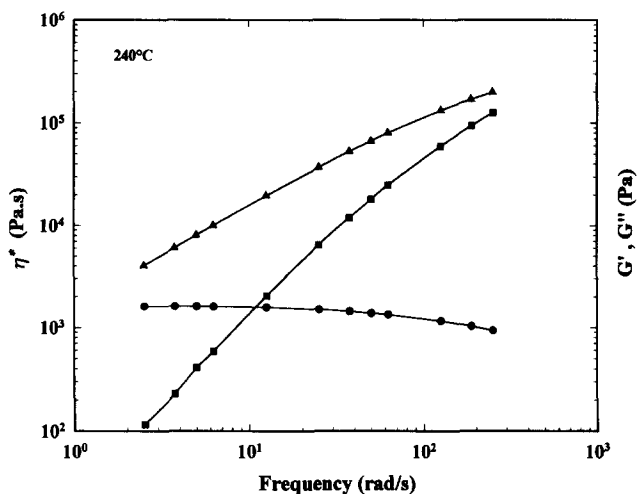


Figure 10 Complex viscosity  $\eta^*$ , storage modulus  $G'$  and loss modulus  $G''$  of PC at 240°C

Table 3 Torque and viscosity ratios of the different blends

	$T$ (°C)	Torque ratio at 50 rpm	Theoretical point of phase inversion	Viscosity ratio at $70 \text{ s}^{-1}$	Theoretical point of phase inversion
PS/PE	180	1.28	62.3	4.13	84.2
	200	0.96	55.4	3.50	81.9
	220	0.50	39.3	3.12	80.2
PMMA/PE	200	1.67	70.9	8.65	92.7
PS/PMMA	220	0.57	33.4	0.79	41.6
PC/PS	240	5.50	86.4	4.12	82.6

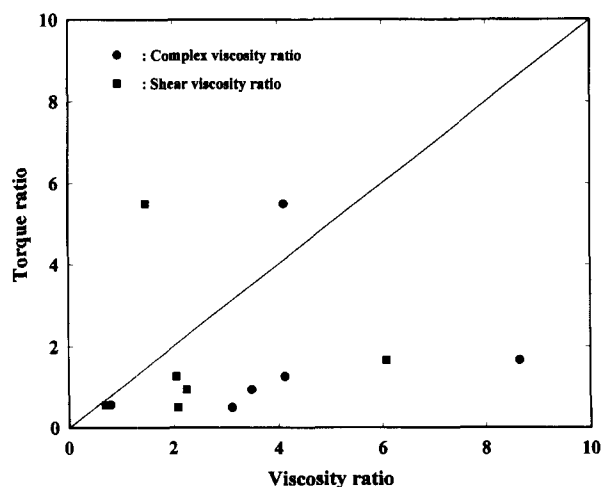


Figure 11 Torque ratio versus viscosity (complex and shear) ratio for the different blends studied

inside the mixing chamber and inside a rotational rheometer are different.

Table 4 shows the values of the points of phase inversion predicted by equation (3) for the different blends. Viscosity ratios estimated at were used for these predictions. This model overestimates the point of phase inversion for all blends, except for PS/PMMA. This is probably due to the fact that the viscosity ratio of the latter blend is close to unity whereas for the others it is away from unity.

The values of the points of phase inversion predicted by equation (5) are also reported in Table 4. Compared to the experimental results, the predictions of equation (5) are in good agreement for PS/PE at 180°C and PC/PS blends. For PS/PE at 200 and 220°C and PMMA/PE blends, the predicted values are within 10% error, whereas for PS/PMMA the theoretical value is considerably overestimated. From the morphological examination of the PS/PE blend prepared at 220°C, it is likely that the predicted value also differs by 10% or more from the experimental point of phase inversion.

The comparison of the experimental values of the points of phase inversion with the predictions of the different models given by equations (1), (2), (3) and (5) clearly demonstrates that the model of Metelkin and Blekht<sup>29</sup> (equation (3)) is not suitable. This might be attributed to the high viscosity ratio of the blends, which is away from unity. One exception is, however, obtained in the case of PS/PMMA blend, for which the viscosity ratio is relatively close to unity.

In general, equation (5) gives better predictions than equations (2) and (3). This is in good agreement with the results presented by Utracki<sup>26</sup>. However, for PS/PMMA blend, equations (2) and (3) seem to give better agreement than equation (5). A similar result was found for PS/PMMA blend with a viscosity ratio of 0.41<sup>38,39</sup>. The comparison between the predictions of equation (1) and equation (5) shows that the first model is more suitable for predicting the point of phase inversion. The predicted values for PS/PE (180 and 200°C) and PMMA/PE using equation (1) are within 5% error and those for PS/PE (220°C) and PS/PMMA are within 10%. On the other hand, only the values for PS/PE (180°C) and PC/PS as calculated with equation (5) are within 5% error, while PS/PE (200°C) and PS/PMMA are within 10%. In the case of PC/PS blend, the prediction of the theoretical point of phase inversion with equation (1) is significantly different from the experimental point. This is attributed to the high torque ratio calculated at this temperature.

Table 4 Comparison of theoretical points of phase inversion, calculated with several models<sup>a</sup>, with experimental results

	Temp. (°C)	Eq. (1)	Eq. (2)	Eq. (3)	Eq. (5)	Expt.
PS/PE	180	62.3	84.2	94.3	70.0	57–67
	200	55.4	81.9	92.6	69.0	50–60
	220	39.3	80.2	91.2	68.0	>47
PMMA/PE	200	70.9	92.7	98.3	77.0	65–70
PS/PMMA	220	33.4	41.6	35.5	61.0	40
PC/PS	240	86/4	82.6	93.6	51.0	55–60

<sup>a</sup> Eq. (1): Avgeropoulos (torque ratio)

Eq. (2): Miles and Zurek at low shear rate (viscosity ratio)

Eq. (3): Metelkin and Blekht at low shear rate (viscosity ratio)

Eq. (5): Utracki at low shear rate (viscosity ratio)

Another interpretation may be based on the fact that this particular blend exhibits a partial miscibility at low PS content<sup>40</sup>. This has the effect of shifting the composition at which phase inversion occurs to higher concentrations of PC.

The effect of interfacial tension on the formation of the morphology of polymer blends has not been well described in the open literature. Taylor derived an equation for predicting the size of droplets in a Newtonian mixture taking into account the interfacial tension and the viscosity of the components together with the shearing force<sup>41</sup>. In the case of viscoelastic materials, it is usually found that the optimum phase diameter is higher than that predicted by Taylor's equation<sup>36,42</sup>. This is due to the fact that the elastic contribution of the individual materials is not taken into consideration. On the other hand, as the phase inversion is approached, coalescence occurs and it is no longer possible to quantify the morphology of the blends using Taylor's equation.

The models used for the prediction of the point of phase inversion do not include the interfacial tension parameter. However, this parameter is of a prime importance in the formation of any type of morphology of polymer blends. Table 5 illustrates the interfacial tension between the different blend components at 200°C. The value of the interfacial tension is estimated to be approximately the same at the mixing temperatures used for the blends since the variation of this parameter with temperature is not significant<sup>43</sup>. For PS/PE and PMMA/PE the interfacial tension is relatively high (5.1 and 9.0 mN m<sup>-1</sup>, respectively), suggesting a sharp interface. This is due to the repulsion forces that prevent the two components from an intimate contact. On the other hand, for low interfacial tension as in the case of PS/PMMA and PC/PS (1.1 and 1.2 mN m<sup>-1</sup>, respectively), a very thin interface as well as an intimate contact can be observed due to the presence of specific interactions. This has been confirmed by several authors for PS/PMMA and PC/PS, for which a partial miscibility between the different polymers was evidenced at low concentrations<sup>40,44</sup>.

If the interfacial tension between two polymers is low, then a droplet-matrix morphology can be obtained up to 40% of the dispersed phase without having a major change in the structure. This might be attributed to the fact that a low interfacial tension prevents the phases from break-up and coalescence. In the opposite case, i.e. high interfacial tension, the repulsion forces contribute to the break-up and therefore coalescence might occur at a lower concentration of the dispersed phase. The PS/PMMA blend was shown to exhibit a droplet-matrix morphology for concentrations of the minor phase (PS) as high as 35 wt%. This agrees well with the data presented by Burns and Kim<sup>44</sup>. The PS/PE blend exhibits a relatively high interfacial tension and shows changes in

the type of morphology for concentrations of the minor phase lower than 20%<sup>5,6</sup>.

As discussed previously, Taylor's equation predicts the phase size in Newtonian multiphase systems. The elastic effects are neglected in this equation since a quasi-Newtonian behaviour is expected for the blend components. However, several authors have attributed the discrepancy between the experimental phase size and that predicted by Taylor to the elasticity of the polymers<sup>36,42</sup>. Therefore, it is important to take into consideration the elastic effects for the prediction of the phase size and also of the point of phase inversion. The use of the torque ratio in equation (1) represents a more direct measurement of the shearing history of the blending step than the viscosity ratio, which is an off-line technique. In this way, the elastic effects are better considered for the prediction of the point of phase inversion.

Hence, the use of equation (1) with the torque ratio is more appropriate to predict the point of phase inversion in polymer blends. The experimental results have shown that substituting the torque ratio by the viscosity ratio leads to an overestimation of the predicted values. Another important point to discuss is the limitation of the model of Avgeropoulos. One should ask: Up to which blend composition is the model valid? According to the percolation theory, the critical concentration for percolation, and therefore coalescence, is 15.6 vol%. Assuming that dual-phase continuity can be obtained at compositions close to the theoretical point for percolation, one can calculate the torque ratio based on this value. In this case, the model of Avgeropoulos is 'theoretically' only valid between a torque ratio of 0.18 and 5.4, since the formation of two continuous phases is impossible below the theoretical point for percolation.

## CONCLUSIONS

Dual-phase continuity is usually obtained at the point of phase inversion, which can be predicted by various semi-empirical models. In this work, the predictions of these models were compared to experimental results obtained from a variety of blends. In general, it was found that the point of phase inversion can be correctly predicted when the torque ratio of the individual components is used. The model proposed by Avgeropoulos was shown to be applicable to blends having torque ratios from 0.6 to 1.7. Theoretically, this model can be used for a torque ratio ranging from 0.18 to 5.4 according to the percolation theory.

It was also found that the model of Avgeropoulos predicts the point of phase inversion better than the models of Metelkin and Blekht, of Miles and Zurek, and of Utracki, in which viscosity ratios are used. The latter model was found to be valid for most of the blends studied, with an error of less than 10%. Our results show that no direct correlation is found between the torque ratio and the shear or complex viscosity ratio.

The results obtained clearly demonstrate that interfacial tension and melt elasticity largely influence the formation of co-continuous structures. Additional terms including the latter effects should be combined with the models to improve their validity.

The validity of the model of Avgeropoulos is satisfactory for blends prepared in internal mixers where the

**Table 5** Interfacial tension between the different polymers

Blends	Temp. (°C)	$\sigma$ (mN m <sup>-1</sup> )	Ref.
PS/PE	200	4.8 - 5.5	16,43,45,46
PMMA/PE	200	8.6	47
PS/PMMA	200	0.8	47
PC/PS	200	0.8 <sup>a</sup>	47

<sup>a</sup> Calculated using the harmonic mean equation (ref. 43)



torque can be easily recorded. The extrapolation from internal mixers to an industrial scale is not yet possible since torque cannot be measured directly on extruders but has to be calculated from the total work expended during blending.

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