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# Effect of sample size on solvent extraction for detecting cocontinuity in polymer blends

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**Abstract**

The effect of sample size on the results of solvent extraction measurements for detecting cocontinuity in polymer blends was investigated. Poly(ethylene oxide)/polystyrene (PEO/PS) blend samples of several thicknesses were analyzed by removing the PEO phase using water extraction. The experimental degree of continuity was shown to have a linear dependence on the reciprocal of sample thickness. A model is proposed to explain this dependence and to allow the bulk or true degree of continuity to be determined. Measurement of the bulk degree of continuity is useful for understanding properties of cocontinuous polymer blends such as electrical conductivity, impact strength, or tensile strength.

*Keywords:* Polymer blends; Cocontinuous morphology; Solvent extraction

## 1. Introduction

Blending of polymers offers an attractive route to new materials with unique combinations of properties not available in a single polymer. In immiscible systems, the morphology (microstructure) has a strong influence on the blend properties. Among the possible blend morphologies are droplet, fiber, lamellar, and cocontinuous [1]. The distinguishing feature of cocontinuous morphologies is the mutual interpenetration of the phases. Cocontinuous polymer blends can have a number of advantageous properties, making them ideal for a wide range of applications. Some of the useful properties of cocontinuous polymer blends include: synergistic mechanical properties [2,3], controlled electrical conductivity [4], or selective permeability [5].

An important challenge in the study of cocontinuous polymer blends is the accurate determination of the blend morphology. A variety of methods have been used for detecting cocontinuity including solvent extraction, microscopy with image analysis, electrical conductivity measurements, and rheological measurements [6–12]. Although numerous techniques have been developed, solvent extraction has been a common choice for characterizing polymer blend morphology [6,8,13–18].

Solvent extraction experiments require one of the phases to be selectively removed from the sample. The degree of continuity of the extracted phase is calculated based on its initial mass and the change in mass during extraction using Eq. (1):

$$\varphi_i = \frac{m_{i0} - m_{if}}{m_{i0}} \tag{1}$$

where $\varphi_i$ is the degree of continuity of component $i$, $m_{i0}$ is the mass of component $i$ originally present in the sample, and $m_{if}$ is the mass of component $i$ present in the sample after extraction. The degree of continuity represents the fraction of the phase that is continuous. Samples in which each phase has a degree of continuity of 1.0 are completely cocontinuous. The primary advantage of solvent extraction is that it is an absolute measurement. The degree of continuity gives a direct measure of the connectivity of each phase for a given composition. Other methods of detecting cocontinuity, such as image analysis, electrical conductivity measurements, or rheological measurements, require

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measurements on blends of several compositions to determine the region of cocontinuity [12].

Solvent extraction has been used to determine the region of cocontinuity in a wide range of blends and to investigate how various conditions affect blend morphology. For example, solvent extraction has been used to determine the effects of mixing time [13], annealing [6,16], steady shear [17], and the presence of block copolymers or other compatibilizers [8,15,18] on the region of cocontinuity.

Although solvent extraction has been widely used and has advantages over other methods of detecting cocontinuity, there are several challenges associated with using solvent extraction for characterizing the region of cocontinuity in polymer blends. One such difficulty is finding selective solvents for both phases (components) in polymer blends. Often one phase is significantly more solvent resistant than the other phase, making it impossible to selectively extract the more solvent resistant phase without affecting the other phase. Another important challenge of using solvent extraction for characterizing polymer blends is the effect of sample size on the results. In particular, samples with large surface area to volume ratios may lead to inaccurate measurements of the degree of continuity because dispersed domains at the surface are extracted. It is also crucial that the sample is large enough that errors in weighing the sample do not result in large errors in the degree of continuity.

Despite the widespread use of solvent extraction for determining polymer blend morphology, there do not seem to be any detailed evaluations of the technique in the literature. In this study, solvent extraction was used to determine the degree of continuity of poly(ethylene oxide) in poly(ethylene oxide)/polystyrene (PEO/PS) blends. Samples of various compositions, from 10 to 65 wt% PEO, were prepared in several thicknesses to evaluate the effect of sample size on the solvent extraction results.

## 2. Experimental procedure

### 2.1. Sample preparation

PEO/PS blends were prepared in a Haake batch mixer. PS ($M_w = 150,000$ g/mol) was blended with PEO (Union Carbide WSR N-3000, $M_w = 400,000$ g/mol) at 35 rpm (maximum shear rate $= 33\ s^{-1}$) and a temperature of 170 °C for 10 min. Immediately following mixing, the product was transferred to a hydraulic press and then compression molded at 170 °C and 5 psi for 1 min followed by 1 min at 100 psi. Several different molds were used to prepare 6.35 cm diameter disks with approximate thicknesses of 1, 2, or 4 mm. The press was then cooled using cold water, reducing the temperature to 55 °C and crystallizing the PEO within 2 min. This quenched the sample and trapped the non-equilibrium microstructure present in the polymer melt.

### 2.2. Solvent extraction

Solvent extraction experiments were used to determine the degree of continuity of the PEO phase. For these experiments, each sample disk was immersed in 250 ml of water for a minimum time of one day. The samples were then removed from solution, and each solution was filtered

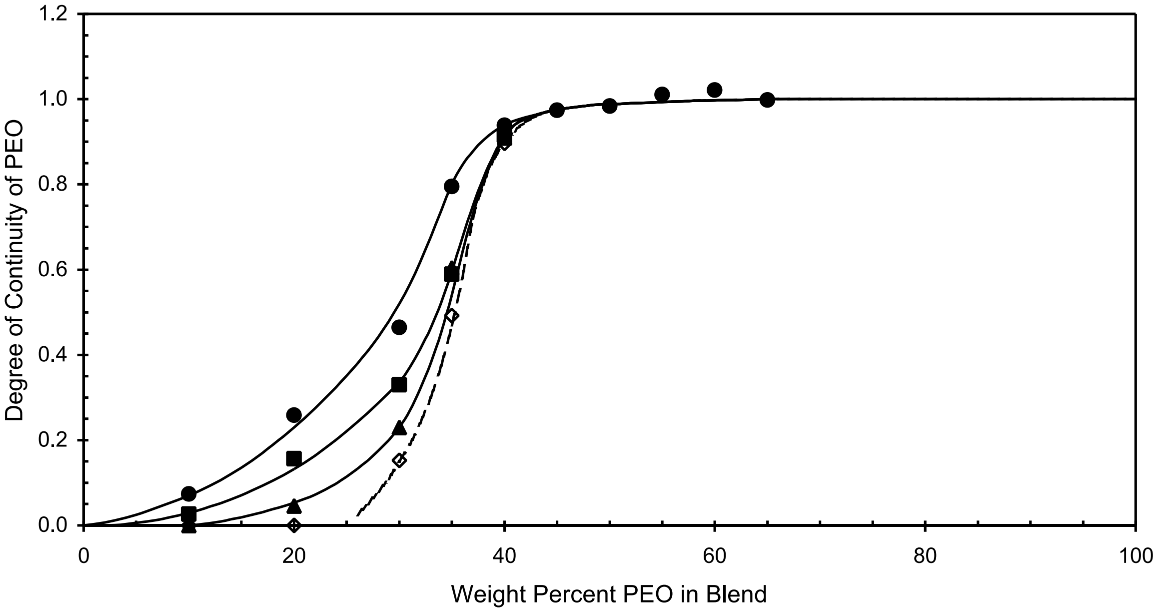

Fig. 1. Degree of continuity of PEO as a function of blend composition for different sample thicknesses. The measured degree of continuity decreases as the sample thickness is increased from 1 mm (circles) to 2 mm (squares) to 4 mm (triangles). The bulk degree of continuity (measured degree of continuity extrapolated to infinitely thick samples, see Fig. 3) is shown as open diamonds. The curves are guides for the eye. Error bars have been omitted, but are shown in Fig. 3.

using a 0.7 μm Whatman FilterCup GF/F before being discarded. The filters allowed small particles that separated from the bulk sample to be recovered for an accurate weight loss measurement. The filters and samples were dried in a vacuum oven at room temperature for a minimum of three days and the mass of the samples after extraction was determined. The extraction process was repeated until a constant sample mass was attained, typically 3–6 times. Several thickness/composition combinations were repeated to determine the reproducibility of the results. The degree of continuity was calculated using Eq. (1).

## 3. Results and discussion

The results of the solvent extraction experiments are shown in Fig. 1. Separate curves show the degree of continuity versus blend composition for various sample thicknesses. As the amount of PEO in the blends increases, its degree of continuity also increases. For each sample thickness, the degree of continuity allows the morphology of the blends to be inferred. At 10% PEO, the degree of continuity is low, in agreement with the expected morphology of dispersed droplets for this composition. For blends containing 30% PEO, the degree of continuity is substantially higher, signifying a more connected morphology. At a composition of 40% PEO, the degree of continuity is nearly 1.0, indicating that the PEO is completely continuous. As the PEO content increases to 65%, the degree of continuity remains close to 1.0, as expected. For blends containing more than 65% PEO, the samples collapsed during extraction, and the degree of continuity was not measured. However, since the PS collapsed, the PEO is completely continuous and the curves have been extended to 100% PEO with a degree of continuity of 1.0.

Fig. 1 also shows the dependence of the degree of continuity on sample thickness. The curve for the 4 mm samples shows some important differences from the curve for the 1 mm samples. First, the degree of continuity for blends with droplet morphologies (10–20% PEO) is essentially zero. This result better represents droplet morphologies, which are not expected to contain any continuous paths of the minor phase. Second, the degree of continuity increases from zero to one more sharply for 4 mm samples than the 1 mm samples. As the thickness of the samples is increased (surface area per unit volume is decreased), the fraction of PEO extracted that can be attributed to domains at the surface decreases. As a result, the degree of continuity is reduced, particularly for blends with droplet morphologies. For a given blend composition, the degree of continuity will approach a limit for large samples. This limit reflects the bulk or true degree of continuity of the sample.

The dependence of the degree of continuity on sample size can be modeled using a simple expression. Since both dispersed and continuous domains at the surface are extracted, there is an average depth into the sample, $\delta$, for which all domains are extracted. For the sample interior, the fraction of the sample extracted corresponds to the bulk degree of continuity, $\varphi$. A schematic diagram of a polymer blend illustrating these regions is shown in Fig. 2. The experimental degree of continuity, $\varphi_e$, is given by:

$$\varphi_e = \frac{2\delta}{h} + \left(\frac{h-2\delta}{h}\right)\left(\frac{R^2-(R-\delta)^2}{R^2}\right) + \left(\frac{h-2\delta}{h}\right) \times \left(\frac{(R-\delta)^2}{R^2}\right)\varphi \tag{2}$$

where $h$ is the thickness and $R$ is the radius of the sample. The first two terms in the expression for $\varphi_e$ represent the complete extraction within a distance $\delta$ of the surface, and the third term represents the extraction equal to the bulk degree of continuity in the interior of the sample. The expression for $\varphi_e$ can be rewritten as:

$$\varphi_e = m\left(\frac{1}{h}\right) + b \tag{3}$$

with the slope, $m$, and intercept, $b$, given by:

$$m = \left(\frac{2\delta}{R^2}\right)((R-\delta)^2(1-\varphi)) \tag{4}$$

$$b = \left(\frac{1}{R^2}\right)(R^2-(R-\delta)^2(1-\varphi)) \tag{5}$$

Since, $\varphi_e$ is linear with respect to $1/h$, the values of $\delta$ and $\varphi$ can be determined from linear regression analysis as follows:

$$\delta = \frac{m}{2(1-b)} \tag{6}$$

$$\varphi = 1 - \frac{(1-b)R^2}{(R-\delta)^2} \tag{7}$$

The reliability of Eq. (3) for modeling the degree of continuity of polymer blends was tested using the solvent extraction results. The degree of continuity as a function of $1/h$ is plotted for five different blend compositions in Fig. 3.

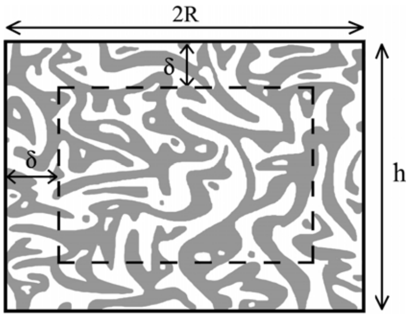

Fig. 2. Schematic diagram of a cocontinuous polymer blend illustrating the variables for Eq. (3). The solvent penetration depth, $\delta$, is the effective depth for which complete extraction occurs. In the interior of the sample, the fraction extracted represents the bulk degree of continuity, $\varphi$, of the sample.

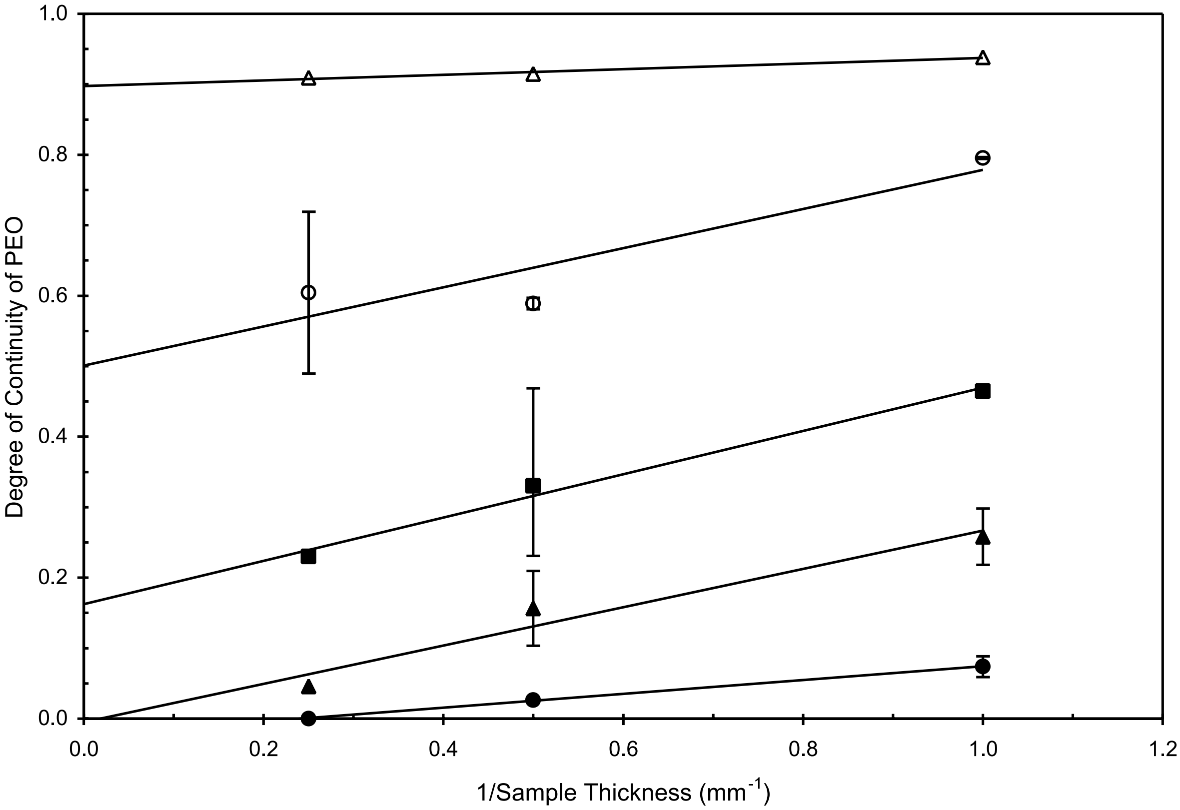

Fig. 3. Degree of continuity of PEO versus the reciprocal of sample thickness. The degree of continuity is linear in $1/h$ and fits to the data are shown. The effect of the sample thickness on the measured degree of continuity grows as the amount of PEO in the blend increases from 10% (filled circles), to 20% (filled triangles), to 30% (filled squares), as shown by an increase in slope. As the degree of continuity approaches 1.0, for 35% PEO (open circles) and 40% PEO (open triangles), the effect of sample size on the results decreases. Error bars represent the range from multiple runs.

The results of fitting the data in Fig. 3 to Eq. (3) are shown in Table 1. For the 10/90 and 20/80 blends, the bulk degree of continuity is essentially zero, in agreement with the expected dispersed morphology. At a composition of 30/70, $\varphi$ is non-zero, signifying the existence of a partially continuous PEO phase. Therefore, percolation of the PEO occurs between 20% and 30% PEO. As the amount of PEO is further increased, the bulk degree of continuity increases to about 0.9 for a 40/60 blend.

The value of $\delta$ also increases as the amount of PEO in the blends increases. This trend reflects the change in morphology of the blends. For 10/90 blends, the PEO exists as droplets and the effect of the surface is minimal, leading to a small value of $\delta$. As the PEO content increases (20/80 and 30/70 blends), the domains become more elongated and allow deep extraction due to surface effects, leading to an increased value of $\delta$. As the morphology becomes cocontinuous (35/65 and 40/60 blends), the value of $\delta$ appears to reach a plateau value (within the uncertainty) of about 0.20 mm. However, it is difficult to draw conclusions about the trends when the blend becomes cocontinuous because both $m$ and $(1\text{-}b)$ approach zero.

As described above, the increase in $\delta$ with the PEO content can be attributed to the domains becoming more elongated as the morphology becomes cocontinuous. However, for blends with a droplet morphology, the value of $\delta$ is significantly larger than the domain size observed in the blends. A possible explanation for these results is the

Table 1
Summary of linear regression analysis

| Weight percent PEO in blend | Slope (mm) | Intercept | Average depth for complete extraction, $\delta$ (mm) | Bulk degree of continuity of PEO, $\varphi$ |
|---|---|---|---|---|
| 10 | 0.10 ± 0.01 | −0.02 ± 0.01 | 0.05 ± 0.01 | −0.03 ± 0.01 |
| 20 | 0.27 ± 0.06 | −0.01 ± 0.04 | 0.14 ± 0.03 | −0.01 ± 0.04 |
| 30 | 0.31 ± 0.03 | 0.16 ± 0.02 | 0.18 ± 0.02 | 0.15 ± 0.02 |
| 35 | 0.28 ± 0.11 | 0.49 ± 0.07 | 0.28 ± 0.15 | 0.49 ± 0.07 |
| 40 | 0.04 ± 0.01 | 0.90 ± 0.01 | 0.19 ± 0.04 | 0.90 ± 0.01 |

The uncertainties in slope and intercept are the standard errors from linear regression analysis. The uncertainties in $\delta$ and $\varphi$ were calculated based on the expressions given in Eqs. (6) and (7).

existence of a different morphology at the surface of the samples than the interior. Examination of scanning electron microscopy images indicates a slightly larger domain size at the surface of the images, but it is not large enough to account for the difference. A more likely possibility is that the value of $\delta$ may have a significant uncertainty since the slope is close to zero.

In addition to affecting the experimental degree of continuity, the sample size is also related to another potential source of error in these experiments. The sample size can impact the accuracy of the results if weighing errors become significant. When the minor phase is extracted, the initial mass and change in mass are relatively small. For example, for a 500 mg sample initially containing 10% PEO with a degree of continuity of 0.05, the total amount of sample extracted would be only 2.5 mg. In this case, a weighing error of just 1 mg corresponds to a 40% error in the degree of continuity. Therefore, it is important to have a sufficiently large sample to minimize the impact of weighing errors on the results. In these experiments, the minimum sample mass was 4 g and the minimum amount extracted from any sample was 20 mg. Although this would limit a 1 mg weighing error to 5%, replicate runs of several thickness/composition combinations were used to evaluate the reproducibility of the results. As shown in Fig. 3, the replicate runs typically were within 20% of the average measurement.

Although the model presented in Eqs. (3)–(5) fits the experimental data well, the edge effects are small if $R \gg \delta$. In this case, Eqs. (3)–(5) can be simplified to:

$$\varphi_e = 2\delta(1-\varphi)\left(\frac{1}{h}\right) + \varphi \tag{8}$$

This approximation allows the intercept to be taken as the bulk degree of continuity, while the relationship between the slope and the value of $\delta$ is unchanged. In these experiments, the approximation is reasonable since $R$ is at least 100 times greater than $\delta$ for all of the compositions tested. As shown in Table 1, the bulk degree of continuity differed from the intercept by 0.01 or less for each of the blends.

## 4. Conclusions

In this study, the effect of sample size on the results of solvent extraction for detecting cocontinuity in polymer blends has been examined. A model to describe the dependence of the degree of continuity on sample dimensions was used to explain the results. Experimental data were shown to match the predicted linear dependence of the experimental degree of continuity on the reciprocal of the sample thickness. The model allowed the bulk degree of continuity of the sample to be determined.

The results of this study are important for understanding different solvent extraction experiments. The effect of the sample size on the results of solvent extraction experiments must be carefully considered when comparing the results of experiments using different sample sizes and shapes. Previous studies involving solvent extraction experiments have used a wide variety of sample shapes including cubes [19], disks [6], or extruded strands [15,20,21]. In some cases (i.e. extruded strands), it is not possible to vary the shape of the sample to determine the bulk degree of continuity. In these situations, the sample size and shape must be kept constant for the best comparison of results.

The results of this study can improve the understanding of other blend properties such as electrical conductivity. In applications requiring conductive materials, blends with a cocontinuous morphology can be useful. These composites require a continuous network of a conductive material throughout the sample. Therefore, the bulk degree of continuity must be greater than zero in order to achieve useful conductive properties. In this study, the minimum amount of PEO required for a non-zero bulk degree of continuity was 30%. This result agrees with previous electrical conductivity measurements that determined the percolation threshold to be 30% [12]. Simulations are being developed to examine the relationship between the degree of continuity of the conductive phase and the electrical conductivity of the blend [22].

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