

Mixed Morphology by the Extrusion of Phase-Separated Blends of a Melt-Processed Polymer and Polymer Solution

Christopher Drew, Suzanne Bosselman, David Ziegler

U.S. Army Natick Soldier Research, Development and Engineering Center, Kansas Street, Natick, Massachusetts 01760

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ABSTRACT: The phase behavior and structure development in immiscible blends of melt-extruded polycaprolactone and a viscous aqueous poly(ethylene oxide) solution were investigated. The coextrusion of an aqueous polymer solution and a molten polymer is a largely unexplored technique and offers exciting potential for creating new materials via the execution of chemical reactions in the aqueous phase. Samples were prepared both with and without a block copolymer acting as a surface-active agent. The resulting morphology was characterized with scanning electron microscopy after the removal of the water-soluble phase. Spheres, rods, fibers, and cocontinuous gyroidal structures were observed, yet the exact phase inversion was not observed, and the changes in the feature shape depended on which component composed the major phase. Significant orientation in the flow direction was

observed when the less viscous poly(ethylene oxide) was the major phase, whereas orientation was minimal when polycaprolactone was the major phase. These observations indicate that control of the feature shape and orientation may be accomplished through the control of the viscosity. The spontaneous formation of an outer layer of polycaprolactone in all samples was observed, suggesting that the morphology could be induced by control of the material interaction with the extruder die wall. The inclusion of a diblock copolymer significantly reduced the feature size but did not alter the morphology type. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 110: 2841–2848, 2008

Key words: block copolymers; compatibilization; composites; phase separation; self-organization

INTRODUCTION

The phase separation of immiscible polymers is a widely studied field, in which research is motivated by the promise of exploiting spontaneous arrangements of materials into desired structures. Technological advances in the development of microstructures and nanostructures via this method may lead to spontaneous low-cost fabrication of novel architectures and even devices such as sensors. Progress depends on gaining an understanding of the evolution of the morphology during processing and exercising subsequent control over the factors that dictate the behavior. To expand the utility of this method, the extrusion of a binary fluid system can be conducted in which one of the immiscible phases is a molten polymer and the other is a viscous aqueous polymer solution. This approach makes possible the execution of a chemical reaction sequestered in the aqueous phase during or after

extrusion. Such a system is expected to find great utility in creating novel composite materials not otherwise possible with conventional melt-processed polymer blends.

Poly(ethylene oxide) (PEO), which was used in this study, has many practical uses that can be exploited by this method. Because of its high water solubility and chelating properties, PEO is used in a number of biological and electronic applications. PEO-based diblock copolymers have been shown to be effective vehicles for controlled drug delivery.¹ The timing and dosage of the drugs contained within the PEO domains can be manipulated with the polymer blend structure. The biocompatibility of PEO makes it a suitable material for topical and *in vivo* medical uses. It has been shown that PEO can be used for live cell encapsulation within a polymer blend scaffold to facilitate tissue regeneration.² PEO has also found use in solid polymer electrolytes. Solid electrolytes consist of ionic species, such as lithium salts, and PEO. By chelating the ions, PEO hinders ionic recombination, yielding higher conductivities than the conductivity of the ionic materials alone.³ The construction of electronic devices requires careful placement of the conductors, insulators, and connectors. Thus, the ability to control the morphology of a PEO phase and an insulating polymer phase, as demonstrated in the work,

Correspondence to: C. Drew (christopher.p.drew@us.army.mil).

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may yield several advantages. Novel device morphologies may be obtained cost-effectively, such as fiber-based batteries.

Immiscible fluids, including molten polymers, have been a topic of interest for many years, and the interest shows little sign of abating. Block copolymers have been cast from a common solvent to generate interesting morphologies.^{4,5} Bicontinuous domains in nonpolymeric fluids have been studied in which surfactants were used to stabilize the interface.^{6–10} Immiscible polymers have been melt-processed as homopolymer blends and as block copolymers, and the resulting morphology has been studied.^{11,12} Common morphologies in all of these approaches include colloidal spheres, lamellae, and cocontinuous (gyroid) structures. Some researchers have developed specialized techniques to impart a desired morphology to an immiscible blend of melt-processed polymers. Chaotic blending, as demonstrated by the Zumbrennen group, is a technique in which two immiscible polymer phases are extruded into a mixing unit comprising two cylindrical rods that rotate either cocontinuously or counter to each other. This rotation creates periodic rotation of the fluid and generates shear forces to stretch and fold the melt domains under control. The morphology adopted by the two materials is progressive along the mixing channel. A wide range of different morphologies have been demonstrated.^{13,14} The Baer group has demonstrated the use of extruder die blocks that combine different melt streams from extruders into stacked layers. By repeatedly dividing the melt streams and directing them to lie on top of one another, they have achieved thousands of alternating polymer layers. In some cases, the reported layer thicknesses have been less than 10 nm.^{15–18} Mixing machinery relies on shear forces to create a morphology and viscosity to hold a material in place while it cools. In contrast, surfactant systems in solvents, such as spin-casting block copolymers, derive their final morphology from the thermodynamic equilibrium interfaces of the components.

The blend morphology of an immiscible binary viscoelastic system depends on many factors, including material characteristics such as the composition ratio, interfacial tension, and viscosity ratio and mixing conditions such as the shear rate and flow field conditions. The domain size of the dispersed phase is dictated partly by the composition ratio. The probability of phase contacts increases with higher concentrations of the minor phase, thereby increasing the domain size.¹⁹ Wu²⁰ developed a relationship between the viscosity ratio, shear rate, and interfacial tension and the dispersed phase particle size for a viscoelastic system using blends of nylon and poly(ethylene terephthalate). Dispersion during mixing was shown to be enhanced by low interfacial ten-

sion, high shear rates, and high viscosity of the matrix. With other processing conditions and component ratios held constant, the minimum size of the dispersed phase occurred when the viscosity ratio approached 1. The deformation of the dispersed droplets also depends on the component elasticity: the dynamic interfacial tension between the phases depends on the difference in the first normal stresses of the dispersed and matrix phases.²¹ Complicated flow fields are generated in twin-screw extruders, caused by both dynamic effects via screw rotation and geometric effects, such as narrow flow passages, variations in the channel/screw geometry, and the die exit. Droplet deformation and breakup in extensional and nonuniform flow in a viscoelastic system have been widely studied, and it has been established that the critical shear rate for breakup is greater when the viscosity of the minor phase is greater than that of the matrix.²² Previous research has demonstrated that the less viscous phase in the molten blend will migrate to the die wall in an extruder where the shear rate is highest, thereby displacing the more viscous phase. For a constant flow rate, this configuration minimizes energy and pressure drop for the system.²³

In this work, a binary fluid consisting of a molten polymer and a viscous polymer solution were extruded together to create various morphologies. A viscous solution of PEO and deionized water was melt-extruded with polycaprolactone (PCL) in a laboratory-scale extruder. Some samples additionally contained a diblock copolymer to act as a surfactant. The morphology dependence on both the surface tension at the interface of the two fluids, controlled by the incorporation of the block copolymer, and the shear forces generated during extrusion was investigated.

EXPERIMENTAL

PEO (100,000 D; Aldrich, St. Louis, MO) was mixed with deionized water in a 1 : 1 weight ratio to form a viscous solution. This solution was then melt-extruded at various ratios with PCL (30,000–80,000 D; Dow, Midland, MI) in a DACA laboratory-scale extruder. Selected samples contained a diblock copolymer comprising blocks of PEO and PCL of equal weights (5000 D; Polymer Source, Dorval, Quebec, Canada) to act as a surfactant. The sample compositions are detailed in Table I. The densities of the PEO/water solution and PCL were both about 1.1 g/mL. Therefore, the weight ratio and volume ratio could be considered equivalent.

A DACA laboratory-scale corotating twin-screw extruder was used in the experiments and is shown in Figure 1. The extruder was equipped with conical single-flight screws, with no mixing elements. For all

TABLE I
Formulations of the Extruded Polymer Samples

Sample number	PCL (g)	PEO (g)	Water (g)	PEO solution (g)	Block copolymer (g)	PEO : PCL ratio
1	0.50	1.25	1.25	2.50	0	5 : 1
2	0.50	1.25	1.25	2.50	0.10	5 : 1
3	1.00	1.00	1.00	2.00	0	2 : 1
4	1.00	1.00	1.00	2.00	0.10	2 : 1
5	1.50	0.75	0.75	1.50	0	1 : 1
6	1.50	0.75	0.75	1.50	0.10	1 : 1
7	2.00	0.50	0.50	1.00	0	1 : 2
8	2.00	0.50	0.50	1.00	0.10	1 : 2
9	2.50	0.25	0.25	0.50	0	1 : 5
10	2.50	0.25	0.25	0.50	0.10	1 : 5

samples, the single heating zone of the extruder was set to 90°C, and the screw speed was set at 80 rpm. The shear rate was estimated at 50 sec⁻¹. Nitrogen gas was fed into the extruder during its operation to minimize degradation. The materials were allowed to recirculate via a selection valve through the extruder for 5 min before being routed through the exit die. The diameter and length of the cylindrical exit die were 2 and 20 mm, respectively. The extrudate was collected as a single round strand, and samples were taken from the middle of the extruded strand to ensure full flow development through the length of the die and uniformity in the strand. For each batch that was extruded and collected, a purge batch of the same polymer composition was run through the extruder with the same residence time. Prior research has shown that dispersion does not increase considerably with mixing times greater than 5 min.²⁴ The strand was not subjected to any post-processing drawing after exiting the die.

Extrudate samples were cryofractured to generate a clean surface free of cutting artifacts for imaging by scanning electron microscopy. Each fractured sample was then washed by immersion in deionized water and ultrasonication for 180 min to remove the PEO phase. The cryofractured surfaces were coated with a 15-nm layer of gold-palladium and imaged at a 10-kV accelerating voltage with a Zeiss EVO 60 scanning electron microscope (Peabody, MA). The mean feature size was directly measured from the scanning electron microscopy images with commercially available pixel counting software.

RESULTS AND DISCUSSION

All the samples showed a generally consistent morphology in the core of the extruded cylinder suggesting uniform mixing within that region. Some samples showed an ambiguous mixed morphology closer to the outer surface of the extrudate. This outermost layer appeared to be pure PCL in all sam-

ples. These observations suggest that PCL showed a greater affinity to the extruder die surface, which in turn changed the local composition ratio of the blend in the regions closest to the die wall. Any temperature difference between the extruder wall and screw channel was sufficiently small to make any differences in the local viscosity of the melt negligible.

The blended morphologies that were observed included spheres, rods, fibrils, and gyroidal structures, depending on the composition ratio of the polymer and polymer solution. The observations are summarized in Table II. These observations were consistent with literature reports of the morphologies in other binary fluid systems, with the exception of lamellae, which have often been reported but were not observed in this work.

In samples 1 and 2, the blend was predominantly a PEO solution with PCL in a 5 : 1 ratio (by weight). The morphology consisted of spheres of PCL in a

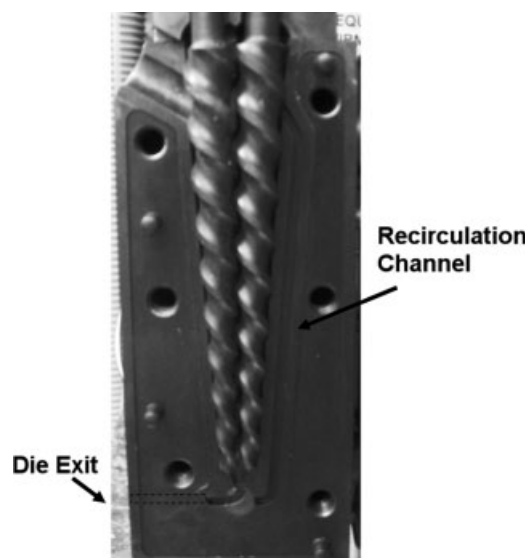


Figure 1 Schematic of the DACA laboratory-scale extruder.

TABLE II
Feature Size and Morphology

Sample number	Block copolymer (g)	PEO : PCL ratio	Mean feature diameter (μm)	Feature type
1	0	5 : 1	5.6	Spheres
2	0.1	5 : 1	0.8	Spheres
3	0	2 : 1	14.1	Rods
4	0.1	2 : 1	1.7	Fibers
5	0	1 : 1	15.7	Gyroids
6	0.1	1 : 1	4.6	Gyroids
7	0	1 : 2	1.8	Spheres
8	0.1	1 : 2	1.3	Spheres
9	0	1 : 5	0.7	Spheres
10	0.1	1 : 5	0.4	Spheres

PEO matrix, as shown in Figure 2, imaged perpendicularly to the direction of flow. In sample 1, which did not contain a block copolymer, the sphere diameters ranged from 1.9 to 14.3 μm with a mean of 5.6 μm . In contrast, sample 2, which had the same

polymer ratio but included a block copolymer, contained slightly elongated spheres ranging from 0.3 to 1.4 μm with a mean of 0.8 μm . The block copolymer residing at the interface of the phases acted as a surfactant or compatibilizing agent, reducing the interfacial tension and thereby thermodynamically stabilizing the larger interfacial area. This accounted for the substantial decrease in the feature size. The difference in the feature size was also indicative of thorough mixing of the blends and significant Ostwald ripening in the blend without the block copolymer. Neither sample 1 nor sample 2 exhibited significant flow-induced order in the mixed region, but both blends had a skin layer of PCL. This was sufficient to hold washed sample 2 together, whereas sample 1, which contained no block copolymer, was completely dispersed in the wash water and had to be imaged without removal of the PEO phase.

A slight decrease in the PEO/PCL ratio to 2 : 1 by weight led to a vastly different morphology, as illustrated in Figure 3. Sample 3 is shown on the top,

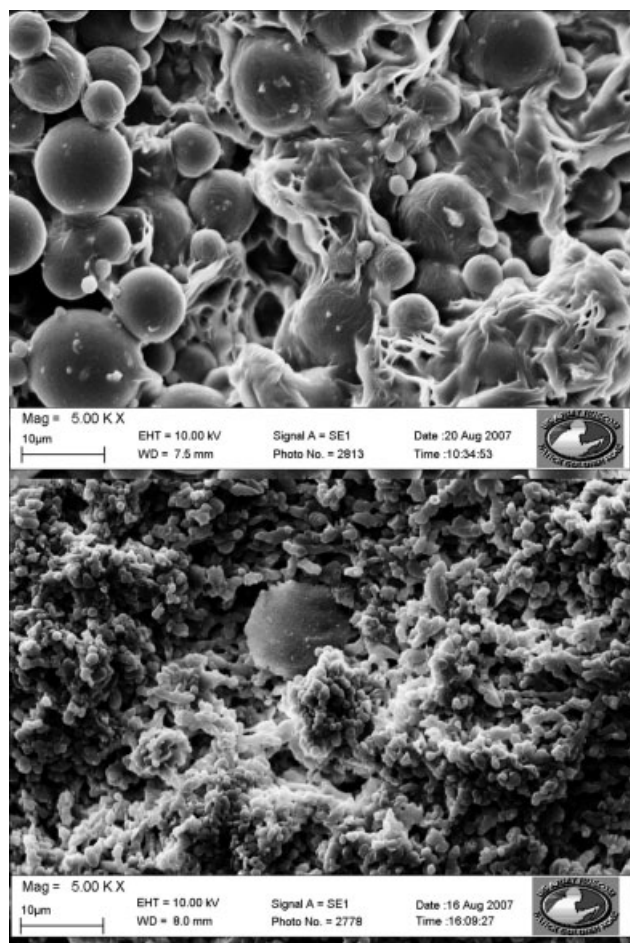


Figure 2 Unwashed sample of PEO and PCL with a 5 : 1 composition ratio (sample 1; top) and the same PEO/PCL composition with the addition of the block copolymer (sample 2; bottom).

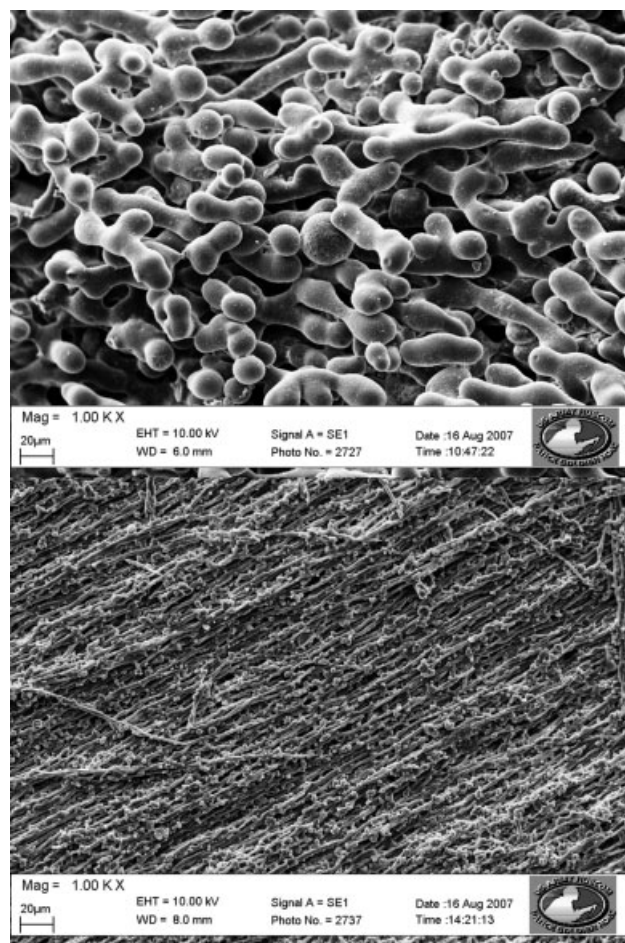


Figure 3 PEO and PCL with a 2 : 1 composition ratio (sample 3; top) and the same composition of PEO and PCL with the addition of the block copolymer (sample 4; bottom).

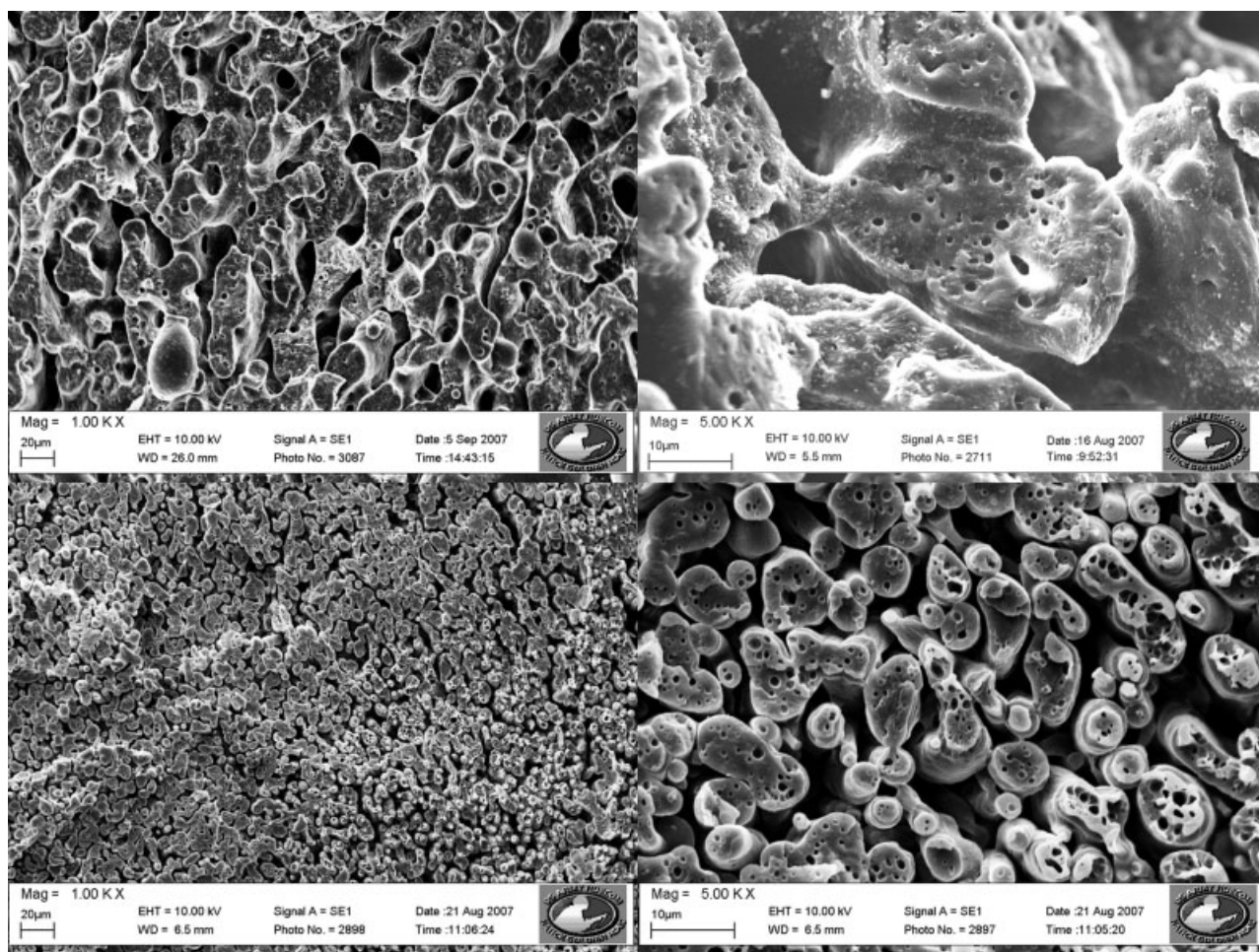


Figure 4 PEO and PCL with a 1 : 1 composition weight ratio at different magnifications (sample 5; top) and the same composition of PEO and PCL with the addition of the block copolymer (sample 6; bottom).

whereas sample 4, containing the block copolymer, is shown on the bottom. The PCL phase adopted an elongated rod shape, which in the case of sample 4 appeared quite long and may have been more akin to a fiber. Figure 3 shows cross sections imaged parallel to the flow direction and exhibits clear orientation in the direction of material flow. The rods in sample 3 had a mean diameter of $14.1\ \mu\text{m}$, whereas the fibrils in sample 4 had a mean diameter of $1.7\ \mu\text{m}$. Again, the difference in feature size was attributed to the block copolymer stabilizing a larger interfacial area by reducing the interfacial tension.

Figure 4 shows the morphologies of samples with a phase ratio of 1 : 1. The gyroidal structure observed in the samples with and without the block copolymer was consistent with the literature on binary fluids. The images show cross sections perpendicular to the direction of flow and suggest that the structure may have some orientation in the direction of material flow through the extruder. The effect of the block copolymer was evident in the observed mean strand thickness, which was $15.7\ \mu\text{m}$ for sam-

ple 5 with no block copolymer and $4.6\ \mu\text{m}$ for sample 6, in which the block copolymer stabilized the interface.

Figure 5 shows cross sections perpendicular to the direction of flow for sample 7 on the top and sample 8 on the bottom. The compositions (PEO solution-to-PCL ratios of 1 : 2) were approximately the inverse of those of samples 3 and 4. Given that samples 3 and 4 showed rods and fibrils of PCL in a PEO matrix, it might be expected that the compositional inverse would likewise consist of rods and fibrils of PEO in a PCL matrix. However, samples 7 and 8 revealed spheres or slightly elongated spheres of the PEO solution in the PCL matrix. This result is a departure from the conventional immiscible binary fluid morphology in which phase inversion has been observed. This result is due to the difference in the viscosities of the molten PCL and the PEO solution and is consistent with reports in the literature for viscoelastic systems. The viscosity of the major phase can dictate the amount of displacement of the minor phase through shear at the interface, and this

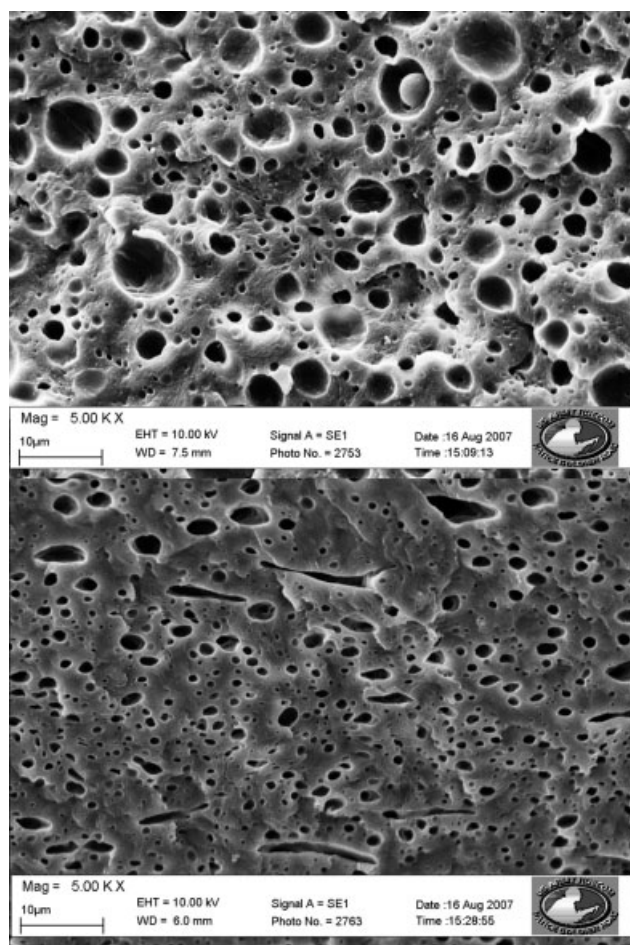


Figure 5 PEO and PCL with a 1 : 2 composition weight ratio (sample 7; top) and the same composition of PEO and PCL with the addition of the block copolymer (sample 8; bottom).

motion, in turn, defines the morphology. The PEO solution is more easily deformed because of its lower viscosity with respect to the PCL matrix. In contrast to samples 3 and 4 (the compositional inverse), in which PCL in the minor phase stretched into longer, more rodlike shapes, here we observe that PEO broke up into smaller droplets because of its lower elasticity. In both the 2 : 1 and 1 : 2 cases, the surface energies were the same; therefore, morphology differences can be attributed to the viscoelastic response. In samples 7 and 8, in which the more viscous PCL was the major phase, we suspect that less displacement was imparted to the minor phase. This, coupled with the likelihood of a less viscous minor phase breakup, resulted in the PEO domains being spherical rather than elongated. The effect of the block copolymer remained apparent, facilitating PEO domains with a mean diameter of 1.3 μm versus a mean diameter of 1.8 μm in sample 7, in which no block copolymer was present.

There was little difference observed in samples in which PEO/water was the minor phase in a 1 : 5

ratio to PCL, as shown in Figure 6. Sample 9, which did not contain the block copolymer, had a mean void size of 0.7 μm , which was only slightly larger than the 0.4- μm void size of sample 10, in which the block copolymer was present. These two samples (shown in Fig. 6) were the compositional inverses of samples 1 and 2, yet the observed feature size was very different. In samples in which PCL was the minor phase or in which the PEO/water : PCL ratio was 1 : 1, the proportion of PCL was observed to be higher at the edge of the extruded strand. This is shown in Figure 7 for a sample with a 1 : 1 PEO/water : PCL composition ratio.

The sessile drop contact angle for water on steel has been reported to be approximately 72°. On bulk PCL, the water contact angle has been reported to be 60°. Because PEO is not surface-active, the surface energy of the PEO solution could be considered very close to that of water alone. Therefore, from the contact angles, one can deduce that the PEO solution had a greater affinity for the PCL

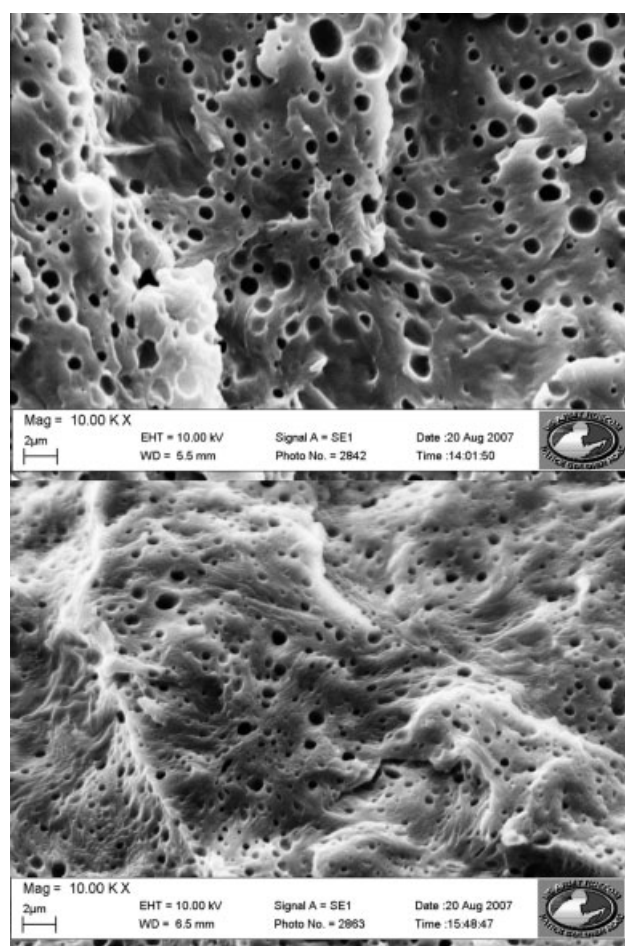


Figure 6 PEO and PCL with a 1 : 5 composition weight ratio (sample 9; top) and the same composition of PEO and PCL with the addition of the block copolymer (sample 10; bottom).

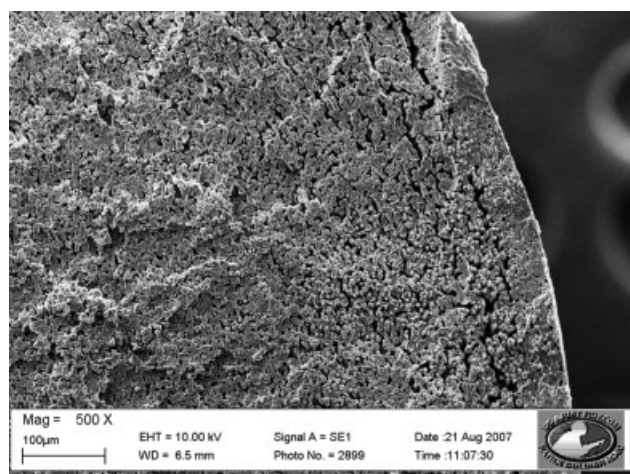


Figure 7 Higher concentration of PCL on the edge of an extruded strand in a 1 : 1 blend. The water-soluble phase was washed away (sample 6).

phase rather than the extruder die wall. In other words, it was energetically unfavorable for a PCL domain to move away from the steel surface to be replaced by a PEO solution domain. As a result, PCL spontaneously formed a sheath structure on the extruded strand. Exploiting the different wall affinities of the blend components may offer a method of generating specific desired structures and configurations within the extruded material.

CONCLUSIONS

Binary blends of molten PCL and a viscous solution of PEO and water were successfully extruded into cylindrical strands with a conventional twin-screw extruder. The presence of the diblock copolymer in the extruded blend significantly reduced the feature size, converting rods into continuous fibrils in the case of a 2 : 1 composition of PEO/water and PCL and converting large spheres into interconnected smaller spheres in the case of a 5 : 1 PEO/water : PCL ratio. These observations suggest that the mixing in the extruder was sufficient for significant amounts of the copolymer to migrate to the polymer/polymer interface, at which it stabilized a higher surface area. It is likely that increasing amounts of the block copolymer will further reduce the feature size up to some saturation point. This effect is currently being investigated.

Several samples showed significant orientation in the flow direction through the extruder die. In one case, the extruded strand consisted of many oriented submicrometer fibers of PCL in a matrix of PEO. The viscosity difference between the phases dictated the resulting morphology. In cases in which the PCL/PEO ratio was 2 : 1, the morphology was very different from that observed when the composition

was inverted with a PCL/PEO ratio of 1 : 2. This difference was attributed to the viscous and elastic response of each phase under interfacial shear forces. Future work will entail measurements of the viscosity and melt strength of the two components.

Because of the abundance of water in the extrudate, it is conceivable that numerous aqueous chemical reactions may be executed in the PEO/water phase during extrusion or immediately thereafter. These reactions, coupled with the morphological control from the addition of interface-active block copolymers, are expected to lead to new and novel microstructures and nanostructures of various materials, including materials not readily melt-processed, such as continuous metal oxide domains. This methodology, coupled with well-established polymer processing techniques, is expected to lead to the facile production of novel composite materials and devices, such as sensors, in large volumes at low cost. Additionally, an understanding of processing conditions on the morphology of immiscible blends may facilitate morphologies that currently require coextruders and other special equipment to be fabricated on simple extruders with the judicious selection of materials.

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