

Phase Morphology Control of the Electrospun Nanofibers from the Polymer Blends

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ABSTRACT

Nanofibers of polybutadiene/polycarbonate blends were electrospun from polymer solutions. The effect of composition on the resulting internal morphology of the nanofibers was studied using Transmission Electron Microscopy (TEM). When the composition ratio of PB/PC blends was larger than 75/25, a co-continuous structure was formed, but when composition ratio of PB/PC blends was changed to 25/75, a core-sheath structure was formed. The effect of type of polymer in the blend on the phase morphology was also investigated. The solubility of the components in the electrospinning solvent was found to play a critical role in phase morphology of nanofibers. Larger solubility differences in components of the blend favor the formation of core-sheath structures, while smaller solubility differences lead to co-continuous structures.

Keywords: electrospinning phase separation blend morphology

1 INTRODUCTION

Electrospinning offers the ability to produce polymer fibers with diameters in the nanometer range.^{1,2,3} The high surface area/volume ratio endows nanofibers with enhanced properties for a variety of applications including tissue growth, protective clothing, thermal insulation, filters for fine particles, reinforcing fibers, wound dressings, and artificial blood vessels.^{4,5} Most of the past and current research efforts have focused on fiber formation mechanisms, electrospinning of different polymer types and blends, and control of mat properties, such as fiber size, type, process, etc.^{6,7} The electrospinning of polymer blends offers the potential to prepare unique materials, but has received more limited investigation. The focus has been primarily on the properties of the overall mat. Blends of polyaniline and polyethylene oxide or sulfonated polystyrene and polyethylene oxide have been used to produce conductive and photo-responsive nanofibers for electronic devices. Nanofibers prepared from Styrene-Butadiene-Styrene (SBS) triblock copolymers showed a two-phase morphology with domains elongated along the fiber axis.⁸ Annealing the nanofibers improved the ordering of the domains of the nanofibers. Co-continuous

phase morphologies were observed in electrospun polylactide/polyvinylpyrrolidone blends and specific surface topologies or fine pores were generated by selective removal of one of the components.⁴ There has been little effort made towards control of the internal morphology of the nanofiber itself. Therefore, the focus of this paper was to study the effect of composition ratio of polymer blend and polymer types in the blends on the resulting morphology within the electrospun fiber. A number of unique morphologies were found, including core-sheath and co-continuous structures.

2 EXPERIMENTAL

2.1 Materials

Polycarbonate (PC) with molecular weight 21.9 kD was supplied by GE Plastics. Polybutadiene (PB) with molecular weight 420 kD, Polymethyl methacrylate (PMMA) with molecular weight 120 kD, Polystyrene (PS) with molecular weight 280 kD, tetrahydrofuran (THF), osmium tetroxide (OsO₄) and ruthenium tetroxide (RuO₄) were purchased from Aldrich. Table 1 presents the physical properties of the polymers used in this research. Polymer blend solutions of PB/PC with 90/10, 75/25, 65/35, 50/50, 65/35, 25/75 and 10/90 wt% in THF, as well as PMMA/PC, PS/PC, PB/PMMA and PB/PS blends with 25/75 wt% were prepared for electrospinning experiments.

2.2 Electrospinning

The electrospinning apparatus consisted of a high voltage power supply (Gamma High Voltage Research Co.), a digitally adjusted syringe pump (Harvard Apparatus, PHD 2000, South Natick Co.), a steel syringe needle, and an electrically grounded aluminum foil target. Polymer solution was fed through the needle tip by the syringe pump at a controlled flow rate. As the electrical field between needle tip and target increased, nanofibers were formed and collected on the target. The applied voltage was 15 kV, the flow rate of the polymer solution was 0.02 ml/min, and the distance between the needle tip and the target was 20 cm in all cases.

	PB	PC	PMMA	PS	THF
Critical surface tension (γ_c) (mN/m)	42	32	39	33	
Solubility parameter (δ) (MPa ^{1/2})	17.2	19.4	19.0	18.6	18.6
Brookfield viscosity (η) at 6% in THF (mPa·s)	320	13	11	24	
Mw (kD)	420	21.9	120	280	

Table 1: Physical properties of polymers.

2.3 Characterization Methods

The morphology of nanofibers was observed using a Transmission Electron Microscope (TEM, Philips EM 400 T). For the preparation of TEM samples, the nanofibers were collected on a carbon coated copper specimen grid, followed by staining in OsO₄ or RuO₄ vapor by suspending them over a 4.0% aqueous solution of OsO₄ or RuO₄ for 30 minutes.

3 RESULTS AND DISCUSSION

The phase morphology of polymer blends depends on a number of factors. The composition, interfacial tension, processing conditions, and rheological properties of the components will all influence the resulting morphology of the blends.⁹ In the electrospinning process, solvent removal takes the mixture from a homogeneous solution across the phase boundary, until two phases are formed. This process of solvent evaporation occurs at time scales in the millisecond range, during the whipping motion of the electrospinning jet.^{2,4} As a result, the rapid fiber structure forming process, coupled with the phase separation process may result in the formation of unique fiber structures.² Due to the high surface to volume ratios in nanofibers, interfaces play a key role. In this paper, polycarbonate and polybutadiene, which have large solubility parameter differences, as well as large viscosity differences, were selected for initial studies. By varying the composition ratio of PB/PC blends, we can study the effect of composition ratio on the resulting phase morphology of PB/PC blends within the electrospun nanofibers. Variations in the compositions of PB/PC blends, as well as blends of PB/PMMA, PB/PS, PMMA/PC, and PS/PC were electrospun to study the factors that had the greatest effect on the phase morphology of nanofibers.

Figure 1 shows the TEM images of PB/PC blends with different weight ratios from 90/10, 75/25, 65/35, 50/50, 65/35, 25/75 to 10/90 after staining in OsO₄ vapor for 30 minutes. OsO₄ is known to preferentially stain the polybutadiene phase, so that the dark regions in the TEM images are identified as the polybutadiene phase, and the light regions are the

polycarbonate phase.⁴ It was observed that there existed a change in morphology around 25/75 weight ratio of PB/PC blends. When the weight ratio of PB/PC blends was larger than 25/75, a co-continuous structure with interconnected PB and PC nanolayers or strands was formed and the nanolayers were oriented along the fiber axis. When the weight ratio of PB/PC blends was increased to 25/75, the nanofibers presented large layers of only one material and evidence of core-sheath structures with PB located in the center and PC located outside.

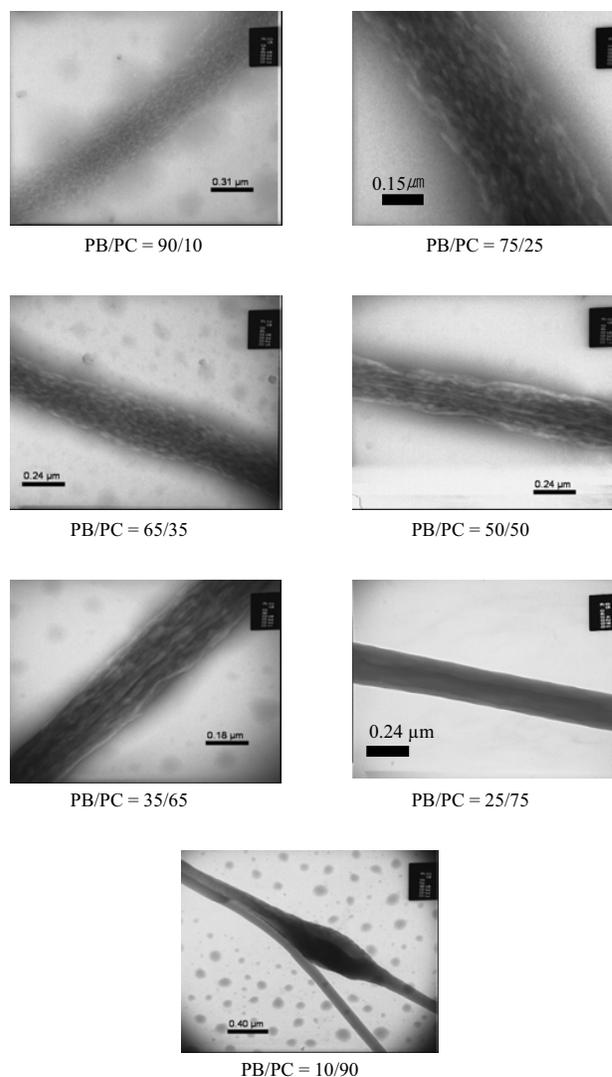


Figure 1. TEM images of electrospun PB/PC nanofibers with different composition ratios.

The formation of these structures is dependent on the ability of the two materials to phase separate during the rapid solvent evaporation process, which may not allow coarsening of the phase separated regions and thus preserving a very fine

phase morphology.⁴ Orientation of the nanolayers is a result of the elongation of the fiber during the whipping process.

The phase separation mechanism involved with rapid solvent evaporation is very similar to that involved with spinodal decomposition.¹⁰ The formation of the unique core-sheath structure may be due to a combination of factors, including viscosity and solubility of the polymers. Although the viscosity of the starting solutions are the same, as the solvent evaporates the viscosity of the system will be lower for the blends with high PC content, because of the increasing fraction of the lower viscosity PC. This decreased viscosity promotes the development of a core sheath structure by two processes. The first is involved with rheological processes and the effect of the viscosity ratio of compositions. Typically, in capillary flow of polymer blends, the lower viscosity material will tend to migrate to regions of highest shear rate. For the capillary flow of a polymer solution in the needle of the electrospinning equipment, the lower viscosity PC component would like to encapsulate the higher viscosity PB component according to the minimum energy dissipation theory of a flow system.³ With increasing PC weight fraction, the decreased viscosity of the whole blend system will give sufficient mobility for this rheological process to occur. Thus, the PC phases will be able to migrate to the outside of the fiber, while the PB phases are located at the center of the fiber forming a core-sheath structure. The second effect is due to solvent effects, or the solubility of the components in the common solvent. THF is a poorer solvent for PC than PB because both PC molecules and THF are nucleophilic, although PC has a lower solubility parameter difference than PB. Therefore, with the evaporation of solvent, the different solubilities of PB and PC in THF would be likely to cause the PC to coalesce, leading to the formation of a core-sheath structure.¹¹ The process of phase separation of PC from PB will also be dependent on the viscosity of the whole blending system, i.e. the mobility of the molecules at high solution concentration as the solvent evaporates.

To further study the influence of the viscosity ratio, solubility of compositions in the common solvent, and the viscosity of the whole blending system on the phase morphology, we investigated several other polymer blend combinations. In the following experiments, we changed the composition of blends to investigate the effect of viscosity ratio and solubility of compositions on the phase morphology. In PMMA/PC and PS/PC blends, PMMA and PS, with much lower viscosity than PB, were used to replace PB in order to study the effect of viscosity ratio on the phase morphology. In PB/PMMA and PB/PS blends, PMMA and PS with better solubility in THF than PC were used to replace PC in order to study the effect of the solubility of components on the phase morphology.

Figure 2 shows TEM images of PMMA/PC, PS/PC, PB/PMMA and PB/PS at 25/75 wt%. PMMA/PC and PS/PC blends were stained by RuO₄ vapor for 30 minutes to darken the PC phase, and PB/PMMA and PB/PS blends were stained by OsO₄ for 30 minutes to darken the PB phase. It was observed that PMMA/PC and PS/PC present core-sheath structures, but PB/PMMA and PB/PS blends present co-

continuous structures. Table 2 presents the molecular weight, approximate interfacial tension, solubility parameter difference, and resulting phase morphology of the electrospun fibers. We found that even with the large viscosity ratio in the PB/PMMA and PB/PS blends, they still presented co-continuous structures, indicating that the viscosity ratio was not the dominant factor for the formation of core-sheath structures. The good solubility of PMMA and PS in THF solvent, leads to the development of co-continuous structures. On the other hand, we observed that any blends having PC in the composition presented core-sheath structures, even with small differences in the viscosity ratio. The interfacial tension and solubility parameter differences between the polymers appear to have little effect on the morphology. Clearly, PC played a key role in the formation of core-sheath structures at certain composition ratios.

4 Conclusions

Core-sheath structures were observed in PB/PC, PMMA/PC, and PS/PC blends and co-continuous structures were observed in PB/PMMA and PB/PS blends at 25/75 wt% by TEM. The effect of interfacial tension, viscosity ratios, and solubility on nanofiber internal morphology were studied using different polymer blend systems. It was found that solubility differences of the polymer components in the electrospinning solvent played a key role in the resulting phase structure of the nanofiber. Larger solubility differences led to the formation of core-sheath structures. Smaller solubility differences for the components of the blends leads to the formation of co-continuous structures.

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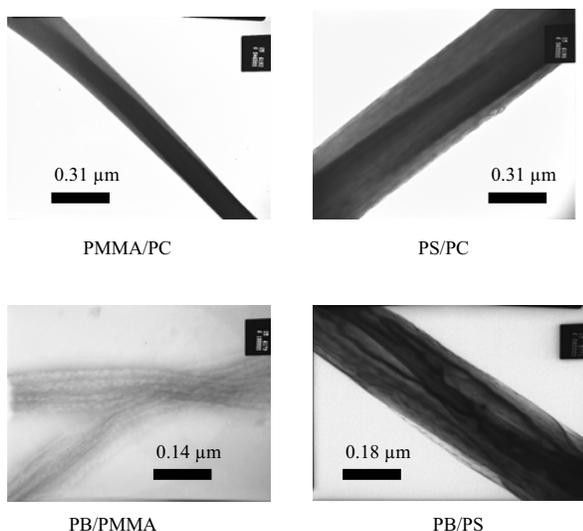


Figure 2. TEM images of PMMA/PC, PS/PC, PB/PMMA and PB/PS blends at 25/75 wt%.

	PB/ PC	PB/ PMM A	PB/ PS	PMMA /PC	PS/ PC
Mw (kD/kD)	420/ 21.9	420/ 120	420/ 280	120/ 280	280/ 21.9
$\Delta\gamma_c$ (mN/m)	10	3	9	7	1
$\Delta\delta^*$ (MPa ^{1/2})	2.3	1.8	0.6	0.4	1.6
$\Delta\delta^{**}$ (MPa ^{1/2})	1.4/ 0.8	1.4/ 0.8	1.4/ 0	0.4/ 0.8	0/ 0.8
$\Delta\eta$ (mPa·s)	307	309	296	2	11
Morphology	Core- sheath	Co- continu ous	Co- contin uous	Core- sheath	Core- sheath

*: The solubility parameter difference between the components of blends

** : The solubility parameter difference between the components of blends and THF solvent.

Table 2 The parameters of for blend compositions and phase morphology.

References

- [1] Pawlowski, K. J.; Belvin, H. L.; Raney, D. L.; Su, J., *Polymer*, 2003, 44, 1309.
 [2] Walters D. A.; Ericson L. M.; Casavant M. J., *Appl. Phys. Lett.* 1999, 74, 3803.
 [3] Salem, D. R., *Structure Formation in Polymeric Fibers*, Hanser Publishers, Munich 2000.
 [4] Bognitzki, M.; Frese, T.; Steinhart, M., *Polym. Eng. and Sci.*, 2001, 41, 982.

- [5] Norris, I. D.; Shaker, M. M.; Ko, F. K., MacDiarmid A. G., *Synthetic Metals*, 2000, 114, 109.
 [6] Doshi, J.; Reneker, D. H., *J. Elec.*, 1995, 35, 151.
 [7] Baumgaarten, P. K., *J. Coll. And Int. Sci.*, 1971, 36, 71.
 [8] Fong, H.; Reneker, D. H., *J. Polym. Sci B: Polym. Phys.*, 1999, 37, 3488.
 [9] Paul, D.R., "Fibers from Polymer Blends" in *Polymer Blends*, Vol. 2., ed. by Paul, D.R., and Newman, S., Academic Press, New York, NY 1978, Ch. 16.
 [10] Lee, J. K., Han, C. D., *Polymer*, 1999, 40, 2521
 [11] Walheim, S., Boltau, M., Mlynek, J., Krausch, G., Steiner, U., *Macromolecules*, 1997, 30, 4995.