

NOTE

Experimental Confirmation of Computer-Aided Polymer Blend Designs

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INTRODUCTION

New polymers are required to fulfill the ever increasing demand for varied applications. The three main methods for creating new polymers are designing new monomers, developing new polymerization mechanisms for old monomers, and synergistically blending existing polymers. Due to an extensive and lengthy process, the development of new commercial polymers is very rare. The use of new polymerization mechanisms for old monomers has been successful but has its limitations. The utilization of polymer blends is increasing in importance from year to year. The technique of polymer blending provides a cost-effective means of fabricating materials with a specific application. Multiphase blends can be made by a variety of methods. The current techniques include melt blending, reaction technologies, and compositional quenching.¹

The possibilities of blending the major polymers are infinite. Without a model, finding the appropriate system of polymers to produce a desired blend can be arduous and costly, especially when more than two components are involved. Previously, Nauman and He² predicted a wealth of morphologies by solving the component continuity equations, which are fourth-order partial differential equations. Despite the complexity of these equations, they contain only a few

adjustable parameters, as follows: volume fractions, interaction parameters, and chain lengths. Nauman and He found that the volume fraction of the components was the most important in determining the morphology of the polymer system. For a ternary system, a component with a volume fraction of 0.6 or higher formed a continuous phase, but no continuous phase was observed for a volume fraction less than 0.33. The semicontinuous structure was limited to the range of 0.3–0.5. The dispersed morphologies were confined to volume fractions less than 0.45. However, many of the predicted morphologies, including those with commercial importance, need further examination.

This article focuses on the preparation of new polymers by solution blending and, in particular, compositional quenching. A combination of solvent dissolution and flash devolatilization is used to achieve the final blend. The morphology of the blend is governed by spinodal decomposition. Cavanaugh et al.³ described a methodology for the computer-aided design of polymer blends. In this work, we provide some confirming results from cast films and bulk samples produced by compositional quenching.

EXPERIMENTAL

Thin films were made by solvent casting from single phase solutions, with xylene as the solvent, and were observed under an optical microscope. Bulk blends were

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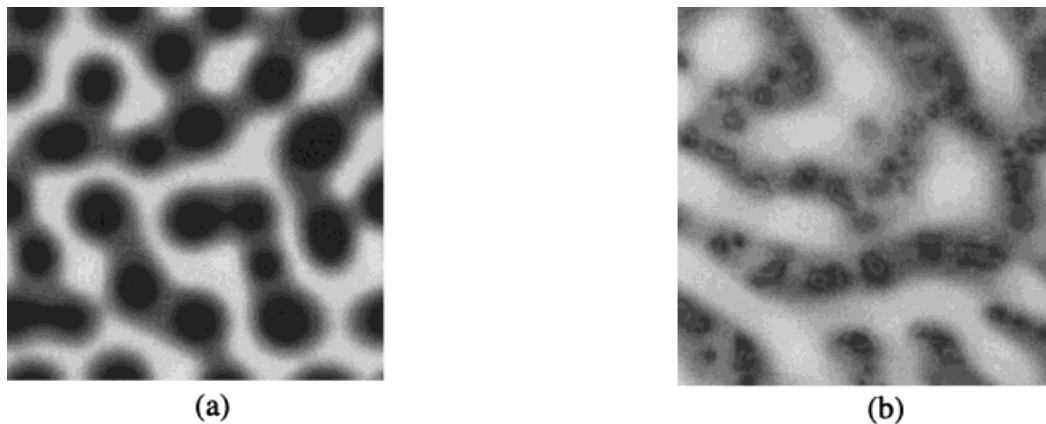


Figure 1 Comparison of (a) simulation and (b) film casting for a 40/40/20 blend of PMMA-PS-PB.

also made by dissolving the polymers in xylene. The homogeneous mixture, typically a 3–5% by weight polymer, was flashed in a vacuum chamber to remove the solvent.¹ The dried polymer blend was then compression-molded. Samples were microtomed and analyzed

using an AEI Mark IV high-voltage electron microscope (HVEM) at 1.2 MeV. In order to provide contrast between the multiphase polymer blends, differential staining techniques using OsO_4 and RuO_4 were utilized.^{4,5}

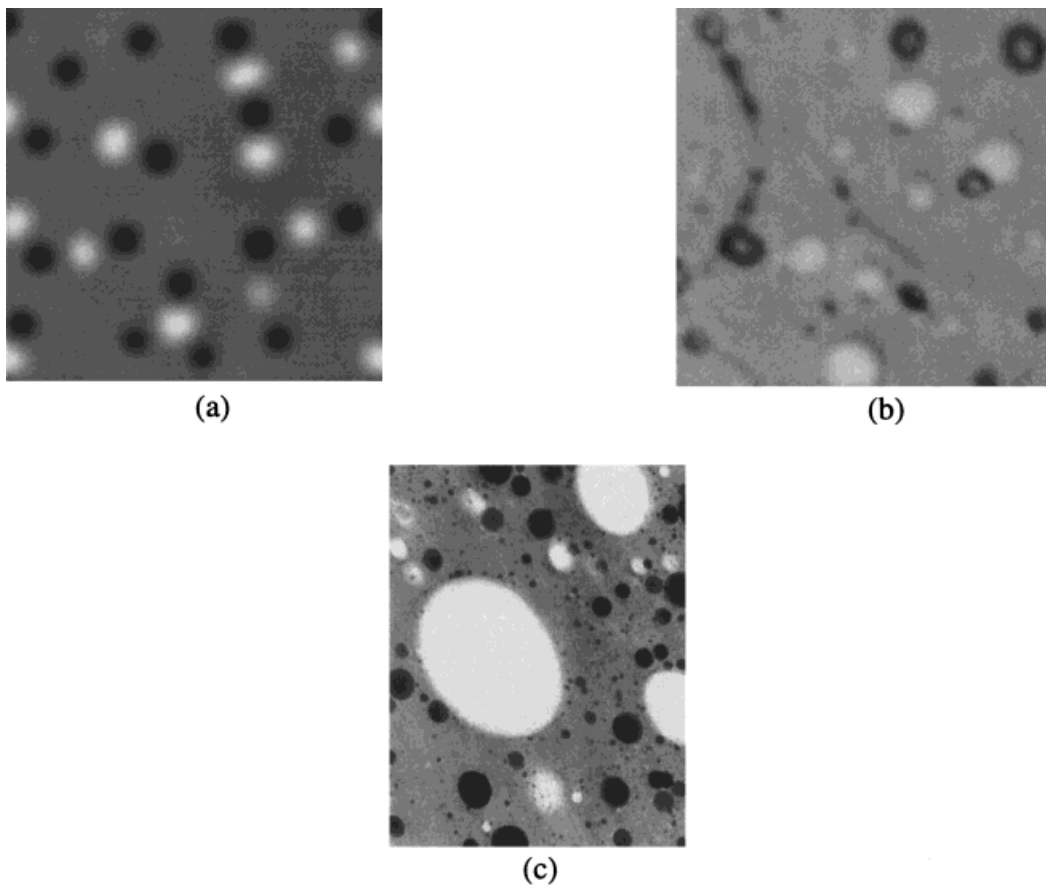


Figure 2 Comparison of (a) simulation, (b) film casting, and (c) bulk HVEM for a 15/77/8 blend of PMMA-PS-PB.

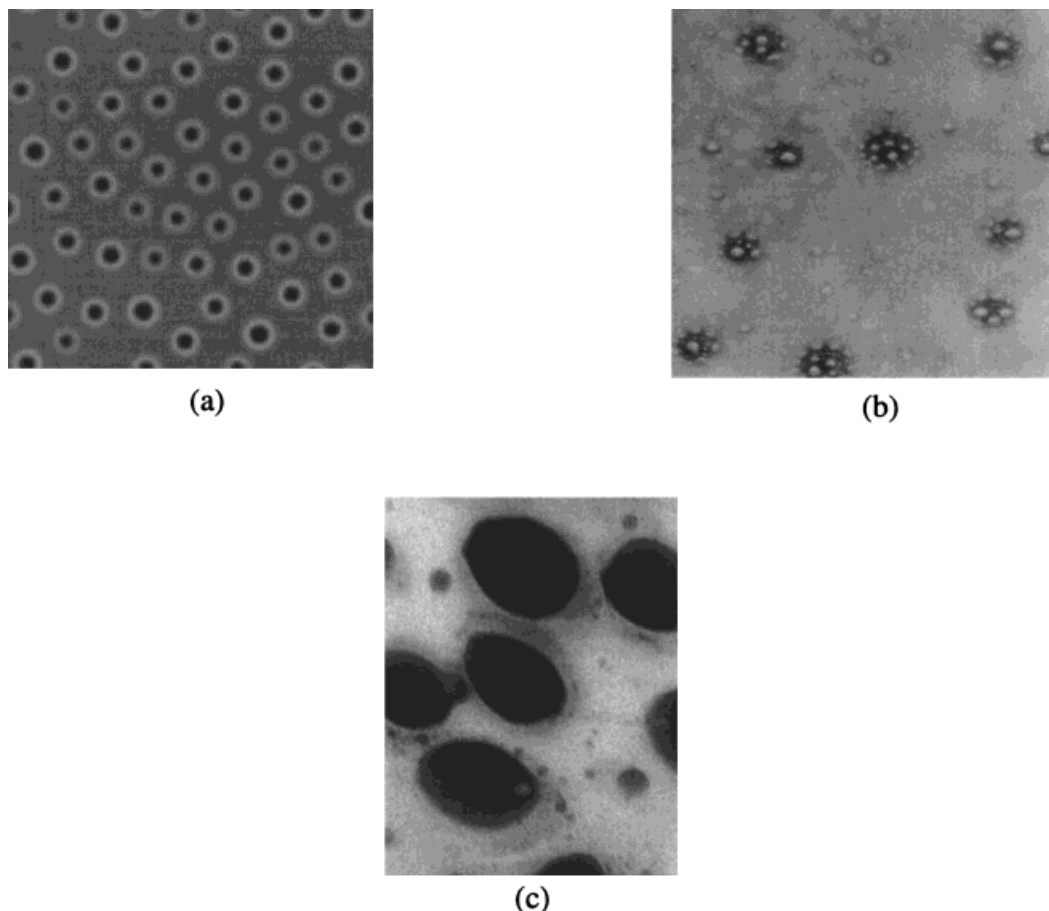


Figure 3 Comparison of (a) simulation, (b) film casting, and (c) bulk HVEM for a 77/15/8 blend of PMMA-PS-PB.

RESULTS AND DISCUSSION

The component continuity equations were solved using a finite difference approach. The initial conditions corresponded to a nearly homogeneous mixture. The interaction parameters were chosen from the literature. Large values of $n\chi$, where n is the polymer chain length, required a smaller time step. This prevented completion of the simulation in a reasonable amount of computational time. Therefore, the interaction parameters were scaled such that the maximum value did not exceed 12. When $n\chi$ is greater than 2, which is the critical value for phase separation, this scaling did not affect the computed morphology. It is the ratios of interaction parameters that are important rather than absolute values. The volume fractions were varied in order to obtain different component morphologies ranging from discrete to continuous. Of the various morphologies, the following three types have significant potential for industrial applications: dual-semicontinuous, multiple discrete particle, and core-shell.

Two ternary systems have been experimentally verified. The first ternary polymer system included

two glassy polymers and one rubbery polymer: poly (methyl methacrylate) (PMMA), polystyrene (PS), and polybutadiene (PB). The interaction parameters used in the simulations were $n\chi_{\text{pmma/ps}} = 3.0$, $n\chi_{\text{pmma/pb}} = 12.0$, and $n\chi_{\text{ps/pb}} = 4.2$. The dual semicontinuous structure created by spinodal decomposition is shown in Figure 1(a). From the simulation, the polybutadiene appears as discrete particles in the semicontinuous polystyrene phase. Figure 1(b) depicts the same blend made by film casting. The overall morphology compares favorably to the simulation.

The multiple discrete particle structures shown in Figure 2(a) also have potential importance due to the possibility of a bimodal particle size distribution. It is believed that for polymers such as Acrylonitrile-Butadiene-Styrene (ABS), which fail by both crazing and shear yielding, the presence of two particle sizes, one above the critical size for craze initiation, and one below the critical size for shearing, would enhance toughness more than a monomodal particle size distribution.⁶ This would be an advantage in materials in which the competing failure mechanisms have an opposite response to particle size. Figure

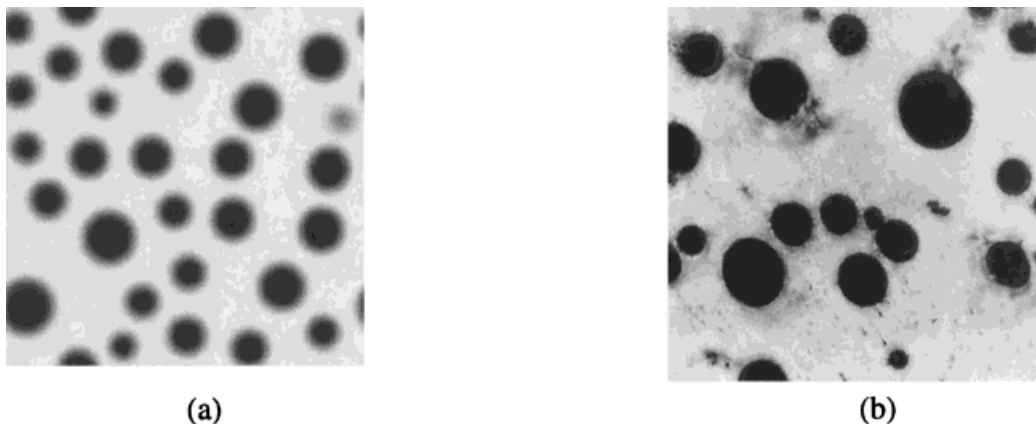


Figure 4 Comparison of (a) simulation and (b) film casting for a 77/15/8 blend of PS-PB-PI.

2(b) shows the multiple discrete particle morphology with PMMA being the larger white spheres and PB being the smaller dark spheres. The PB spheres appear to be unstained in the center, which may be attributed to insufficient staining. The lines in Figure 2(b) are crazes that develop in the film as the solvent evaporates. Figure 2(c) is the bulk blend in which the unstained PMMA constitutes the white spheres. Both blends match the simulation.

The core shell structure, as seen Figure 3(a), was produced using three homopolymers, although such structures are more commonly produced using a block copolymer of the two homopolymers. Figure 3(b) is the experimental attempt to produce a core shell structure by film casting. As observed, the core, which consists of PB with some polystyrene (PS) inclusions, is surrounded by PS particles. It is possible that internal hydrodynamics, which are not accounted for in the model, cause the shell to break up. Other models,^{7,8} which include hydrodynamics, may be able to predict

such a structure. Figure 3(c) is the blend produced in bulk. The PS appears as the shell around the dark PB particles.

The second ternary blend studied was PS, PB, and polyisoprene (PI). In this case, two rubbers were mixed with a glassy polymer. The interaction parameters for this case were $n\chi_{ps/pb} = 4.2$, $n\chi_{ps/pi} = 5.4$, and $n\chi_{pb/pi} = 0.3$. Since the interaction parameter between polybutadiene and polyisoprene was less than the critical value for phase separation, the two components will not phase separate. Figure 4 shows the mixed rubbers as discrete particles in a PS matrix. With the addition of more PB and PI, the rubber becomes a semicontinuous phase, as shown in Figure 5. As the composition of the polystyrene is decreased, PS forms discrete domains in the continuous rubber matrix (see Fig. 6). The small dots in the micrograph are apparently tiny bubbles in the film, which may have been caused by the casting process. The experimental results show good agreement with the simulations.

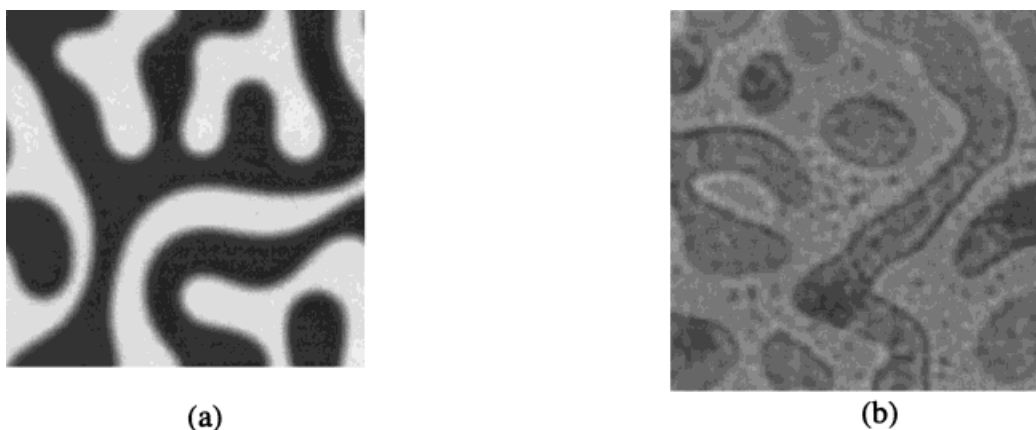


Figure 5 Comparison of (a) simulation and (b) film casting for a 50/25/25 blend of PS-PB-PI.

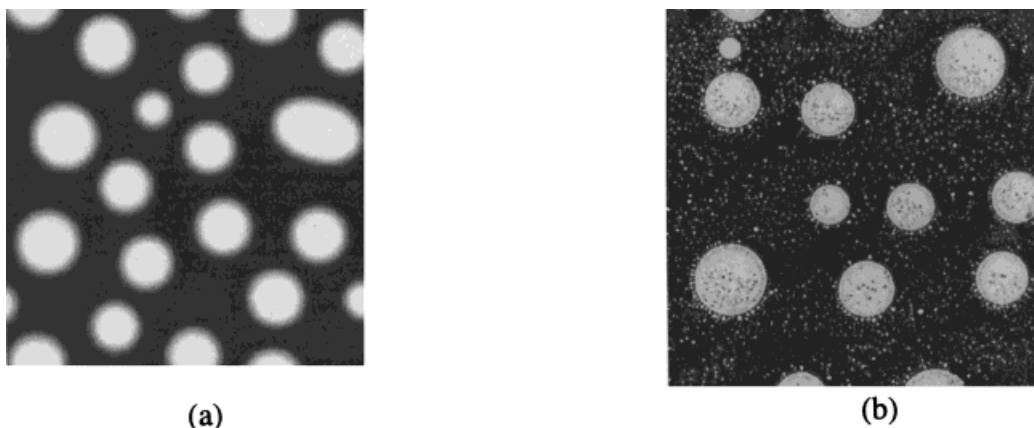


Figure 6 Comparison of (a) simulation and (b) film casting for a 34/33/33 blend of PS-PB-PI.

CONCLUSIONS

The morphologies of ternary blends, cast as films or quenched in bulk from solution, closely resemble predicted morphologies obtained from spinodal decomposition theory. This result makes it possible to design polymer blends with a minimal amount of experimentation. Although additional confirmation is desirable, it appears that the morphologies of blends can be predicted from computer simulations requiring only three adjustable parameters: component volume fractions, chain lengths, and binary interaction parameters.

Additional work must also be done to correlate the physical properties of blends with their predicted morphologies. Upon completion of this aspect of blend simulation, a powerful computational tool for the design of polymer blends with desirable physical characteristics will be available.

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