

Encapsulation and Compatibilization by Random Copolymers

Moo Sung Lee

Department of Textile Engineering, Chonnam National University

C. W. Macosko and T. P. Lodge

Department of Chemical Engineering and Materials Science,

University of Minnesota

Introduction

Blends of immiscible polymers often require the addition of a compatibilizer to improve the dispersion and adhesion of phases and to stabilize the morphology. Block or graft copolymers having the same monomeric units as the blend components have been successfully used for this purpose. Such compatibilizers can be introduced by adding a pre-made copolymer, or by in-situ formation during melt processing [1].

Random copolymers may offer an alternative method for compatibilization because they can enhance the interfacial adhesion between immiscible phases and encapsulate the dispersed domain during drying of solvated blend samples [2,3]. However, it is not yet clear whether random copolymers can move to the interface during melt processing, and stabilize the resultant morphology during melt annealing.

In this study we investigate the compatibilizing performance of random copolymers in the melt state. As model polymers, a styrene-methyl methacrylate random copolymer (SMMA), PS, PMMA, PC, PPO are chosen. Using melt mixing we prepare four blend systems; PS/PMMA/SMMA, PS/PC/SMMA, PPO/PMMA/SMMA, and PPO/PC/SMMA blends.

Experimental

The characteristics of the polymers used in this study are listed in Table 1. All polymers are commercially available. Except for PPO which was in powder form, all polymers were provided as pellets. Before melt blending all polymers were dried overnight under vacuum at room temperature. Blend samples were prepared using a Haake Rheomix 600 batch mixer. After mixing, the samples were quenched in ice water. To investigate the melt stability as blended samples were annealed in a home-

made annealing oven for specified period of time. Specimens were wrapped in aluminum foil to prevent flow during annealing.

Table 1. Polymers used in this study

Polymers	Source	Mw (g/mol)	T _g (°C)	η ₀ * ^a (Pa.s)
PS	DOW (Styron666)	200,000	99	624
PMMA	Polysciences, Inc.	100,000	94	661
PC	GE Plastics	-	150	7,860
PPO	GE Plastics	40,000	208	-
SMMA	Polysciences, Inc	270,000	104	1,870

^a Measured using a Rheometrics DSR rheometer at 240°C.

The blend morphology of as-blended and annealed samples was characterized using a JEOL 1210 transmission electron microscope (TEM), operated at 120 kV. Sections of about 70 nm thickness were microtomed at room temperature with a Reichert Ultracut S ultramicrotome. The sections were stained for 10 or 15 min with the vapor of 0.5 % RuO₄ in water solution. As benzene rings are preferentially stained under the conditions used in this study [4], PS, PC, PPO appears dark, SMMA gray, and PMMA white in bright field TEM. Moreover, although PS, PC, and PPO are stained with RuO₄, it is possible to differentiate PPO, PC and PS phases in blends due to different staining rate.

Results and Discussion

Figure 1 shows TEM micrographs of 70/10/20 (by weight) PS/PMMA/SMMA blends before and after annealing at 200 °C for 60 min. Almost all PMMA domains are encapsulated by a layer of SMMA. Since SMMA has the highest melt viscosity under the mixing conditions employed, this observation suggests that encapsulation by SMMA is controlled by thermodynamic factors such as interfacial tension. After annealing the encapsulating layer is well developed, but the domain size is increased significantly.

Figure 2 shows representative TEM micrographs of 70/30/10 (by weight) PC/PS/SMMA blends. Similarly to Figure 1, SMMA encapsulates the minor PS domains and also the domain size increases significantly after annealing. These two figures clearly demonstrate that the encapsulating layer of SMMA does not provide stability against static coalescence, which calls into question the effectiveness of random copolymers as practical compatibilizers.

The other two blends studied, PPO/PMMA/SMMA and PC/PPO/SMMA systems, have the similar morphologies to Figures 1 and 2. This means that random copolymers have the strong tendency

to encapsulate minor phase when they A/B/A-r-B, C/B/A-r-B, or C/D/A-r-B ternary blends. In here A/C and B/D pairs are miscible or compatible.

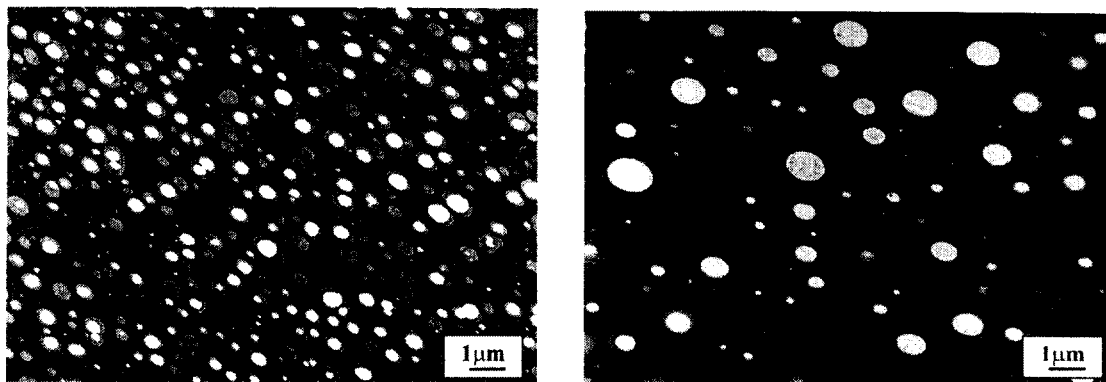


Figure 1. TEM micrographs of as-blended (a) and annealed (b), at 200 °C for 60 min, PS/PMMA/SMMA (by weight) 70/10/20 blends.

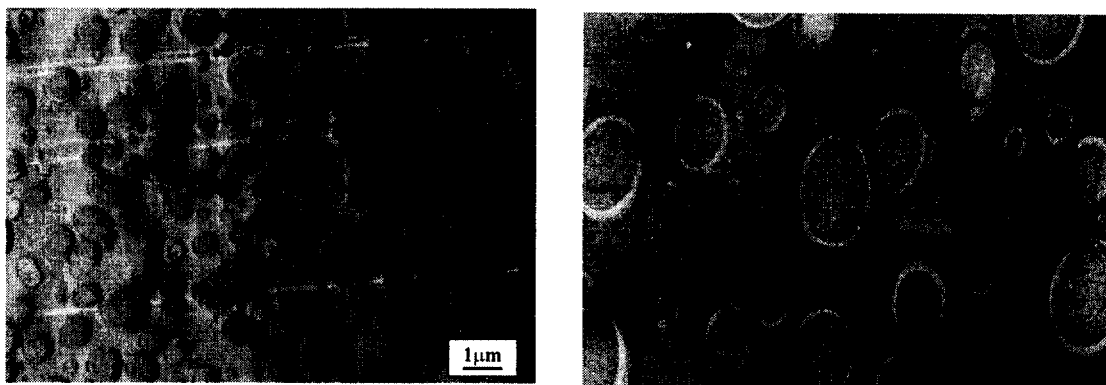


Figure 2. TEM micrographs of as-blended (a) and annealed (b), at 240 °C for 60 min, PC/PS/SMMA (by weight) 70/30/10 blend.

Concluding Remarks

All blend systems studied have interesting morphologies, in which SMMA encapsulates the minor phases during melt mixing. The encapsulation behavior of SMMA can be explained in terms of a spreading concept [5] combined with the Flory-Huggins interaction parameter. After annealing the encapsulating layer of SMMA is well developed although the domain size is increased. These may cause opposite effect to the mechanical properties of the blends. It is not yet clear whether the coarsening

behavior observed in this study is fatal for the physical properties of polymer blends compatibilized by random copolymers or not. More elaborate experimental works will be required to answer the question.

References

1. S. Datta and D. Lohse, *Polymeric Compatibilizers*, Hanser Publishers, Munich, 1996.
2. H. R. Brown, K. Char, V. R. Delin, and P. F. Green, *Macromolecules*, **26**, 4155 (1993).
3. K. I. Winey, M. L. Berba, and M. E. Galvin, *Macromolecules*, **29**, 2868 (1996).
4. J. S. Trent, J. I. Scheinbeim, and R. R. Couchman, *Macromolecules*, **16**, 589 (1983).
5. S. Y. Hobbs, M. E. Dekkers, and V. H. Watkins, *Polymer*, **29**, 1598 (1988).