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13. ABSTRACT (Maximum 200 words)

Mechanical properties of polymer blends can be improved by addition of block copolymers as compatibilizers. The objective of this study has been to systematically investigate the effect of added block copolymer in order to gain understanding of the factors, such as the amount, size and structure of block copolymer, that control the efficacy of the compatibilization. The rate of particle coarsening that occur at the late stage of phase separation has been shown to be affected sensitively by the presence of even a very small amount of block copolymer. On the assumption that the late stage proceeds by the Lipshitz-Slyozov mechanism, one can estimate the change in the interfacial tension resulting from the adsorption of block copolymer at the interface. The larger the block copolymer size is, the more pronounced is the reduction in the particle coarsening rate. When polymers are melt-blended, a larger block copolymer additive is again found to be more effective than smaller copolymers.

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USE OF BLOCK COPOLYMER
AS POLYMER BLEND COMPATIBILIZER

FINAL REPORT

R. J. ROE

1/30/93

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CINCINNATI, OH 45221

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FORWARD

This is the final report of the research project conducted from February 1, 1989 to October 31, 1992 under the ARO contract DAAL03-89-K-0040. The title of the project is "Use of Block Copolymer as Polymer Blend Compatibilizer."

A. STATEMENT OF THE PROBLEM STUDIED

Mechanical properties of polymer blends can be improved by addition of block or graft copolymers. The additive helps to "compatibilize" the blend by reducing the size of the phase-separated domains and increasing the adhesion between the phases. Despite the great amount of effort that has gone into the technology of polymer blends in recent decades, little systematic information is available about the factors that control the efficacy of the compatibilizers. The objective of this study has been to systematically investigate the effect of added block copolymer on polymer blends in order to gain understanding of the mechanism of compatibilization in more scientific terms. The key to the compatibilization lies in the interfacial activity of the block copolymer, that is, its tendency to accumulate at the interface between two incompatible polymer phases. Once accumulated at the interface, it enhances the interfacial adhesion, on the one hand, and lowers the interfacial tension, on the other hand. The lowering of the interfacial tension is responsible for the reduction in the size of the phase-separated particles to the degree required for good mechanical performance. The

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interfacial activity of the block copolymer can be demonstrated by its effect on the particle coarsening in the very late stage of phase separation. A quantitative measure of the amount of block copolymer adsorbed at the interface, and the resulting reduction in the interfacial tension could be obtained from measuring the rate of growth of particle sizes and analyzing the result by application of available theories. The validity of such an approach can be assessed by comparing the interfacial tension values thus evaluated against the values obtained by direct measurements. The interfacial activity of the added block copolymer can also be demonstrated by noting the change in the morphologies of melt-mixed polymer blends when block copolymers of various sizes are added to the system. The properties and morphologies exhibited by these melt-blended materials present many interesting and intriguing features that require further exploration.

B. SUMMARY OF THE MOST IMPORTANT RESULTS

The use of block or graft copolymer as compatibilizer of polymer blends is widespread in practice. A large number of published literature articles report experimental observations demonstrating the efficacy of block copolymers. The experimental results reported are, however, mostly qualitative observations, and very few studies have been directed toward obtaining systematic understanding of the factors that govern the efficacy of the compatibilizing effect. In order to be economically beneficial the amount of the additive required to achieve a sufficient

compatibilizing effect has to be small, and obviously there is a need to optimize the efficacy of the compatibilizers.

A direct consequence of the interfacial activity of block copolymer is the reduction in the size of the phase-separated particles in the blend prepared. Two separate processes contribute to this outcome: on the one hand, the reduced interfacial tension, resulting from the accumulation of block copolymer at the interface, facilitates breaking-up of the incompatible blends into smaller particles during melt-mixing, and on the other hand, the same lowered interfacial tension brings about a decrease in the tendency for the phase separated particles to coalesce and grow in size. The second process is much more clearly defined and amenable to precise measurements. The first part of the present study was directed toward assessing the effect of the added block copolymer on the coarsening of phase separated particles. A clearer understanding of the effect of the amount and the molecular weight of the added block copolymer has emerged. In the later phase of the project, the influence of the size of the added block copolymer on the dispersion of the phases during melt mixing was investigated. The result clearly demonstrates the profound influence the added block copolymer exerts in producing the blend morphology. A number of very interesting features have been observed, suggesting a need for further systematic exploration to understand the molecular processes leading to them.

To optimize the efficacy of the block copolymer for compatibilization it is important to insure that as large a fraction of the added copolymer as possible is actually driven to the polymer-polymer interface. One way of assessing the amount of interfacially adsorbed block copolymer is to measure the extent of reduction in the interfacial tension

between two immiscible polymers achieved by addition of a block copolymer. Another method, which has been developed in this project, is to determine the rate of particle coarsening in the presence of added block copolymer in the late stage of phase separation of polymer blends. It turns out to be a very sensitive method, and both light scattering measurement and optical microscopic observations demonstrated that the dynamics of particle coarsening is indeed affected by the presence of even a very small amount of block copolymer. Figure 1 shows an example¹ of such optical micrographs of phase separated particles of polystyrene in the matrix of polybutadiene, both of low molecular weights. When the average particle diameter, determined from such micrographs, are plotted against time, results exemplified by Figure 2 are obtained. The average diameter R increases as $\sim t^{0.4}$, in fair agreement with theoretical predictions $t^{1/3}$. What is striking is that the presence of an even very small amount of block copolymer markedly reduces the rate of particle coarsening. This particle growth retardation effect is also very sensitive to the molecular weight of the added block copolymer. When the block copolymer molecular weight was increased by a factor of two from 25000 to 47900, the amount required to produce the same extent of retardation was reduced by nearly an order of magnitude.

The particle coarsening in the late stage of phase separation may proceed either through the collision-coalescence process discussed by Smoluchowski,² Siggia³ and others⁴ or through the evaporation-condensation mechanism elaborated on by Lifshitz-Slyozov,⁵ Wagner⁶ and others.⁷ The latter is the dominant mechanism under our experimental conditions, as judged from the observed temperature dependence of the phase-separation rate and the particle size distribution. When the

Lifshitz-Slyozov mechanism is dominant, the rate of particle volume growth, dR^3/dt , is expected to be directly proportional to the interfacial tension. The data, such as those given in Figure 2, can therefore be analyzed to show how far the interfacial tension γ in the presence of block copolymer is reduced in comparison to the interfacial tension γ_0 in its absence, as shown in Figure 3. Application of the available theory, such as the one due to Leibler,⁸ then enables us to estimate the amount of adsorbed block copolymer at the interface and thence the fraction of block copolymer that is actually utilized for lowering the interfacial tension. The extent to which the result of such an analysis could be relied upon can be checked by comparing the interfacial tension values deduced by our method (for example those presented in Figure 3) with the interfacial tension valued determined by direct means such as the pendant drop method. The only experimental data of this kind available in the literature, those due to Koberstein and others,⁹ were, however, obtained under fairly different conditions than ours (with respect to temperature and the size of the block copolymer), and do not allow a direct comparison with our results. We sent some of our polymer samples to Professor Koberstein's group at University of Connecticut for interfacial tension measurement with their pendant drop set-up, but have not received any results yet.

The more enhanced efficacy of larger block copolymer in its compatibilizer role is in line with our expectation that the block copolymer becomes less soluble in the homopolymer as the size of the copolymer increases and are hence driven more toward the interface. This reduced solubility, however, also drives the block copolymer molecules toward formation of micelles by themselves. The two

processes, adsorption at the interface and formation of micelles, compete with each other, and as a result, beyond a certain point, an increase in the size of the block copolymer or an increase in the amount of added copolymer may not produce any additional beneficial effect. Our study in pursuit of this upper limit of efficacy has not been concluded at the time of this writing. It appears that as the amount of added block copolymer is increased much beyond the critical micelle concentration, the particle coarsening retardation is apparently reversed,¹⁰ suggesting that an additional process that have not been so far taken into consideration might be setting in.

The adsorption of block copolymer at the phase interface and the consequent reduction in the interfacial free energy makes it easier for the interfacial areas to increase as the dispersed phase is broken up during mechanical mixing. The process of melt-mixing is complex, and there is very little work published that addresses the relationship between the characteristics of the block copolymer and the ease of dispersion. In our work,¹¹ we have taken a blend of equal amounts of polystyrene (40K MW) and polybutadiene (40K MW) and added to it 10 weight percent of styrene/butadiene diblock copolymer of various sizes. The importance of the block copolymer size is again clearly demonstrated. With 10K/10K block copolymer added, the melt-mixed material did not achieve fine dispersion of the two phases, as was evident from the electron micrograph shown in Figure 4 (left frame), and also from the mechanical properties exhibited. On the other hand, with the block copolymer of 60K/60K block lengths, one of the phases (polystyrene) is totally broken up into small, ellipsoidal particles and thoroughly dispersed in the continuous matrix of the other phase

(polybutadiene), as is seen in the electron micrograph in Figure 4 (right frame). This blend exhibits an unusual mechanical behavior in that, although it is solid-like at short time observation, it eventually flows under its own weight to conform to the shape of the container. This phase of the study had to be curtailed by the termination of the present project, but it is felt that a systematic study of the structure of melt-mixed blends as a function of the amount, size, and structure of the block copolymer is highly desirable.

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11. K. Kerr, D. Melik, S. D. Smith, and R. J. Roe, presented at the ACS Midwestern Regional Meeting, May 1992.

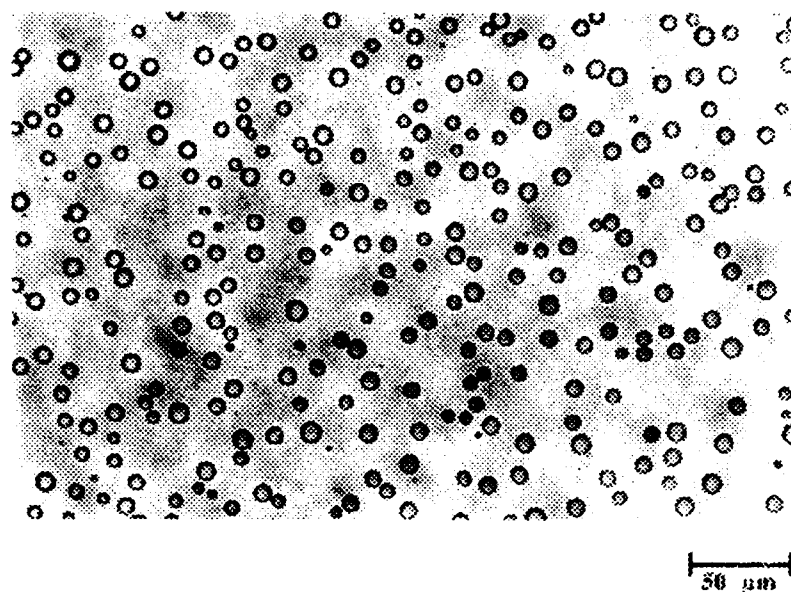


Figure 1. Optical micrograph of particles of polystyrene in the matrix of low molecular weight polybutadiene in the late stage of phase separation.

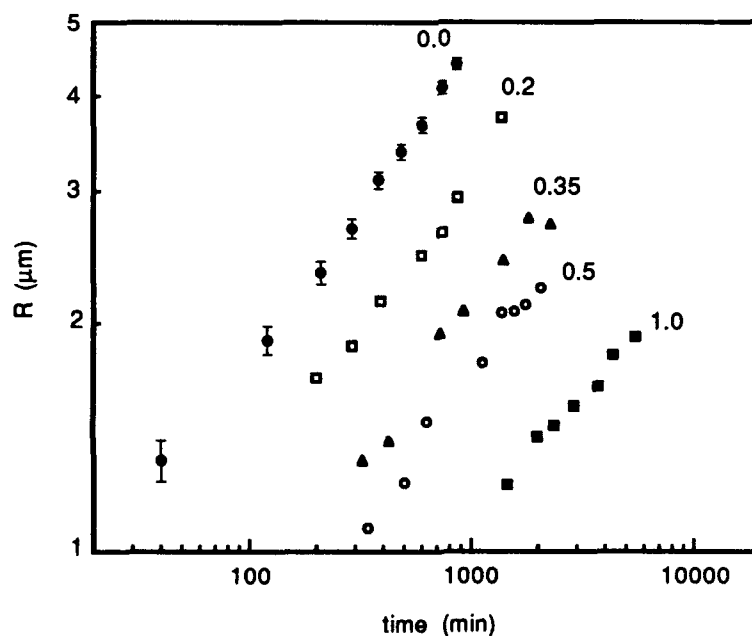


Figure 2. Average radius R of the dispersed polystyrene-rich particles plotted as a function of time, in the mixtures containing the indicated amounts (wt %) of styrene/butadiene diblock copolymer.

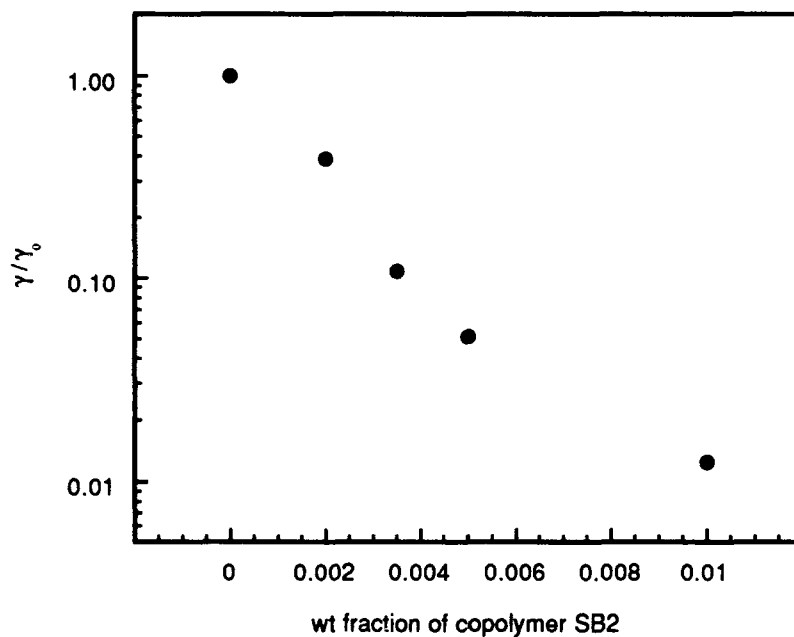


Figure 3. Reduction in the interfacial tension against the amount of block copolymer added, evaluated from the data in Figure 2 on the assumption that the Lipshits-Slyozov mechanism of particle coarsening is valid.

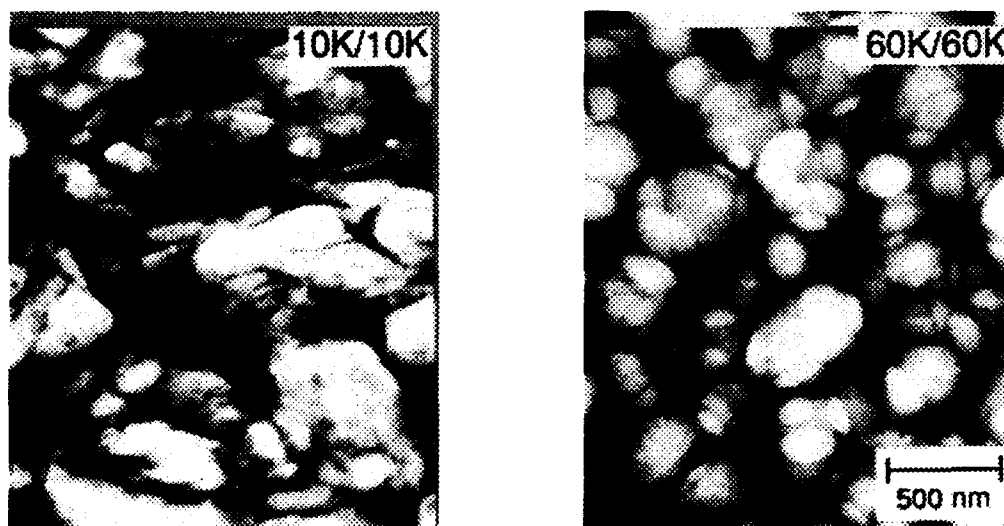


Figure 4. Morphology of the blend of polystyrene (40K MW) and polybutadiene (40K MW) melt-mixed in the presence of 10 % of styrene/butadiene diblock copolymer of block lengths 10K/10K (left) and 60K/60K (right).

C. LIST OF PUBLICATIONS RESULTING FROM THE PROJECT

Effect of Added Block Copolymer on Phase Separation Kinetics of Polymer Blend. I. Light Scattering Study, by R. J. Roe and Ch. M. Kuo, *Macromolecules*, **23**, 4635 (1990).

Light Scattering Study of Phase Separation Dynamics of Polymer Blends in the Presence of Block Copolymer, by R. J. Roe and C. M. Kuo, *Bull. Am. Phys. Soc.* **35**, 746 (1990).

Effect of Added Block Copolymer on Phase-Separation Kinetics of Polymer Blend. 2. Optical Microscopic Observations, by D. W. Park, R. J. Roe, *Macromolecules*, **24**, 5324 (1991).

Effect of Added Block Copolymer as Compatibilizer of Polymer Blends, by D. W. Park and R. J. Roe, *Bull. Am. Phys. Soc.* **36**, 788 (1991).

The Effect of Added Block Copolymer as Compatibilizer of Polymer Blend, by R. J. Roe, C. M. Kuo, and D. W. Park, *Preprint of Division of Polymeric Materials: Science and Engineering, American Chemical Society*, **64**, 119 (1991).

Block Copolymer as Compatibilizer of Polymer Blend: Effect on the Late Stage Phase Separation Dynamics at Different Temperatures, by D. W. Park and R. J. Roe, *Bull. Am. Phys. Soc.* **37**, 412 (1992).

Study of the Effect of Added Diblock Copolymers on Polystyrene/Polybutadiene Blends, by K. Kerr, D. Melik, S. D. Smith, and R. J. Roe, abstract of paper presented at the ACS Midwestern Regional Meeting, May 1992.

Particle Coarsening Process in the Late Stage of Phase Separation of Polymer Blends, by D. W. Park, D. Ping, and R. J. Roe, manuscript in preparation.

D. LIST OF PARTICIPATING SCIENTIFIC PERSONNEL

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Ph.D. degree awarded: 12/1991.

Dissertation title: Block Copolymer as Compatibilizer of Polymer Blends and Its Effect on Phase Separation

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