Distribution of MBS Emulsion Particles in Immiscible Polystyrene / SAN Blends

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Synopsis

The effect of mixing technique and sequence on the distribution of methacrylated-butadiene-styrene (MBS) emulsion particles in immiscible blends of polystyrene (PS) and a styrene/acrylonitrile copolymer (SAN) was examined using transmission electron microscopy. The shell of the emulsion particle is essentially poly(methyl methacrylate) (PMMA), which is miscible with SAN but immiscible with PS. In simple thermodynamic terms, the MBS particle should have an affinity for SAN over PS. It was found, however, that the sequence of mixing had a strong influence on the location of the MBS particles. If the PS-SAN interface is established before the addition of the MBS particles, the MBS particles are located exclusively in the SAN phase. If the MBS particles are present at the time the PS-SAN interface is formed, then the particles line up at the interface.

INTRODUCTION

Many glassy polymers are brittle and require incorporation of a rubbery phase in some manner to achieve an appropriate level of toughness for broad commercial application.[1-6] In some cases, this is accomplished by dissolving the rubber in the monomer followed by polymerization, as in the case of high impact polystyrene (HIPS) or certain types of acrylonitrile-butadiene-styrene materials (ABS). Melt blending of preformed impact modifiers into the matrix polymer is an alternate route. Often these modifiers consist of emulsion-made rubber particles having a grafted shell of a rigid polymer that adhesively bonds the particles to the matrix, for example by miscibility of the shell with the matrix polymer. The size of these particles and their distribution in the matrix are some of the many factors influencing the effectiveness of this approach.

The need to broaden the performance spectrum of plastics has stimulated much interest in blending different types of polymers to obtain materials having balanced combinations of specific properties, such as heat and chemical resistance, or a more favorable performance/price ratio. Most polymer pairs are immiscible and form multiphase mixtures. Because of this incompatibility or because of the inherent limitations of either or both components, such blends also frequently lack adequate toughness and the addition of rubbery particles to obtain toughening is an option to be considered. This case then raises interesting questions about how the blending process will distribute the modifier particles in the multiphase matrix and the important issue of where they should be located for optimal performance. No doubt many factors are involved in each of these considerations. This paper reports results of a

limited nature dealing with how the mixing process affects distribution for one particular system.

This study was stimulated by an earlier examination[4,5] of blends of HIPS and ABS to which additional rubber was added in the form of small emulsion-made rubber particles to which a second stage of methyl methacrylate (MMA) had been grafted. While HIPS and ABS each have high impact resistance alone, the resulting blends were found to be brittle. Interestingly, toughness was re-established by addition of the grafted rubber particles. Microscopy revealed these particles were for the most part lined up at the interface between the HIPS and ABS with only a few stray particles distributed in either phase.[5] It was felt that this interesting and unexpected morphology deserved further examination. It seems reasonable that the rubber phases of either HIPS or ABS have little to do with the resulting morphology, so we selected blends of their matrix phases, polystyrene (PS) and styrene/acrylonitrile copolymer (SAN), for further investigation. For the rubber particles we selected a commercially available methacrylate-butadiene-styrene impact modifier. The object was to learn how blending technique and sequence influenced the distribution of these particles in the two phase PS-SAN matrix.

EXPERIMENTAL

The polymers used in this study are described in Table I. The impact modifier is a grafted emulsion polymer manufactured by the Rohm and Haas Co. with the designation of Acryloid KM-680. It is described as a methacrylated butadiene-styrene (MBS) product, and it is essentially a butadiene-based rubber core with a poly(methyl methacrylate) shell. The ultimate particles are rather uniform in size with a diameter of 0.18 μm. The rubber content is approximately 80%. Further details about this material are given elsewhere.[7,8]

Blends were prepared by both extrusion and batch mixing as a means of varying the mixing technique. A one-inch Killion extruder (L/D = 30) outfitted with a high shear mixing screw having a compression ratio of 3:1 was used for continuous mixing at a screw speed of 50 rpm. A Brabender Plasti-Corder equipped with a 50 cm^3 sample chamber was used for batch mixing at a rotor speed of 40 rpm. In both cases, a processing temperature of 200°C was used.

TABLE I
Polymers Used in This Study

Polymer	Abbreviation	Source	Molecular weight
Polystyrene	PS	Cosden Oil and Chemical Co. 550P	$M_n = 100,000$ $M_w = 350,000$
Poly(styrene-co-acrylonitrile) 25% AN	SAN	Dow Chemical Co. Tyril 1000	$M_n = 77,000$ $M_w = 152,000$
Methacrylated-butadiene-styrene modifier	MBS	Rohm & Haas Co. Acryloid KM-680	

The PS and SAN were dried at least 12 h at 75°C before mixing. In some cases, blending of the component polymers was carried out in two stages. In the case of extrusion, this meant extruding the appropriate blend components to form a premix and then mixing the premixed pellets with the remaining component in a final extrusion step. Similarly, the appropriate premixes were blended in the Brabender, chopped into small pieces, and subsequently blended together with the remaining component to generate the final blend. Sheets 0.125 inch thick were compression molded at 200°C from either pelletized extrudate or material prepared in the batch mixer. From these moldings, ultrathin slices were microtomed at room temperature and stained in a 4% solution of OsO_4. This staining procedure allows ready identification of the
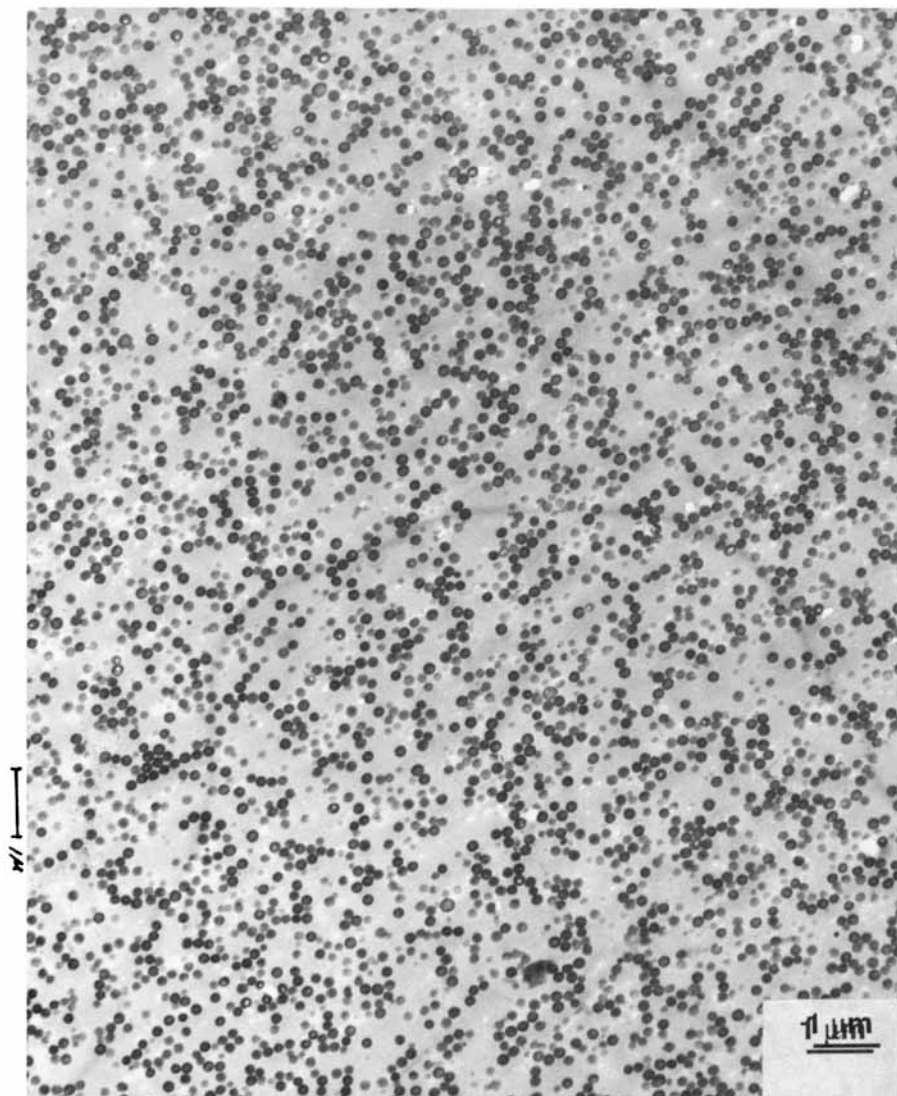

Fig. 1.   Transmission electron photomicrograph of an SAN/MBS (70/30 by weight) extrusion blend. Dark particles are MBS.

modifier particles because of the unsaturation of the rubber core; however, some differential staining also provided adequate contrast to delineate the PS and SAN phases of the matrix. A Phillips Model EM 300 electron microscope was used to obtain the transmission photomicrographs presented here.

RESULTS AND DISCUSSION

The MBS particles, like the experimental MMA-grafted elastomer used in the earlier work,[5] are readily dispersed into various matrix polymers. Figure 1 shows a relatively uniform dispersion of MBS particles in an SAN for an
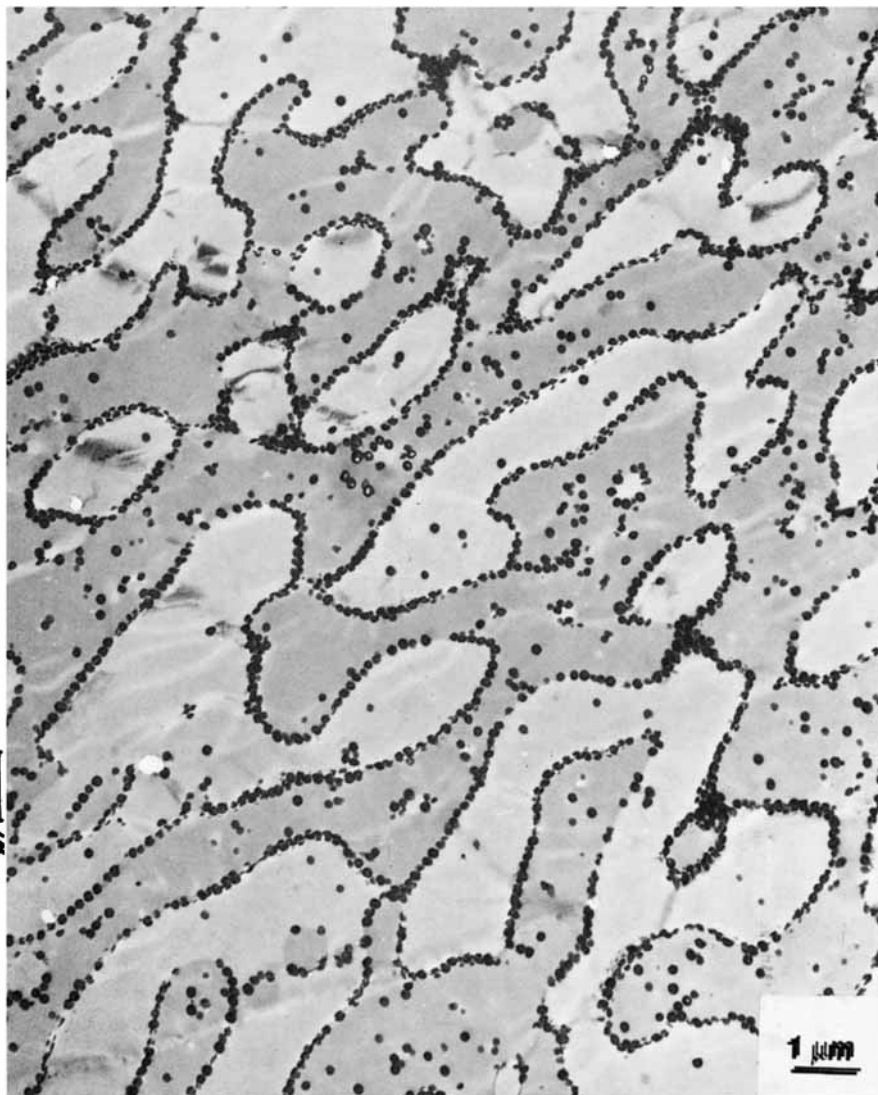

Fig. 2. Transmission electron photomicrograph of a PS/SAN/MBS (41/41/18) blend prepared by simultaneous mixing of the components in a Brabender mixer. Darker phase in SAN. Small particles are MBS.

extruded sample. While there are some areas of low particle concentration and in some areas the particles appear to touch, overall the particle distribution is uniform and no agglomeration is apparent. The same blend was made in a Brabender with similar results. The experimental MMA graft mentioned earlier was found to be equally well distributed in a PS matrix.[9]

Melt blending MBS, SAN, and PS simultaneously in the Brabender resulted in the unusual morphology shown in Figure 2 which is similar to that obtained from a blend of ABS, HIPS, and MMA graft as reported earlier.[4,5] Essentially all the MBS particles are at the PS–SAN interface, while some occasional stray particles exist within both the PS and the SAN (darker) phases. However, there are more stray particles in the SAN phase. This is

Fig. 3. Transmission electron photomicrograph of a PS/SAN/MBS (41/41/18) blend prepared by simultaneous mixing of the components in an extruder.

probably due to a preference of the PMMA shell of MBS for SAN compared to PS. Note that PMMA has been found to form miscible blends with SAN of this composition and to be immiscible with PS.[10-15] Figure 3 shows the morphology of a sample having the same proportion of ingredients as that shown in Figure 2 prepared by melt blending in the extruder. Again, all components were introduced simultaneously. Extruder mixing produced a much finer and possibly more elongated PS-SAN phase structure than did the batch mixing. As a consequence, the dimensions of these domains are more similar to the diameter of the MBS particles and the total SAN-PS interfacial area is much larger than that in Figure 2. Due to these factors, Figure 3 is not as dramatic as Figure 2 but there is the same basic propensity for the MBS
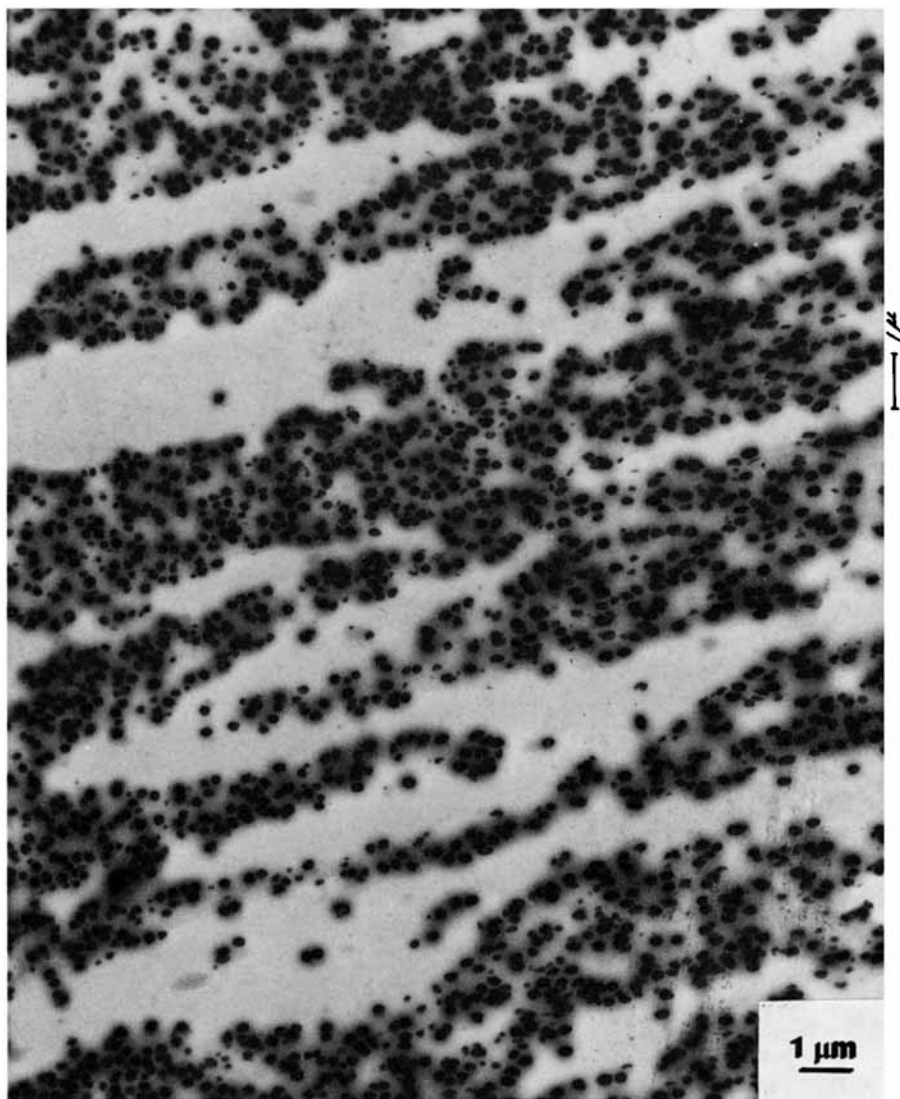
Fig. 4. Transmission electron photomicrograph of a PS/SAN/MBS (41/41/18) blend. It was prepared by first extrusion blending of PS and SAN, followed by the addition of MBS in the second extrusion step.

particles to locate at the PS-SAN interface. The amount of MBS is not sufficient to cover the entire interfacial area in Figure 3 as it more nearly does in Figure 2.

The affinity for the SAN phase by the MBS particles is illustrated by the morphology shown in Figure 4 for a sample prepared as follows. First equal amounts of PS and SAN were mixed by the extrusion process. This pelletized extrudate was then re-extruded along with MBS to produce the composition shown. Virtually all of the MBS particles were finally located in the SAN phase. An equivalent composition was arrived at in yet another way. Half of the MBS was premixed with PS and separately the other half of the MBS was premixed with SAN using the Brabender. These premixes were mixed in the
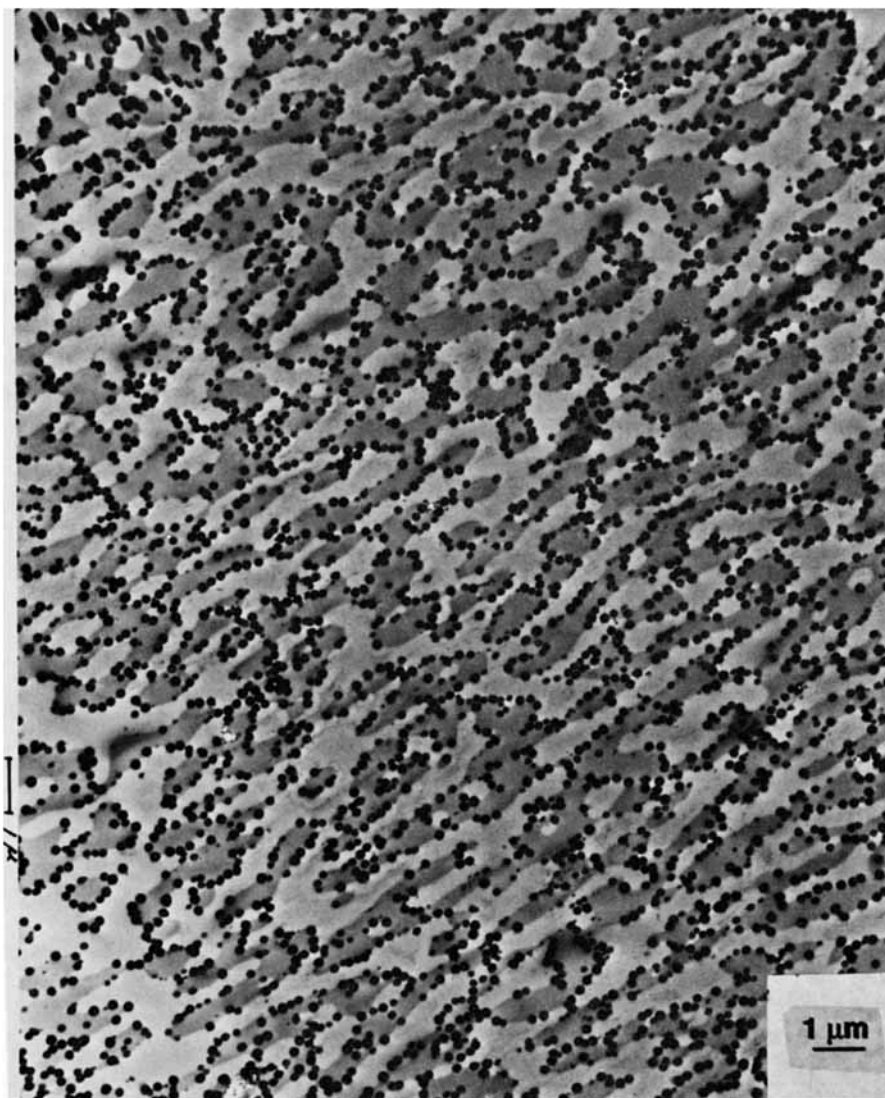

Fig. 5.   Transmission electron photomicrograph of a PS/SAN/MBS (41/41/18) blend. It was prepared in a Brabender by first preparing separate blends of PS/MBS and SAN/MBS followed by blending the two premixes together.

Brabender to produce the final material having the morphology shown in Figure 5. In this case, however, the MBS particles are located primarily at the PS-SAN interface as described earlier.

SUMMARY AND CONCLUSIONS

These experiments have not considered all of the possible combinations or variations for mixing that might be conceived. They have not covered a broad range of mixing patterns or stresses. The relative rheological properties of the two matrix components have not been varied. The particles used should, from a simple thermodynamic point of view, prefer to reside in the SAN phase rather than in the PS phase. Clearly, the location of these particles are not governed by thermodynamic factors alone, but kinetic issues or interfacial forces must also be considered for a practical mixing protocol like those used here. These results clearly demonstrate that such particles may preferentially locate at the interface of the matrix components which to our knowledge is a novel observation. Whether they do so or not seems to be most influenced by when this interface is formed. When SAN-PS interfaces already exist, the MBS particles seem to locate in the SAN phase as expected from the thermodynamic preference of the PMMA shell for SAN rather than PS (see Fig. 4). However, when SAN-PS interfaces are being created for the first time by the final mixing step, then the MBS particles seem to prefer locating at the interface regardless of whether the particles were added previously to each phase (Fig. 5) or simultaneously with these components (Fig. 2 and 3). Definitive explanations for such behavior cannot be rationally constructed or reasonably defended from such a meager base of experimental observations. We offer these observations more in the spirit of initiating discussion than ending it.

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