A novel approach to polymeric microdispersions

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Novel microdispersions of one polymer in another have been created by solvent devolatilization. Two incompatible polymers are first dissolved in a common solvent. The solvent is then rapidly evaporated, causing the residual polymeric solution to enter the two-phase region. Depending on the relative amounts of the two polymers and the rate of evaporation, polymer blends of widely differing morphologies are formed. Unlike previous methods employed for their production, polymer dispersions created by devolatilization have remarkably uniform particles, with the average size controllable in the range of 0.5 μm to 20 μm. If the solvent free volume fractions of the two polymers are more ore less equal, co-continuous networks are formed.

(Keywords: impact modification; microdispersions; solvent devolatilization; blends)

INTRODUCTION

It is frequently desired to create a microdispersion of one polymer in another incompatible polymer. Impact modification of brittle, glassy polymers such as polystyrene, poly(styrene-acryonitrile) and poly(phenylene oxide) are examples of major commercial importance. Impact polystyrene, for example, has an annual worldwide production of over 50 000 000 tons, and is a two-phase system consisting of small rubber particles dispersed in a polystyrene matrix[1-3]. In existing methods for the production of such dispersions, the particulation of the dispersed phase (rubber) is incorporated in the polymerization step[4,5] (conversion of styrene to polystyrene). It has proven difficult if not impossible to control either the average particle size or the particle size distribution over an adequately broad range. This is because the particulation is inextricably linked to the course of the polymerization. In particular, average particle sizes less than 1 μm have not been achieved in a bulk process.

The present study describes a new method for creating these polymer blends. This method not only produces particles which are uniform in size, but also allows independent control over the particle size. The particle sizes range between 0.5 μm and 20 μm.

MECHANISM OF PARTICULATION

Two incompatible polymers are dissolved in a common solvent so as to form a homogeneous solution. The solvent is then rapidly evaporated causing the residual polymeric solution to enter the two-phase region. This process is best illustrated on a ternary phase diagram (*Figure 1*). The system under consideration is a mixture of polystyrene, polybutadiene and *o*-xylene. This phase behaviour is broadly representative of many polymer systems[6]. The phase diagram is remarkably insensitive to temperature. Thus temperature changes cannot be used to initiate phase separation, as is common practice with low molecular weight species. However, phase separation will occur when the solvent is removed by evaporation. Spinodal decomposition is believed to be the primary mechanism of phase transformation[7].

If one of the polymers (say polymer A) is present in excess of the other (polymer B), the net result of the phase transformation is a dispersion of B in a matrix of A. The solvent is distributed in both phases. The droplets thus formed collide with each other and grow by agglomeration. As the depletion of the solvent continues, the viscosity of the matrix increases. A point is reached when viscous forces prevent further agglomeration. This seems to occur when the solvent concentration is reduced to about 60% and the viscosity of the matrix is 10~100 Pa s. No further growth of particles take place as

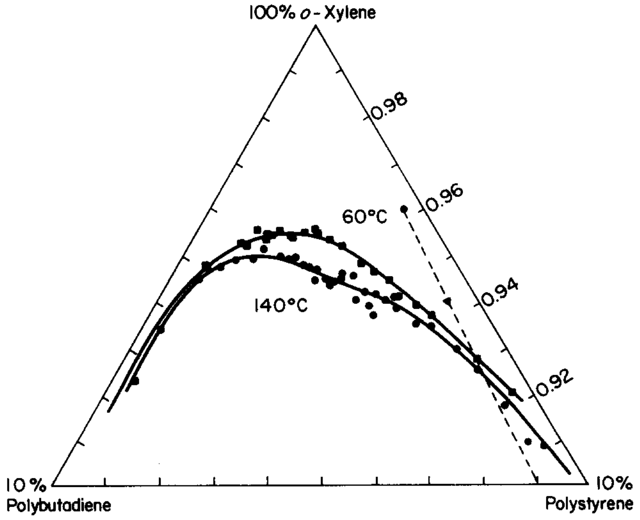

Figure 1 Liquid phase diagram for the ternary system (*o*-xylene, polystyrene, polybutadiene) at 60°C and 140°C. The solvent devolatilization process is represented by the dotted line. Note that only the solvent-rich portion with less than 10% total polymer is illustrated

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solvent removal continues, until we have essentially a two-component dispersion.

Particle size control

The final particle size is dependent on the rate of evaporation of the solvent. As the solvent is removed, the residual polymer solution moves from the stable region through the metastable region characterized by nucleation and growth into the unstable region characterized by spinodal decomposition. As has been recognized[8], nucleation and growth is a slow process. Results of solvent casting experiments conducted by Inoue *et al.*[8] suggest that the time spent by the solution in the metastable region is not enough for substantial phase separation and that spinodal decomposition is responsible for the ultimate phase transformation. As the depletion of the solvent proceeds, the wavelengths of the growing concentration fluctuations decrease. However, fluctuations of larger wavelengths take a longer time to grow. Hence, the lower the evaporation rate, the larger the average wavelength of the growing fluctuations. Subsequent growth of the droplets by agglomeration is also enhanced by slow evaporation. As a result, slow evaporation yields larger particles, while rapid evaporation leads to smaller particles. Thus, by controlling the rate of evaporation, it is possible to control the particle size of the dispersion.

EXPERIMENTAL

Two different experimental techniques were employed to effect the removal of the solvent.

(1) Rapid evaporation of the solvent was achieved by flash devolatilization. Flash devolatilization is a continuous process wherein the polymer solution is heated under pressure and throttled across a valve into a flash chamber which is operated under vacuum (see *Figure 2*). The polymer solution must be heated under pressure to prevent the solvent from boiling prior to entering the flash chamber. When the hot solution enters the flash chamber, the vapour pressure of the solvent is much greater than the pressure inside the chamber. This causes spontaneous, homogeneous boiling of the solvent and leaves behind the two-phase polymer dispersion. The evaporation rate, which determines the particle size of the dispersion, can be controlled by varying the temperature prior to the flash or the pressure inside the flash chamber.

(2) Slow evaporation was achieved by placing a drop of polymer solution on a microscope slide and evaporating the solvent at a more or less constant temperature under atmospheric pressure. The rate of evaporation was controlled by varying the temperature.

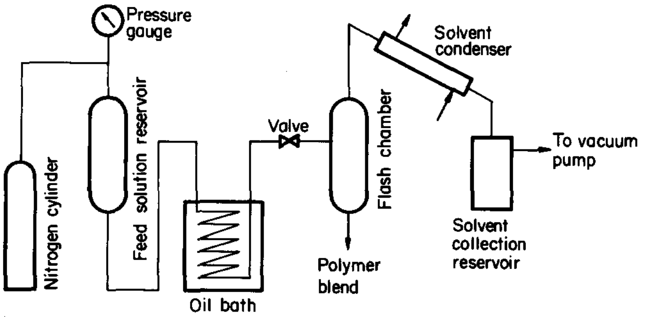

Figure 2 Schematic of the flash devolatilization process. Nitrogen pressure is used to force the feed solution into the heated oil bath. The hot polymer solution is then throttled across the valve into the flash chamber

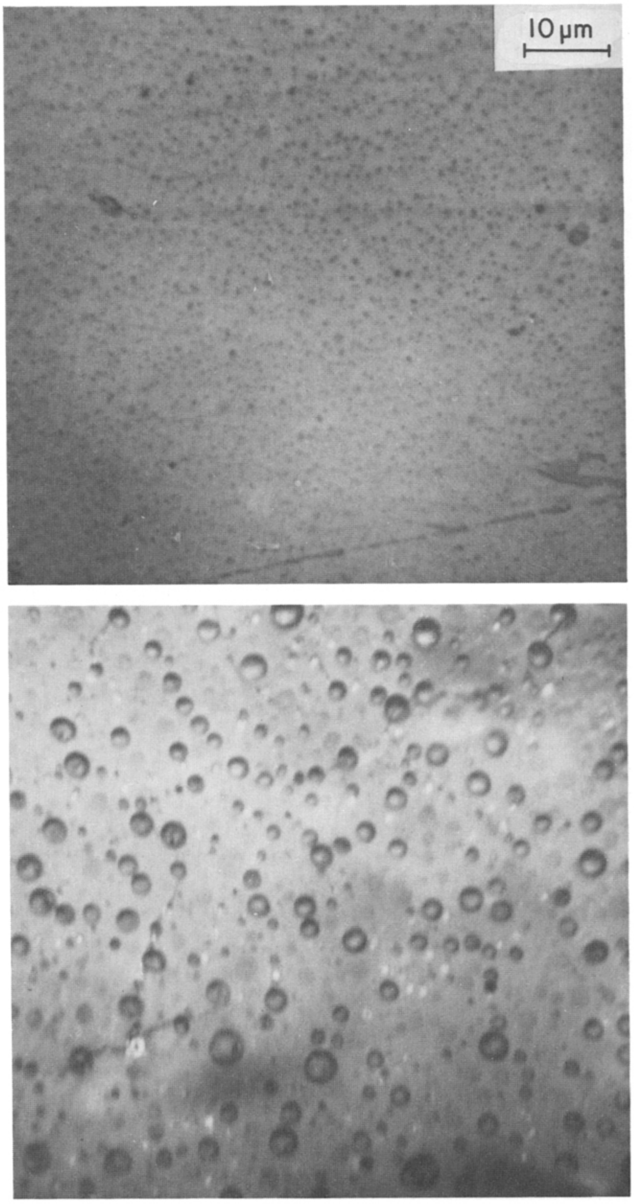

Figure 3 Effect of vacuum chamber pressure on the particle size in polybutadiene/polystyrene microdispersions formed by flash devolatilization. A 5% polymer solution containing 10% polybutadiene on a solvent-free basis was flash devolatilized to a 45% solution. (top) Using a vacuum chamber pressure of 200 Torr. (bottom) Using a vacuum chamber pressure of 300 Torr. The pre-flash temperature for both runs was 245°C. Both photographs are at the same scale

RESULTS

The majority of the results reported here are for the system polystyrene (major component)/polybutadiene (minor component)/*o*-xylene. The starting solution contained 4% total polymer and 96% common solvent.

Microdispersions formed by flash devolatilization at two different pressures are shown in *Figure 3*. Both the dispersions contain 10% polybutadiene and 90% polystyrene. It is apparent that control over the average particle size can be achieved by varying the flash chamber pressure.

The effect of evaporation rate on particle size, when the solvent is evaporated from a glass slide is shown in *Figure 4*. As expected, higher evaporation rates yielded smaller particles.

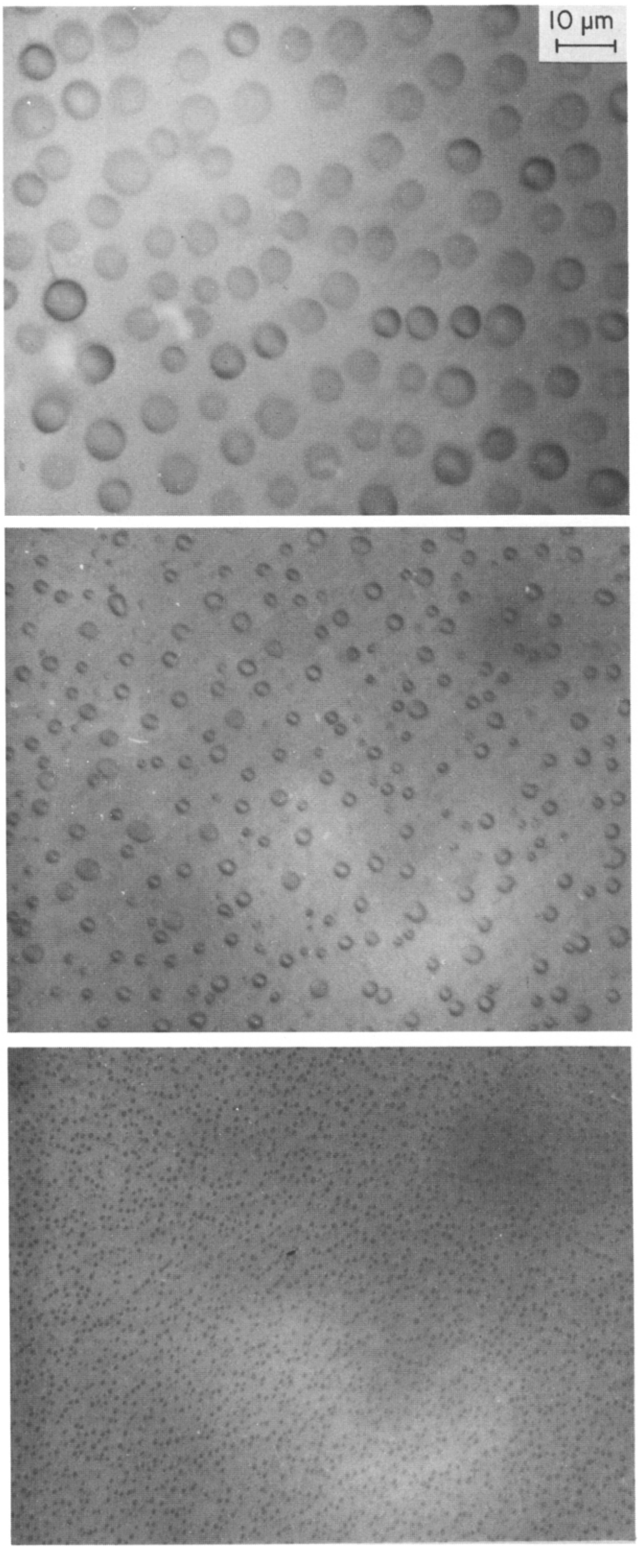

Figure 4 Effect of solvent evaporation rate on the particle size in polybutadiene/polystyrene microdispersion. Samples were created by slow evaporation of the solvent on a microscope slide, at normal pressure and temperature of (top) 25°C, (middle) 65°C and (bottom) 100°C. The solvent free polybutadiene concentration in each photograph was 10%. All photographs are at the same scale

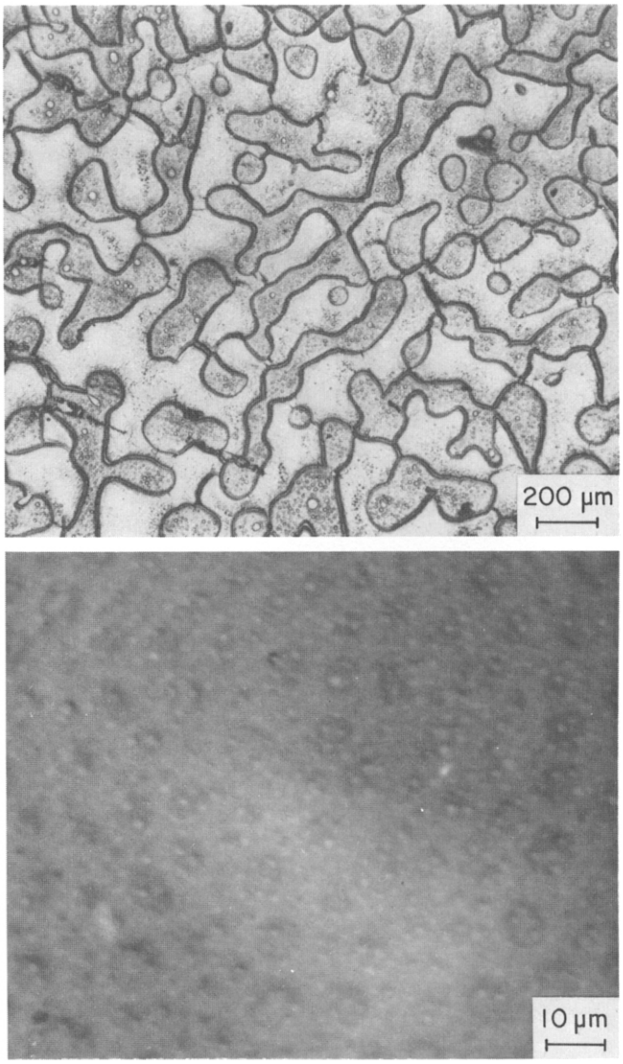

Figure 5 Resulting morphologies when the solvent free concentration of polybutadiene and polystyrene are more or less equal. (top) Slow solvent evaporation of a 35% polybutadiene solution results in a highly interconnected structure. (bottom) Solvent flash devolatilization of a 50% polybutadiene solution yields three phases. The white particles are polystyrene. Black particles are polybutadiene. The grey continuous phase is believed to be a non-equilibrium mixture

The effect of increasing the amount of polybutadiene to 30% of the total polymer concentration is shown in *Figure 5*. When the evaporation is carried out on a microscope slide, the resulting polymer blend exhibits a high degree of interconnectivity (*Figure 5a*). However, if the same solution is flash devolatilized, it appears possible to precipitate a third non-equilibrium phase (*Figure 5b*). This would occur if the polymer chains were 'frozen' before phase separation could be completed.

CONCLUSION

This study has shown that solvent devolatilization can be used to create novel polymer dispersions. This method, unlike existing methods, allows easy control over the particle size and can generate particles less than 1 μm in diameter. Another major advantage of the flash devolatilization process is that it is readily scalable. Commercial application of this technology would require an unusually large amount of solvent to be removed, but

Table 1 Example systems for new microdispersion technique

Matrix polymer	Dispersed polymer	Solvent
EPDM rubber	Polybutadiene	Tetrahydrofuran
High M. wt. alkylated phenolic resin	Polybutadiene	Tetrahydrofuran
Phenolic resin	Polystyrene	*o*-Xylene
Phenolic resin	Polysulphone	1,2-Dichlorobenzene
Polybutadiene	EPDM rubber	Tetrahydrofuran
Polybutadiene	Phenolic resin	*o*-Xylene
Polybutadiene	Polystyrene	*o*-Xylene
Polybutadiene	Polysulphone	1,2-Dichlorobenzene
Poly(methyl methacrylate)	Polybutadiene	Tetrahydrofuran
Poly(methyl methacrylate)	Polystyrene	Tetrahydrofuran
Poly(phenylene oxide)	Polybutadiene	1,2-Dichlorobenzene
Poly(phenylene oxide)/ polystyrene (50/50 compatible blend)	Polybutadiene	1,2-Dichlorobenzene
Poly(phenylene oxide)/ polystyrene (50/50 compatible blend)	EPDM rubber	1,2-Dichlorobenzene
Polysulphone	Phenolic resin	1,2-Dichlorobenzene
Polystyrene	Phenolic resin	*o*-Xylene
Polystyrene	Polycarbonate	Chloroform
Polystyrene	Poly(methyl methacrylate)	Tetrahydrofuran
Polystyrene	Polybutadiene	*o*-Xylene or styrene or tetrahydrofuran or toluene
Polystyrene	Low density polyethylene	*o*-Xylene
Styrene–acrylonitrile copolymer	EPDM rubber	1,2-Dichlorobenzene

the energy cost needed for evaporation is moderate, about \$0.02/kg for a typical solvent.

The phase separation technique described here has broad applicability. It is applicable to almost any pair of incompatible polymers, the major requirement being the existence of a mutual solvent which introduces a single phase region of at least 1% total polymer concentration. *Table 1* illustrates some systems to which the method has been successfully applied. Microdispersions with a dispersed phase particle size less than 10 μm have been created in all of these systems.

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