Concentrated emulsions pathways to polymer blending

E. Ruckenstein* and J. S. Park

Department of Chemical Engineering, State University of New York at Buffalo, Buffalo, NY 14260, USA

A new method of preparation of polymer composites involving the concentrated emulsion polymerization is described. In this kind of emulsion, the volume fraction of the dispersed phase is very large (as large as 0.99), while the volume fraction of the continuous phase is very small. In the present case, a monomer containing an appropriate initiator constitutes the dispersed phase and a dilute solution of surfactant in water constitutes the continuous phase. In a first step, two such concentrated emulsions containing different monomers were prepared and each of them was subjected to heating at 40°C for partial polymerization. Subsequently, the two partially polymerized systems were mechanically mixed, and the mixture was subjected to additional polymerization, drying, and sintering by heating at various temperatures for various time intervals. Partially polymerized concentrated emulsions of polystyrene, poly(buthyl methacrylate), poly(buthyl acrylate), and cross linked polystyrene, whose conversions were less than 5%, were employed. Conversions higher than 5% led to large increases in the viscosity of the concentrated emulsions, making their mixing difficult. N.m.r. spectroscopy was used to obtain information about the extent of copolymerization between the two monomers. Electron microscopy examination of the surfaces obtained by the fracture of the composites revealed that the latex particles aggregated with relatively slight changes in size and shape.

(Keywords: emulsion pathways; polymer composites; polymerization)

INTRODUCTION

Multiphase polymer blends of two or more structurally dissimilar polymers often exhibit a synergistic behaviour due to their different chemical structure and to the existence of various phase domains[1-3]. Because of their superior mechanical properties, such as high impact strength, the combination of dissimilar polymers by chemical or physical methods has been frequently exploited. The chemical methods include the copolymerization[4,5], the interpenetration of two networks[6], and the concentrated emulsion[7] and colloidal[8] pathways, while the physical method[9] involves mechanical blending, without covalent bonding, between the different species. The preparation method affects the morphology of the multiphase polymer composite and plays an important role in its physical properties. Of course, the properties of the polymer composites are also dependent on the properties of the component polymers.

In this paper, a new approach to composites, involving partially polymerized concentrated emulsions and their subsequent blending, is described. Partially polymerized concentrated emulsions of polystyrene (PS), poly(buthyl methacrylate) (PBMA), poly(buthyl acrylate) (PBA), and cross linked polystyrene (PS) were prepared by the concentrated emulsion polymerization method[7,10]. In concentrated emulsions, which have the appearance of gels, the volume fraction of the dispersed phase (in the present case a monomer containing an appropriate initiator) can be as high as 0.99 and the continuous phase (in the present case water containing surfactant) is in the form of a network of thin liquid films that

separate polyhedral cells of the dispersed phase. In a first step, the concentrated emulsion is partially polymerized by heating at 40°C until a conversion of about 5% is achieved. The length of this heating time depends upon the nature of the monomer. A greater conversion should be avoided because it increases the viscosity of the system, making the next step, the blending, very difficult. A composite can be prepared by blending two or more different partially polymerized concentrated emulsions and then subjecting the mixture to additional polymerization, followed by drying and sintering. The additional polymerization involves some copolymerization, which might occur either because of the coalescence of the latex particles, and/or because of copolymerization near the surfaces of contact between the latex particles. Information about copolymerization was obtained by n.m.r. spectroscopy. The microstructure of the polymer composites was investigated by scanning electron microscopy. The mixing of the gels without their preliminary partial polymerization, followed by polymerization, led to the formation of almost only copolymer and not polymer composites.

EXPERIMENTAL

Materials and preparation

Concentrated emulsions of styrene (Aldrich), buthyl methacrylate (Aldrich), and buthyl acrylate (Aldrich) were prepared at room temperature by dropwise addition of vacuum distilled monomers that contained recrystallized azobisisobutyronitrile (AIBN, Alfa) to a stirred distilled and deionized water containing sodium dodecyl sulphate (SDS, Aldrich). For the preparation of cross

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*To whom correspondence should be addressed

linked PS latexes, a mixture of distilled divinyl benzene (Polysciences) and styrene was employed. A concentrated emulsion mildly packed by centrifugation into a 15 ml capacity tube was immersed into a 40°C water bath for partial polymerization, in the presence of air. Two different partially polymerized gels were mixed by magnetic stirring, in the presence of air, at room temperature. The mixture of gels thus obtained was further heated at 40°C for 24 h for completing the polymerization. Finally, the polymer composite thus obtained was slowly dried at 80°C for 24 h and then sintered at 120°C for 6 h in a temperature controlled oven.

N.m.r. measurements

The solutions for n.m.r. measurements were prepared by dissolving 0.15 g of purified and well dried polymer in 3 ml chloroform-d (CDCl$_3$, Aldrich). The polymer solutions were introduced into pyrex n.m.r. tubes. A Varian Gemini-300, 300 MHz proton FTn.m.r. instrument was employed.

Molecular weight measurements

Gel permeation chromatography (g.p.c., Waters) was used to determine the molecular weight of the polymer with methylene chloride (Aldrich) as the mobile phase. Very dilute solutions (0.2 g l^{-1}) of polymer in chloroform (Aldrich) were prepared and injected in the g.p.c. The calibration curve of the g.p.c. was obtained by using polystyrene standards (Polymer Laboratories) with molecular weights in the range of 10^4–12×10^6.

Electron microscopy investigation

Polymer latexes, obtained by dispersing small amounts of partially polymerized gels in water, were examined with a SEM (Amray 100A). The specimens were prepared by placing drops of highly diluted latex solutions on clean cover glasses. After drying they were coated with gold. Surfaces obtained by fracturing polymer composites of cross linked PS and PBMA were contacted for 12 h with acetone (Aldrich), which is a good solvent for PBMA. Both the fractured and solvent treated surfaces were coated with gold before examination.

RESULTS AND DISCUSSION

Figure 1, in which the rate of the concentrated emulsion polymerization of PS, PBMA, and PBA is compared with that of the bulk polymerization, shows that the former rate of polymerization is higher than the latter. The molecular weights of the obtained polymers, listed in *Table 1*, are greater for the concentrated emulsion polymerization method. Both the higher molecular weight and the higher reaction rate are probably due to a gel like effect induced by the higher rigidity of the monomer in the emulsion cells[10]. The concentrated emulsion becomes more viscous with increasing conversion and transforms into a solid at high conversion. A too high viscosity produces difficulties in the uniform mixing of two different partially polymerized concentrated emulsions.

Two different partially polymerized concentrated emulsions were blended under high shear. The partially polymerized latex particles rearrange and aggregate during the blending process. During the additional
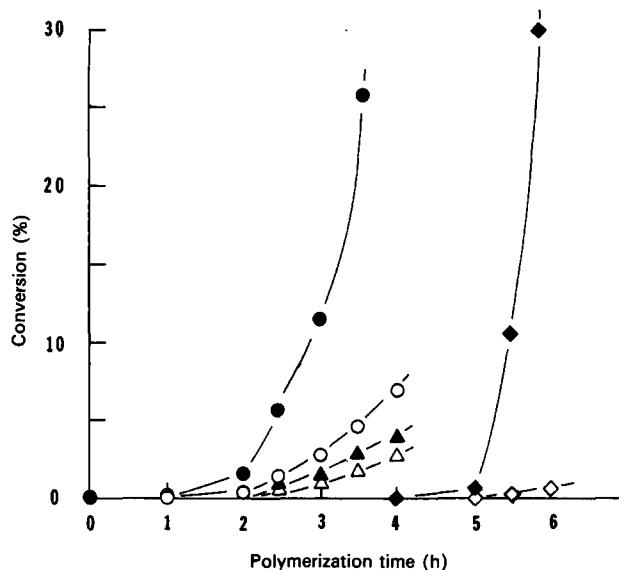

Figure 1 Polymer conversion at 40°C against polymerization time. ●, Styrene; ▲, buthyl methacrylate; and ◆, buthylacrylate in concentrated emulsion polymerization (monomer 50 ml, AIBN 0.30 mol l^{-1} monomer, SDS 0.35 g, water 4 ml). ○, Styrene; △, buthyl methacrylate; and ◇, buthylacrylate in bulk polymerization (monomer 40 ml, AIBN 0.30 mol l^{-1} monomer)

Table 1 Molecular weights obtained by concentrated emulsion polymerization (monomer 50 ml, AIBN 0.30 mol l^{-1} monomer, SDS 0.35 g, water 4 ml) and by bulk polymerization (monomer 50 ml, AIBN 0.30 mol l^{-1}) at 40°C for 8 h of polymerization

	Molecular weight	
	bulk	concentrated emulsion
Polystyrene	6.7×10^5	4.2×10^6
Poly(buthyl methacrylate)	2.1×10^4	6.1×10^4
Poly(buthyl acrylate)	3.2×10^4	8.5×10^4

heating at 40°C for 24 h of the mixture of the two partially polymerized gels, polymerization inside the latex particles, copolymerization inside the coalesced particles, and/or copolymerization near the surfaces of contact between particles take place. The extent of copolymerization in the polymer composite was investigated by employing high resolution n.m.r. spectroscopy. *Figure 2* presents the proton n.m.r. spectra of the polymers. *Figure 2a* and *b* are for the PS and PBMA, respectively, while *Figure 2c* is for a polymer blend of equal weights of PS and PBMA prepared by solution blending. The resonance peaks between 2.8 and 3.8τ in *Figure 2a* are due to the phenyl protons of the styrene units. The proton n.m.r. spectrum of the copolymer of equal weights of styrene and buthyl methacrylate, is given in *Figure 2d*, where the resonance peaks between 6.4 and 7.8τ are due to the butoxyl protons. Similar complexities (several peaks) in the methoxyl region of the spectra of the copolymers styrene-methyl methacrylate[11] and styrene-methylacrylate have been reported[12].

Figure 3 presents the proton n.m.r. spectra of the polymer composites prepared by blending equal weights of two different partially polymerized concentrated emulsions. Depending upon the extent of conversion of the latex particles in the first polymerization step, changes in the resonance peaks between 6.4 and 7.8τ occur. This indicates that the extent of copolymerization which

first step. As the conversion of the latex particles increases over 5%, the blending of the partially polymerized concentrated emulsions by mixing becomes difficult, due to the increase of their viscosities.

Figure 4 presents some scanning electron micrographs of the latex particles prepared by the concentrated emulsion polymerization, and shows that the concentrated emulsion polymerization leads to spherical latexes whose diameters range from submicrons to microns.

In order to examine the microstructure of the two phase polymer composites, the sintered polymer composites were fractured. *Figure 5* presents scanning electron micrographs of the surfaces thus obtained. It shows that the polymer composites contain latex particles whose sizes are not drastically changed when compared to those of the latexes in *Figure 4*. In the polymer composite containing cross-linked PS and PBMA, the polymer latexes were found to aggregate without change.

The toughness of a composite is expected to be higher when one of the components has a high and the other a low glass transition temperature. The glass transition temperatures of the polymers employed in the present experiments: PS, PBMA, and PBA are 100, 20, and $-55°C$ respectively[13]. The combination of PS and PBA is therefore expected to be tough, while the combination

Figure 2 Proton n.m.r. spectra of curve a, polystyrene; curve b, poly(buthyl methacrylate), curve c, polymer blend of equal weight of polystyrene and poly(buthyl methacrylate) prepared by solution blending, and curve d, copolymer of equal weights of styrene and buthyl methacrylate

Table 2 The ratio of the n.m.r. peaks area of buthoxyl protons resonance to phenyl protons resonance

	Peaks area between 6.4–7.8τ/ peaks area between 2.8–3.8τ
Copolymer, *Figure 2d*	0.41
Polymer composite, *Figure 3a*	0.38
Polymer composite, *Figure 3b*	0.32
Polymer composite, *Figure 3c*	0.27
Polymer composite, *Figure 3d*	0.10
Polymer blend prepared by solution blending, *Figure 2c*	0.0

occurs depends, as expected, upon the extent of polymerization in the first step. To evaluate the extent of copolymerization of the mixed partially polymerized concentrated emulsions, the ratio of the areas of the peaks between 6.4 and 7.8τ of the butoxyl protons to those between 2.8 and 3.8τ of the phenyl protons of the styrene units was calculated and the results are listed in *Table 2*. As expected, the amount of copolymer in the polymer composites decreases with increasing conversion in the
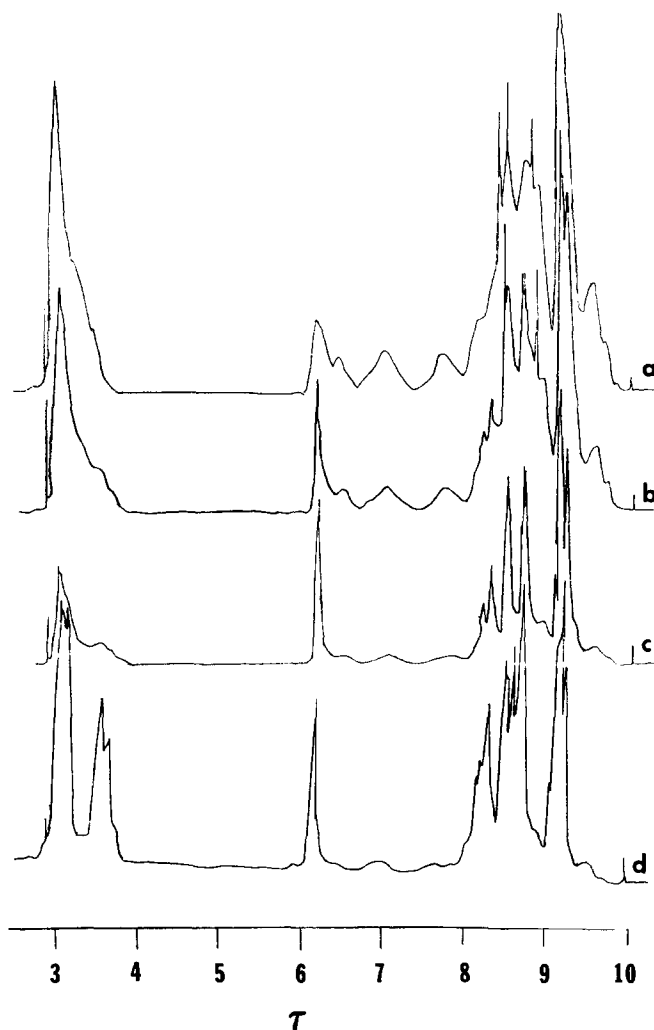

Figure 3 Proton n.m.r. spectra of polymer composite of polystyrene and poly(buthyl methacrylate), prepared from equal weights mixtures of partially polymerized concentrated emulsions. Curve a, 0%; curve b, 1%; curve c, 3.5%; curve d, 5% conversions of the monomers
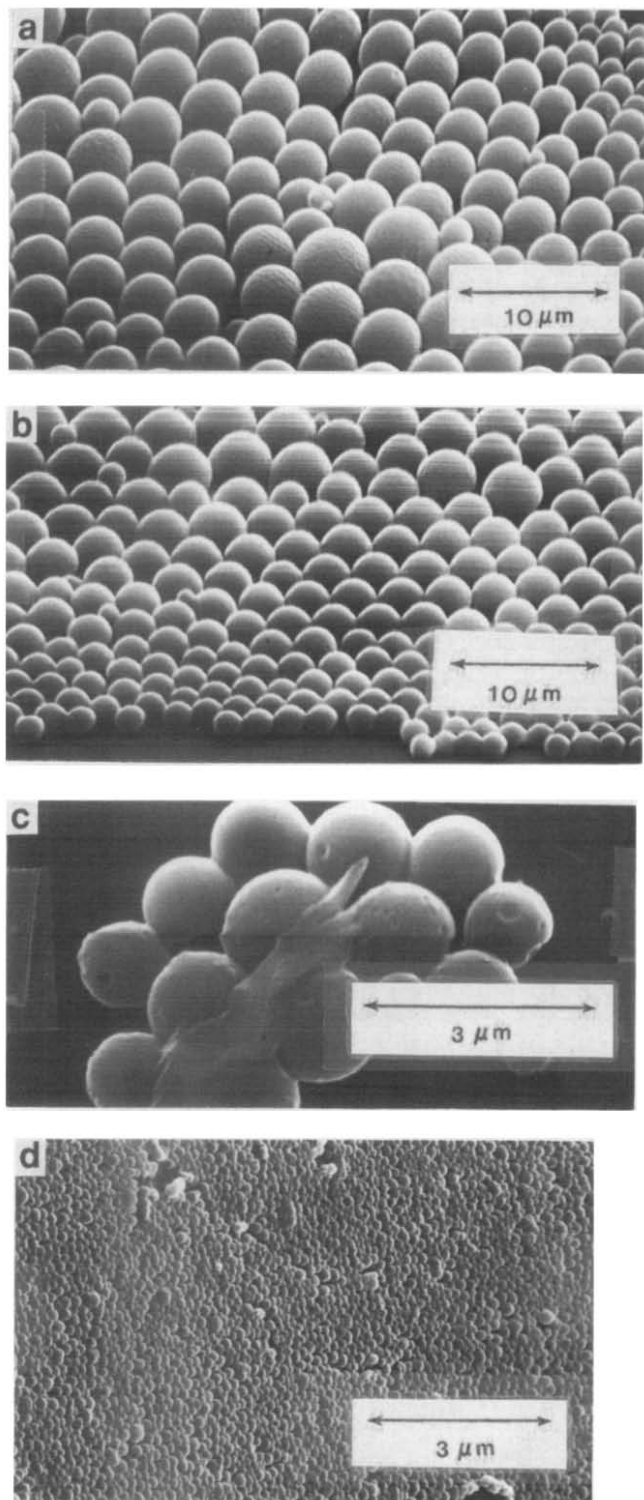
Figure 4 Electron micrographs of polymer latexes (monomer 50 ml, AIBN 0.30 mol l^{-1} monomer, SDS 0.35 g, water 4 ml, at 40°C). (a) Polystyrene, (b) poly(buthyl methacrylate), (c) poly(buthyl acrylate), (d) cross-linked polystyrene (40 ml of styrene and 10 ml of divinyl benzene, total 50 ml of monomer)

between PS and PBMA less tough. This was indeed observed. In addition, also as expected, the combination between cross-linked polystyrene and PBMA is less tough. Both the morphology of the multiphase polymer composite and the physical properties of the component polymers play important roles in determining its mechanical strength. *Figure 6* presents a solvent treated surface obtained by fracturing a composite formed of cross linked PS and PBMA. The solvent dissolved the PBMA; the

remaining cross-linked PS particles are seen to be in contact and well interconnected.

CONCLUSION

Two different partially polymerized latex particles prepared by the concentrated emulsion method can be blended by the mixing of the corresponding concentrated emulsions, if their conversion is lower than about 5%. For larger conversions, the viscosities of the concentrated emulsions become high and the mixing difficult.
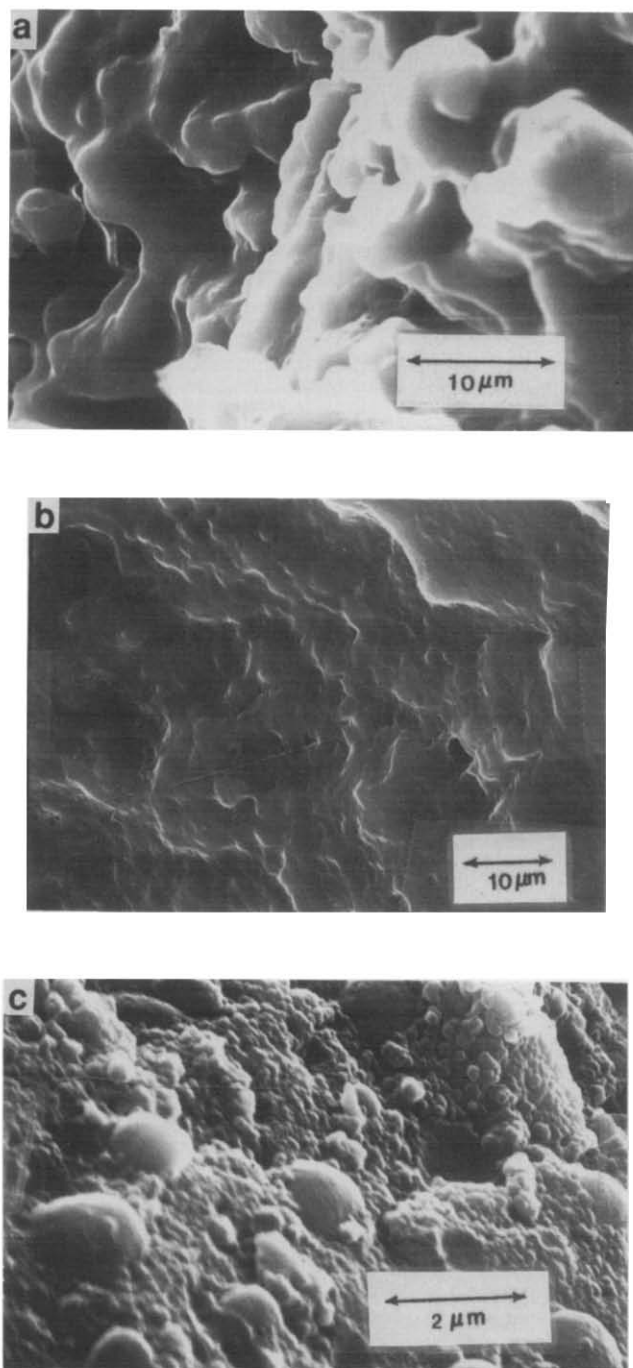

Figure 5 Electron micrographs of surfaces obtained by fracturing the polymer composite, which was prepared by blending two different 5% conversion concentrated emulsions. (a) polymer composite of polystyrene (80 wt%) and poly(buthyl acrylate) (20 wt%); (b) polymer composite of polystyrene (50 wt%) and poly(buthyl methacrylate) (50 wt%); (c) polymer composite of cross linked polystyrene (50 wt%) and poly(buthyl methacrylate) (50 wt%)
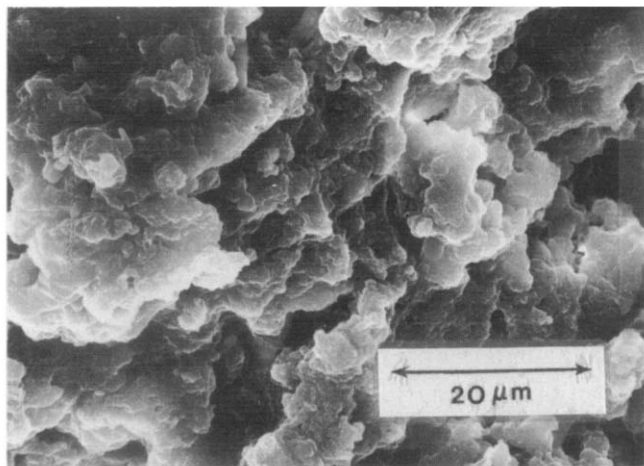
Figure 6 Electron micrograph of a solvent treated surface obtained by fracturing the polymer composite of cross linked polystyrene and poly(buthyl methacrylate) of *Figure 5c*

Aggregation of the two kinds of latex particles takes place after heating the mixture at 40°C for 24 h and further at 80°C for 24 h and at 120°C for 6 h. During these additional heating periods, homopolymerization inside the particles and copolymerization inside the coalesced particles and at the contact between particles

take place. A high resolution n.m.r. spectroscopy was employed to determine the extent of copolymerization in the polymer composites. Electron microscopy examination reveals that the microstructure of the two phase polymer composite is determined by the nature of the latex particles employed and that the aggregation during the blending and sintering processes occurs with slight changes in size and shape.

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