Novel polymeric composites from microemulsions

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(Received 16 July 1993; revised 20 February 1994)

A novel approach to prepare composites of different porosity and morphology is demonstrated. Instead of blending two polymers, hydrophilic and hydrophobic monomers are solubilized in microemulsions and then polymerized to obtain composites with the desired properties. This technique is exemplified by the polymerization of microemulsions containing styrene and acrylamide as the hydrophobic and hydrophilic monomer, respectively. Different types of surfactants were used in formulating the microemulsions: anionic sodium dodecyl sulfate (SDS), cationic cetyltriethylammonium bromide (CTAB) and zwitterionic octadecyl dimethyl betaine (C18DMB). The clear or bluish microemulsions were stable at room temperature and at the polymerization temperature of 55°C. No gross phase separation was observed during polymerization. The morphology and thermal behaviour of the composites resulting from microemulsion polymerization are strongly influenced by the surfactant, which is trapped inside the solid. C18DMB produced the largest pore size and most rigid composite. Use of SDS or CTAB led to a random copolymer, poly(styrene-*co*-acrylamide), with a single glass transition temperature (T_g) of 151 ± 2°C, which is intermediate between the T_g values of the two homopolymers. The composite obtained using C18DMB was more heterogeneous, with polystyrene-rich and polyacrylamide-rich domains in addition to the copolymer. The T_g values of the polystyrene-rich (89 ± 1°C) and polyacrylamide-rich (171 ± 1°C) domains are lower than those of the corresponding homopolymers (99 ± 1°C and 175 ± 1°C, respectively). Apparently, C18DMB acts as a plasticizer in the composite.

(Keywords: composites; microemulsions; surfactants)

INTRODUCTION

Polymer blends and composites are obtained by combining two or more polymers in order to achieve improvements in thermal stability, mechanical properties or chemical resistance[1]. A wide range of random or structural morphologies can be visualized. However, high interfacial tension and high viscosity cause difficulties in achieving the desired degree of dispersion or control of microstructure. The lack of stability leads to gross separation during subsequent processing of the blends. The interfacial behaviour between the phases plays a key role in determining the blend properties. Bulk or solution copolymerization of two monomers at various ratios may result in a heterogeneous mixture of the two homopolymers along with the copolymer. The blend composition depends on the concentrations of the monomers, their reactivity ratios and the polymerization conditions.

A microemulsion may be defined as a thermodynamically stable isotropic solution of two immiscible fluids, generally oil and water, containing one or more surface-active species[1,2]. Microemulsions can be lower phase (water-continuous or oil-in-water type), upper phase (oil-continuous or water-in-oil type) or middle phase. The middle-phase microemulsions can be bicontinuous in microstructure[3]. The domain size in microemulsions is in the range 100–1000 Å (1 Å = 0.1 nm). Microemulsions are usually prepared with water, surfactant (~10%), cosurfactant (e.g. a short-chain alcohol) and a hydrocarbon. The surfactant molecules are mostly confined to the oil–water interface as an oriented film. The partitioning of cosurfactant into the oil–water interface increases the flexibility of the surfactant film[4]. Microemulsions have been extensively investigated for enhanced oil recovery[5]. Interactions between surfactant and polymer solutions are also important because of the use of polymer solutions for mobility control. Polymerization in microemulsions has gained considerable attention because microemulsions provide suitable media for reacting the monomer in either the dispersed or the continuous phase. Owing to chain transfer of the cosurfactant in microemulsion polymerization, however, the polymers obtained have lower molecular weights than those prepared by bulk or emulsion polymerization[6,7].

Microemulsion polymerization has been investigated primarily using either a hydrophobic monomer, e.g. styrene, or a hydrophilic monomer, e.g. acrylamide, to obtain nanoparticles. This topic has been recently reviewed by Candau[8]. Qutubuddin and coworkers[9,10] have used microemulsions to obtain porous solids with interesting properties and morphology. Hydrophilic–hydrophobic composites have been prepared by Ruckenstein and Park[11,12] using styrene and acrylamide

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0032-3861/94/21/4606-05

Table 1 Compositions and phase behaviour of microemulsions and glass transition temperatures of polymeric solids obtained from microemulsion polymerizations

	M-1	M-2	M-3
Composition (wt%)			
Surfactant	10.0(SDS)	10.0(CTAB)	10.0(C18DMB)
2-Pentanol	15.0	15.0	15.0
H_2O	22.0	22.0	22.0
Acrylamide	31.0	31.0	31.0
Styrene	22.0	22.0	22.0
Phase behaviour			
Before polymerization	Bluish	Bluish	Clear
After polymerization	Opaque	Opaque	White
T_g of dried polymer (°C)			
Before purification	152 ± 1	150 ± 1	$89 \pm 1, 149 \pm 1, 171 \pm 1$
After purification	152 ± 1	150 ± 1	–[a]

[a] T_g measurement was not available owing to incomplete dispersion in DMSO used for copolymer purification

monomers in concentrated emulsions. The emulsions, unstable above 50°C, were polymerized at 40°C and examined using a transmission electron microscope. The application of microemulsions as media to obtain new types of polymeric composites is demonstrated in this paper. Polymeric composites are obtained by formulating microemulsions which contain a hydrophobic monomer as the oil phase along with a hydrophilic monomer in the aqueous phase, and then polymerizing both monomers. The microemulsions used contain an alcohol as a cosurfactant. The term composite is preferred over copolymer or blend since the product obtained is a solid mass rather than a dispersion or powder. Also, the surfactant is trapped in the composite and may act as a compatibilizer and/or plasticizer.

EXPERIMENTAL

Materials

Inhibited styrene (99% pure; Aldrich) was purified by distillation at 28–30°C under reduced pressure to give a clear, colourless liquid. It was stored at 0°C until used. Acrylamide (AM; Fluka) was used without further purification. Potassium persulfate ($K_2S_2O_8$; Aldrich) and 2,2′-azobisisobutyronitrile (AIBN; Du Pont) initiators were recrystallized twice from methanol. Sodium dodecyl sulfate (SDS; $T_m = 203$–207°C; Aldrich) and cetyltrimethylammonium bromide (CTAB; $T_m > 230$°C; Sigma) were used without further purification as anionic and cationic surfactant, respectively. Octadecyl dimethyl betaine (C18DMB) was used as a zwitterionic surfactant[13]. Poly(ethylene glycol) dimethacrylate (PEG 400) and divinylbenzene (DVB) were obtained from Polysciences and used as crosslinking agents. 2-Pentanol, dimethyl sulfoxide (DMSO), toluene and other solvents were all reagent grade. Deionized water was employed in formulating the microemulsions.

Phase behaviour of microemulsions

Microemulsions were prepared in 16 ml test tubes with phenolic caps. The compositions of the microemulsions are given in *Table 1*. The hydrophilic monomer (acrylamide) and water-soluble surfactant (SDS, CTAB or C18DMB) were dissolved in H_2O, then 2-pentanol was added. The mixture was vortex mixed and sonicated for ca. 10 min to give a clear surfactant solution to which styrene was added with mixing. The phase behaviour of the microemulsions containing inhibited styrene was observed at room temperature and at 55°C in a water bath.

Microemulsion polymerization

Purified styrene was used in formulating microemulsions for polymerization. Small amounts of $K_2S_2O_8$ (0.25 wt% based on acrylamide) and AIBN (0.25 wt% based on styrene) were added to each microemulsion as initiators. The microemulsions were purged with nitrogen for 10 min, sealed in capped test tubes with Teflon tape and polymerized at 55°C in a water bath for 24 h without stirring. They were further polymerized at 80°C in an oven for another 48 h.

Characterization of composites prepared by microemulsion polymerization

The morphology of solid polymers prepared from microemulsions (samples M-1, M-2 and M-3; *Table 1*) was observed using a scanning electron microscope (JEOL JSM-35CF). The sample was broken into small pieces and then dried slowly overnight at 60°C and atmospheric pressure. A small sample was placed on a metal holder and sputter coated with carbon (3 nm in thickness) before being examined in the microscope.

A differential scanning calorimeter (Perkin–Elmer DSC-7) was used to determine the glass transition temperature (T_g) of each dried sample after polymerization. Temperature calibration was performed at a $10°\mathrm{C\,min^{-1}}$ heating rate with nitrogen purging using mercury (onset of $T_m = -38.9$°C) and indium (onset of $T_m = 156.6$°C) as standards. Samples were partially dried at 60°C under reduced pressure for 4 h to remove most of the water and alcohol, cooled to room temperature, ground to fine powders and further dried overnight under reduced pressure. A small sample (2–5 mg) of each dried, fine powder was hermetically sealed in an aluminium sample pan, heated at $10°\mathrm{C\,min^{-1}}$ from 30 to 200°C, cooled at $10°\mathrm{C\,min^{-1}}$ to 30°C and then heated to 200°C at the same rate. The T_g was determined at the midpoint of the change in heat capacity. The T_g values for the second scan are reported (*Table 1*).

Removal of surfactant

The translucent or opaque product (~1.0 g; polymer content ~53%) obtained via microemulsion polymerization was dried at 80°C under reduced pressure to remove water and 2-pentanol. A very slightly yellowish solid was obtained. To remove the surfactant, the dried solid was magnetically stirred overnight in 20 ml of DMSO. Samples M-1 and M-2 were completely dispersed in DMSO, resulting in bluish dispersions. However, sample M-3 could not be completely dispersed and hence was not purified. To reprecipitate the polymers from M-1 and M-2, the fine dispersion in DMSO was added dropwise to 500 ml of magnetically stirred methanol. The polymer precipitated while the surfactant (SDS or CTAB) remained dissolved in the DMSO–methanol mixture. The use of a larger amount of DMSO resulted in an almost clear solution but made polymer reprecipitation in methanol difficult. The precipitated polymer was filtered and then washed with fresh methanol. The polymer was redispersed in DMSO, reprecipitated and then dried at 60°C under reduced pressure for 4 h. The white solid was ground to a fine powder and redried at 80°C under reduced pressure overnight. A white powder (yield about 0.5 g, 96%) with highly electrostatic character was obtained after purification of samples M-1 and M-2.

RESULTS AND DISCUSSION

Phase behaviour and polymerization of microemulsions

The phase behaviour of the microemulsions was studied before and after polymerization. Before polymerization, sample M-1 was a two-phase system at room temperature with a very small amount of a clear organic phase (~3% by volume) on top of the microemulsion (~97% by volume). The excess phase almost disappeared at 55°C, indicating an increase in solubilization of styrene in the microemulsion. Samples M-2 and M-3 were single-phase microemulsions at both room temperature and 55°C. Drops of the microemulsions could be dispersed completely in water without shaking but remained immiscible in toluene. Hence, the microemulsions were not oil continuous.

No gross phase separation was observed for the three microemulsions during polymerization at 55°C. However, the samples became either opaque or white, indicating different domain sizes for the dispersed phase and, hence, heterogeneity at the microscopic level. It is likely that gelation occurs quickly even as a small fraction of the acrylamide monomer is polymerized to polyacrylamide (PAM). The resulting high viscosity prevents gross phase separation of styrene and 2-pentanol as an excess phase. The system becomes microscopically unstable because of a considerable change in solubility of the polymer relative to the monomer. Before polymerization, both acrylamide and styrene monomers are solubilized by the surfactant and 2-pentanol. During polymerization, the molecular weights of the polymers increase with time, reducing their compatibility with the surfactant and 2-pentanol. Because of increased incompatibility, the surfactant and 2-pentanol can no longer orient as a monolayer at the interface between aqueous and organic domains. Thus, both surfactant and 2-pentanol are displaced from the interface. The kinetics and degree of phase separation, the latter of which depends on the surfactant type, affect the bulk properties of the composite.

The microemulsions became unstable with the addition of a small amount (~5%) of a crosslinking agent (PEG 400 for acrylamide or DVB for styrene). Phase separation during polymerization resulted in a liquid phase (water and 2-pentanol) on the top and a polymer phase on the bottom. The heterogeneous polymers with crosslinking agents were not further characterized.

Morphology of polymer composites

The microstructure of the microemulsion changes during polymerization depending on the surfactant type. The morphology is expected to be porous owing to the large amount of unpolymerizable liquids (water plus 2-pentanol, totalling 38 wt% of the sample) which can be removed by drying. The evaporation of these components may cause the collapse of some pores originally present. Thus, the resulting morphology is sensitive to the sample-drying and preparation protocol used for the scanning electron microscopy (SEM) study.

SEM micrographs of composites prepared from microemulsions containing SDS, CTAB and C18DMB are shown in *Figures 1a, 1b* and *1c*, respectively. *Figure 1a* shows a collapsed microstructure of the polymer obtained using SDS. SEM micrographs at higher magnification reveal a film-like morphology for sample M-1. This is because water and 2-pentanol were evaporated from the continuous phase. In contrast, distinct pores in the range 1–10 μm are observed in the composite prepared using C18DMB, as shown in *Figure 1c*. It is likely that phase inversion occurred during polymerization to result in a polystyrene-rich continuous composite which is expected to be rigid. After the 2-pentanol and water were evaporated from the dispersed phase, the rigid structure still remained along with many spherical pores. C18DMB acts as an oil-soluble surfactant because it is less hydrophilic than SDS. During polymerization, phase inversion results in an oil-continuous or co-continuous composite from a water-continuous microemulsion. The large pore size in *Figure 1c* is consistent with the bulk appearance of M-3, which scatters more light than M-1 and M-2 solids. *Figure 1b* shows an intermediate morphology for the sample obtained from a CTAB microemulsion. It is obvious that the surfactant type (anionic, cationic or zwitterionic) strongly influences the morphology of the composite resulting from microemulsion polymerization.

Thermal behaviour

Glass transition temperatures of the dried polymers are listed in *Table 1*. The differential scanning calorimetry (d.s.c.) curves for samples M-1, M-2 and M-3, as well as for pure polystyrene (PS) and pure PAM, are shown in *Figure 2*. The T_g of PS is around 99°C on the second, third or fourth scan. A non-equilibrium value of T_g as high as 106°C may be obtained on the first scan owing to enthalpy relaxation[14] or poor contact between the sample and the aluminium pan. Different values have been reported for the T_g of PAM: 153°C[15], 165°C[16], 188°C[17], 194°C[18] and 204°C[18]. The variation in T_g may be ascribed to differences in the molecular weight, crosslinking density or amount of absorbed water. Since PAM is a hydrophilic polymer, it retains water strongly during ordinary drying and rapidly picks up moisture from the environment when dry[19]. Furthermore, gases (H_2, CO_2 and NH_3) are evolved on heating PAM at elevated temperatures, indicating cyclization or oxidation[20].

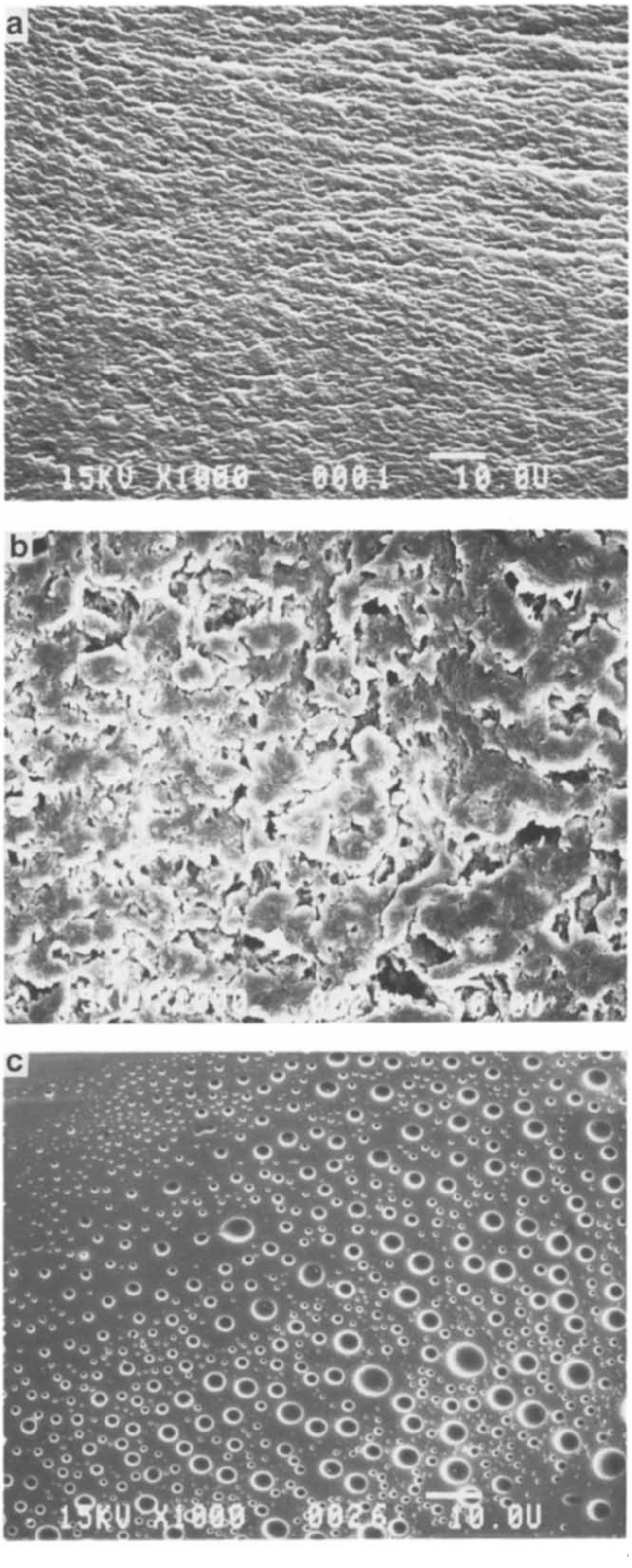

Figure 1 SEM micrographs (magnification × 1000) of dried polymers prepared from microemulsion polymerizations using (a) anionic SDS, (b) cationic CTAB and (c) zwitterionic C18DMB as surfactants

A single T_g was obtained for each of samples M-1 (152 ± 1°C) and M-2 (150 ± 1°C), indicating random copolymerization of styrene with acrylamide with relatively small amounts of PS-rich and PAM-rich domains, if any. Three glass transitions were observed for sample M-3 obtained using the zwitterionic surfactant C18DMB. As previously mentioned, solubility tests showed that samples M-1 and M-2 can be completely dispersed in DMSO. For sample M-3, the white precipitates in DMSO could be the PS-rich and PAM-rich copolymers which are not soluble. According to the d.s.c. curve, composite M-3 contains considerable fractions of PS-rich (hydrophobic) and PAM-rich (hydrophilic) domains. No organic solvent has been found to dissolve this heterogeneous copolymer completely at room temperature or 60°C. No extract was obtained using hot water or chloroform. After the dried M-1 and M-2 composites were further purified to remove the surfactant, the T_g values of the surfactant-free copolymers were not much different from those of the unpurified samples. With C18DMB as the surfactant, the T_g values of the PS-rich (89 ± 1°C), PAM-rich (171 ± 1°C) and poly(styrene-*co*-acrylamide) (149 ± 1°C) phases are lower than those of pure PS (99 ± 1°C), pure PAM (180 ± 1°C) and samples M-2 and M-3 (151 ± 2°C), respectively. With C18DMB, there is a considerable decrease in the T_g (89 ± 1°C) for the PS phase. This indicates that, unlike SDS and CTAB, C18DMB may act as a chain-transfer agent during polymerization or as a plasticizer in the composite.

CONCLUSIONS

Microemulsions were prepared containing a hydrophobic monomer (styrene) and a hydrophilic monomer (acrylamide) using SDS (anionic), CTAB (cationic) or C18DMB (zwitterionic) as the surfactant. The microemulsions are stable at both room temperature and 55°C. Polymerization at 55°C produced opaque, porous composites. The morphology and thermal behaviour of the composites strongly depend on the surfactant type. With an ionic

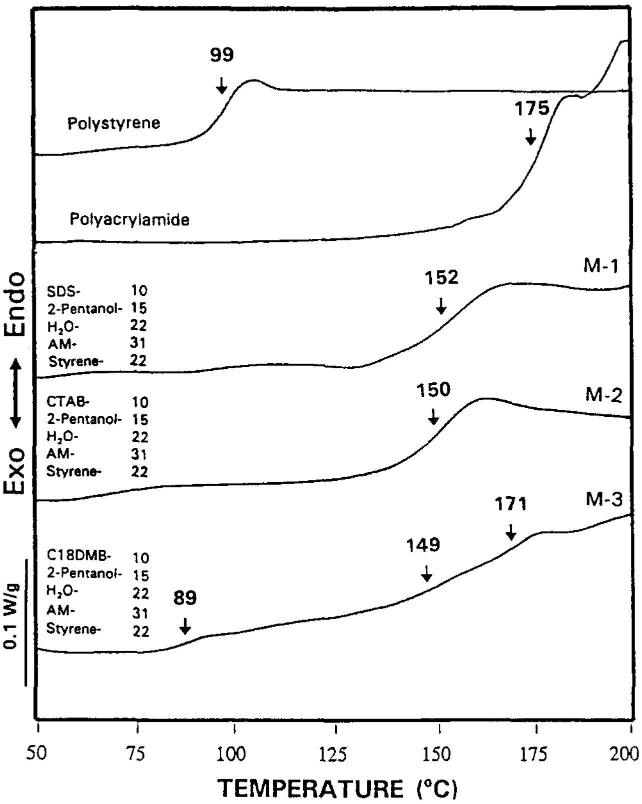

Figure 2 D.s.c. curves of dried polymers prepared from microemulsion polymerizations (curves for pure PS and pure PAM shown for comparison)

surfactant (SDS or CTAB), the composite has only one T_g (about 151±2°C) which is intermediate between the T_g values of the PS (99°C) and PAM (175°C) homopolymers. With a zwitterionic surfactant, three T_g values are observed corresponding to PS-rich, poly(styrene-*co*-acrylamide) and PAM-rich domains. The T_g values of the PS-rich and PAM-rich domains are lower than the T_g values of the corresponding homopolymers, indicating that C18DMB acts as a plasticizer in the composite.

ACKNOWLEDGEMENTS

The authors thank Edison Polymer Innovation Corporation (Ohio), NSF (CTS-8905919, PYIACBT-8552882) and Perkin–Elmer for their financial support of this work. Preliminary work by E. Haque is also acknowledged.

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