RAPID PAPER

Stable Surfactant-Free Toluene-Polyethylene-in-Water Emulsion Prepared by Ultrasonication at High Temperature

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Abstract: A toluene-polyethylene (PE) mixture, only partially miscible at room temperature (RT), was ultrasonically dispersed in hot water, followed by immediate cooling to give a highly stable surfactant-free oil-in-water (O/W) emulsion. This temperature effect was correlated with physical gelation of the bulk mixture. Prolonged stabilization was achieved only through dispersion at a temperature (T_d) above the gelation temperature (T_{gel}) of the toluene-low-density PE (LDPE) mixture and subsequent rapid cooling. These stabilized emulsions exhibited characteristics such as a small droplet size with a narrow size distribution, low ζ -potential, and round-shaped droplets, which were not observed for the emulsions prepared at $T_d < T_{gel}$ or those at $T_d > T_{gel}$ that had been subjected to slow cooling. From these results, physical gelation through crystallization and modification of the droplet surface by PE were concluded to be essential for the prolonged stability of a surfactant-free toluene emulsion.

Key words: hydrophobic polymer, oil, surfactant-free emulsion, gelation, rapid cooling

1 INTRODUCTION

An oil-in-water (O/W) emulsion is an unstable mixture in which immiscible oil is dispersed as droplets in an aqueous medium. Fine droplets with sizes below a micrometer can be prepared with rigorous disruption like mechanical or ultrasonic homogenization. Once prepared, droplets start to increase in size through a variety of processes such as flocculation, coalescence, and creaming, eventually resulting in phase separation¹⁾. To inhibit this increase in size, surfactants or surface-active macromolecules are added to emulsions to decrease the interfacial energy. However, contrary to this generalized scheme, relatively stable O/W emulsions have been prepared with hydrophobic oils by ultrasonication²⁻¹⁴⁾, even in the absence of surfactants. The stabilization mechanism of such surfactant-free emulsions (SFEs) is considerably different from those established for surfactant-stabilized emulsions. Namely, stabilization of SFEs has been achieved with (1) an increase in the hydro-

phobicity of the oil phase with the addition of other hydrophobic oils⁴⁾ or hydrophobic polymers¹⁴⁾, (2) an increase in viscosity with the addition of viscous hydrophobic polymers¹⁴⁾, and (3) an increase in monodispersity with ultrasonic irradiation at midsonic (~ 100 kHz) to megasonic (~ 1 MHz) frequencies⁸⁾. These demonstrations imply that SFEs are kinetically stabilized systems opposing to flocculation and coalescence.

A thermal stabilization technique for O/W emulsion has also been studied extensively. Stability improvement by emulsification in hot water has been reported for a docosane suspension¹⁵⁾. A glycerin trioleate (triolein)/water emulsion was markedly stabilized by ultrasonic dispersion in hot water and subsequent immediate cooling¹⁶⁾. Triolein remained fluid upon cooling; hence, the stabilization seemed to be a transient effect. While the oil phase consisted of a single component in these studies, a similar temperature effect is expected for multi-component

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Accepted November 24, 2011 (received for review November 4, 2011)

Journal of Oleo Science ISSN 1345-8957 print / ISSN 1347-3352 online

<http://www.jstage.jst.go.jp/browse/jos/> <http://mc.manuscriptcentral.com/jjoecs>

systems, which will open wide applicability for emulsification of volatile compounds that are difficult to disperse in water alone. In particular, if the thermal effect is compatible with the polymer stabilization effect at room temperature (RT)¹⁴⁾, it will be possible to stabilize such oil-polymer/water emulsions through a dual effect.

This dual stabilization, which makes use of both the polymer effect and the temperature effect, might occur remarkably when the polymer solubility in the oil decreases significantly upon cooling and the polymer solidifies above RT. For instance, aromatic oils are regarded as a good solvent for polyethylene (PE) at higher temperatures but not at RT. In this study, the effect of the addition of PE on the stability of a surfactant-free toluene emulsion was examined^{17, 18)}. We adopted PEs with various melting points and studied the effect of the melting points of PE on the emulsion stability. Furthermore, we investigated the mechanism of “dispersion in hot water and subsequent rapid cooling” stabilization for the toluene-PE-water emulsions.

2 EXPERIMENTAL PROCEDURES

2.1 Materials

Highly purified Milli-Q water was used in the experiments. The hydrophobic polymers used in this study were a low-density polyethylene (LDPE) with an average molecular weight (M_w) of 3,000 from Tomen Inc., a medium-density polyethylene (MDPE) with $M_w = 6,300$, and a high-density polyethylene (HDPE) with $M_w = 125,000$. The medium- and high-density polyethylene samples were from Aldrich Chemical Company Inc. These polymer samples were used as received. Reagent-grade toluene from Wako was used as the solvent.

2.2 Preparation of O/W emulsions

Polyethylene was mixed with toluene, and the mixture was heated to 100°C for complete dissolution. The solutions were added to water in a flask that was kept at either 30 or 70°C. The mixtures were then emulsified for 8 min with an ultrasonic cleaner NEOCLEANER 1505 (Japan Alex Company, 150 W at 40 kHz) at the temperatures indicated. After sonication, the emulsions were rapidly cooled to RT with cold water in the fast-cooling process or with air in the slow one.

2.3 Measurements

Particle size distribution was measured using a NICOMP 380 ZLS analyzer from Particle Sizing Systems Inc., in the dynamic light-scattering mode. Once prepared, the emulsion samples were placed in a cuvette with a bottleneck for measurements.

The dissolution and melting temperatures were analyzed for the polymer-oil solutions with differential scanning calo-

rimetry (DSC). The viscosity of the polymer-oil solutions was measured using a stress-control rheometer (Type CSL from I.T.S., Japan) and the Ostwald viscometer for the low-viscosity samples. The turbidity was assessed photographically as a measure of emulsion stability. The crystallinity of a polymer-oil domain was observed photographically with a Nomarski-type differential interference contrast (DIC) microscope. For ¹H-NMR measurements, emulsion samples were prepared by dispersing the oil-polymer mixture in NMR-grade deuterated water from Wako. The sample was sealed in a 5 mm diameter NMR tube and subjected to measurements using a JEOL-EX-400 spectrometer (JEOL). The shapes of the emulsion droplets were observed by freeze-fracture microscopy with a transmission electron microscope Hitachi H-7650, in which sliced samples were prepared using an FR-7000A microtome.

3 RESULTS AND DISCUSSION

3.1 Polyethylene-toluene systems

The “dispersion in hot water and subsequent rapid

Fig. 1 Visual observation of LDPE-toluene emulsions prepared at $T_d = 70^\circ\text{C}$ (right) and by $T_d = 30^\circ\text{C}$ (left) preparation, (a) right after preparation, and (b) 12 months after preparation.

cooling" technique was examined for the LDPE-toluene mixture at a 1:10 weight ratio. When the emulsion was prepared at 70°C ($T_d = 70^\circ\text{C}$) and subjected to rapid cooling, the appearance of the dispersion did not change for 1 year, as shown in Fig. 1. In contrast, the same mixture processed at $T_d = 30^\circ\text{C}$ underwent phase separation during the same period, as expected from the incomplete dissolution. Stabilization was also noticed over a longer period (four months) for the MDPE-toluene emulsion processed at $T_d = 70^\circ\text{C}$, but stabilization was not obtained for the HDPE mixture, even at $T_d = 70^\circ\text{C}$. For every PE mixture, emulsions prepared at 30°C were not stable.

For the stabilized emulsions, fluidity remained visually unchanged. The entire phase was not solidified as was the case with liquid crystalline emulsions or gel emulsions^{19, 20}. Instead of bulk solidification, crystallization or a sol-gel transition is expected for the droplet domain. In the gelation scheme, polymer segments are cross-linked with each other and the polymer network is swollen with the solvent^{21–23}. With respect to the linking, gels are grouped into two categories: chemical gels and physical gels. In a chemical gel, polymer segments are firmly linked by covalent bonds, while in a physical gel, the segments are weakly cross-linked by hydrogen bonding or van der Waals interaction, such that the network structure is easily formed and melts. Physical gelation has been found for LDPE mixtures with toluene, decalin, benzene, and xylene^{24–29}. Therefore, physical gelation is presumed for the PE-toluene mixture.

To verify that physical gelation was involved in the processing at $T_d = 70^\circ\text{C}$, LDPE-toluene stock solutions were subjected to an inclination test upon rapid cooling. Solidification was observed for the LDPE-toluene 1:10 mixture, while deposition and partial gelation was noticed for the 1:100–1:300 mixtures. Therefore, a sol-gel transition is highly expected to occur in the PE-oil/water emulsion prepared from the 1:10 stock solution.

Droplet diameter is an indicator of the microscopic stability of emulsions. Figure 2 shows the droplet size distribution measured by dynamic light scattering for the LDPE-toluene emulsion prepared at $T_d = 30$ and 70°C. For emulsions prepared at $T_d = 70^\circ\text{C}$, droplet size remained at approximately 100 nm even for 112 days, while the value increased to 100–1000 nm for emulsions prepared at $T_d = 30^\circ\text{C}$. The averaged droplet size was compared among the emulsions prepared at various T_d , and the results are shown in Fig. 3. The growth can be sorted into two types: (A) a slow, monotonous increase for LDPE-toluene droplets prepared at $T_d = 50$ –70°C and MDPE-toluene droplets prepared at $T_d = 60$ –70°C and (B) a fast increase for LDPE-toluene droplets prepared at $T_d = 30$ –40°C and MDPE-toluene droplets prepared at $T_d = 30$ –50°C. The emulsions assigned to type (A) showed high dispersion stability.

In the earlier reports on PE-oil gels, the gel melting point (T_{gm}) or the gelation temperature (T_{gel}) had some correla-

Fig. 2 Droplet-size distribution vs. retention time (t) for LDPE-toluene emulsions prepared at $T_d = 70^\circ\text{C}$ (a) and 30°C (b). Each curve from the bottom was obtained at $t = 0$ (solid line), 14 days (dotted line), and 112 days (broken line).

Fig. 3 Averaged droplet diameter vs. retention time (t) for (a) LDPE-toluene and (b) MDPE-toluene (right) emulsions prepared at $T_d = 30$ (●), 40 (■), 50 (▲), 60 (▼), and 70 (◆)°C.

tion with the molecular weight (M_w) of PE^{30, 31}. In the present study, MDPE and HDPE had a higher M_w than LDPE; hence, MDPE and HDPE should have higher T_{gel} than LDPE. As a consequence, we conceive that gelation of the PE-oil mixture is a key condition for the prolonged stabilization of the emulsion. It suggests that extended stabilization of PE-toluene emulsions is not observed if dispersed at T_d below T_{gel} . The values of T_{gel} determined with DSC, as well as the stability of the processed O/W emulsions, are summarized in Table 1. As seen in the table, the PE-toluene emulsions are apparently stabilized as long as $T_d > T_{gel}$ stands and vice versa. This criteria was also evidenced by

Table 1 Gelating temperature (T_{gel}) of toluene-PE mixtures and emulsion stability.

PE samples	LDPE	MDPE	HDPE
Gelating temperature	45.5°C	55.4°C	77.6°C
emulsion prepared at 30°C	unstable	unstable	unstable
emulsion prepared at 40°C	unstable	unstable	unstable
emulsion prepared at 50°C	stable	unstable	unstable
emulsion prepared at 60°C	stable	stable	unstable

the droplet growth in Fig. 2, where the slow increase in droplet size was characteristic of PE emulsions prepared at $T_d > T_{\text{gel}}$. Therefore, dispersing the liquid-oil mixture and rapid cooling to solidification is an essential scheme for prolonged stabilization.

3.2 Characterization of LDPE-toluene droplets

Microscopic and interfacial properties are the next concern regarding thermally stabilized emulsions in order to understand the structure of the gelated droplets. Figure 4 represents the ζ -potential of LDPE-toluene and MDPE-toluene droplets prepared at various T_d as a function of standing time. The initial value was as low as -60 mV for the two emulsions prepared at T_d (50–70°C) $> T_{\text{gel}}$, and it remained stable at -50 mV for 112 days. Meanwhile, the potential value for emulsions prepared at T_d (30–40°C) $< T_{\text{gel}}$ was approximately -43 to -45 mV initially and subsequently increased to approximately -30 to -35 mV. In addition, the ζ -potential value varies from -37 mV for pure toluene droplets to -60 mV with an increase of PE fraction. Referring to the low ζ -potential values of long n-alkane droplets³²⁾, such a low potential of the PE-toluene droplet reveals hydrophobic modification of the droplet surface upon gelation. Plausibly, the CH_2 framework of PE is certainly exposed to water surrounding the droplet surface. Those polymer tails would induce steric repulsion with each other and increase resistance against flocculation and

coalescence¹⁴⁾. Steric repulsion has been reported for hydrophilic polyethylene glycol tails^{33, 34)}.

The presence of toluene molecules and their microscopic environment can be perceived in the chemical shift in the ^1H -NMR spectra shown in Fig. 5. The toluene/water emulsion gave spectra consisting of ring-H and methyl-H peaks located close to the peaks in CDCl_3 ³⁵⁾, accompanied by a side peak at a 0.6 ppm higher field. These shifts suggest

Fig. 4 Value of ζ -potential for (a) LDPE-toluene and (b) MDPE-toluene emulsions vs. retention time (t) prepared at $T_d = 30$ (●), 40 (■), 50 (▲), 60 (▼) °C, and 70 (◆) °C.

Fig. 5 NMR spectra of LDPE-toluene mixture and emulsions by $T_d = 30^\circ\text{C}$ and 70°C preparations. (a) LDPE-toluene SFE prepared at $T_d = 70^\circ\text{C}$, (b) LDPE-toluene SFE prepared at $T_d = 30^\circ\text{C}$, and (c) pure toluene SFE.

hydration of the toluene molecules. For the LDPE-toluene/water emulsion prepared at $T_d = 70^\circ\text{C}$, the side peaks appeared strongly with the shift of 0.9 ppm. This new peak was located at a 0.4 ppm higher field than the methylene-H peak of LDPE in the literature³⁶⁾ and was absent for emulsions prepared at $T_d = 30^\circ\text{C}$. It is assignable to the methylene-H peak of LDPE immersed inside the droplet. The positive shift indicates hydration of the CH_2 frameworks. This evidence is consistent with the view discussed from the ζ -potential.

Direct observation of the droplets showed that spherical shapes were observed for the droplets prepared at $T_d = 70^\circ\text{C}$, while deformed or broken shapes were found for those prepared at $T_d = 30^\circ\text{C}$. The round shape shows that a liquid-oil interface was formed in hot water and frozen instantaneously.

3.3 Effect of cooling rate on LDPE-toluene emulsion

In contrast to the reversible sol-gel transition in microgels like poly(N-isopropylacrylamide) (NIPAM) and the solid-liquid transition in wax emulsions, we must consider the dynamic aspect of crystallization-induced gelation²²⁾ for the present systems. The cooling rate of the hot emulsion especially would determine the emulsion stability at room temperature. A comparison was made between the LDPE-toluene emulsion prepared by fast cooling and that by slow cooling. The PE-oil mixture was preliminarily subjected to a tube inclination test after cooling. Solidification was observed for the rapidly cooled sample but not for the slowly cooled one. As anticipated from the difference, fast cooling gave a stable emulsion for seven months, while slow cooling resulted in phase-separation during the same period. This will give some applicability of controlled destabilization for the gelated droplets to release the oil.

The appearance of crystallization is another concern in the droplet gelation. Nomarski differential interference optical microscopy was adopted for differentiation of the LDPE-toluene mixture prepared by fast and slow cooling (Fig. 6). In the case of fast cooling, fine crystals 1-2 μm in size were widely spread around large crystals 10 μm in size having irregular shapes, while in the case of slow cooling, larger round-shaped crystals grew and the small crystals almost disappeared. From this observation, crystallization of PE should also occur in the gelated droplets, although the size and shape of the crystal strongly depends on the cooling rate.

4 CONCLUSION

A highly stable, surfactant-free toluene/LDPE-in-water emulsion was prepared using a hot-water-dispersion/immediate-cooling method. Such a stable emulsion was very difficult to obtain using ordinary dispersion methods at room

Fig. 6 Nomarski differential interference optical microscopic images of LDPE-toluene droplets after rapid (upper) and slow (lower) cooling processes. Scale bar indicates 10 μm .

temperature. Rapid cooling of the hot emulsion is the principal condition for the effective collaboration of gelation and polymer-assisted equilibratory stabilization. For successful stabilization, the T_{gel} of the PE-toluene mixture should be controlled between T_d and the retention temperature. Because PE is a common type of synthetic polymer, this method is promising for implementing low-cost, recyclable, and controllable emulsification/de-emulsification of aromatic oils in water.

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