Emulsifying and Self-Emulsified Properties of Siloxane Polymer Grafted with Easy Hydrophile

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ABSTRACT: A series of siloxane polymers (SHE) with varying weight percents of simple nonionic hydrophilic groups have been synthesized and characterized by FTIR and ^{13}C-NMR. Emulsions have been made by self-emulsification of those polymers in pure water and also by emulsifying silicone oil using those polymers as oil-in-water type emulsifiers. The stability of those emulsions have been examined apparently from the phase separation and also from the particle size increase on storage by Transmission Electron Microscopy (TEM) and photo microscopy. The results reviled that SHE 40, having 40 wt % grafted hydrophile, formed the most stable self-emulsified emulsion, and SHE30 and SHE40 could be used as effective emulsifiers for silicone oil emulsification. The possible use of those emulsions as a defoamer for water-borne systems has also been investigated by measuring the reduction of foam height of a strongly foamed aqueous solution of sodium lauryl sulfate (SLS). The defoaming ability decreases with the increase in hydrophile wt % in the polymer backbone; however, it increases with the emulsion (defoamer) concentrations. When compared with respect to the total wt % of hydrophobe contents in the emulsion defomer, the self-emulsified emulsion has shown better defoaming than the silicone oil emulsion, and the results are well in accord with the difference in size of the respective emulsion particles. © 2002 Wiley Periodicals, Inc. J Appl Polym Sci 86: 2408–2415, 2002

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INTRODUCTION

Various surface-active hydrophilic-grafted polysiloxanes have been synthesized by a simple reaction, and their colloidal behaviors have also been extensively studied.[1] Their performance as dispersants in chemical mechanical polishing (CMP) slurries has already been reported.[2] It is known that when the hydrophobic and hydrophilic components contained in these types of polymers reach an appropriate balance, the polymers can be expected to act as an effective emulsifier for oil-in-water systems.[3] When the hydrophilicity is controlled at a level so that the polymer is insoluble in water but hydrophilicity is strong enough to enable the polymer chain suspended in the water, these polymers should have a strong affinity to form self-emulsified emulsions also.[4]

Polysiloxane (or silicone oil) has the great ability to restrain the foams by lowering the surface tension. This polymer has widely been used as defoamer for many decades.[5–7] However, this polymer does not possess any hydrophilic property to migrate to the oil–water or air–water interface, thus it cannot be compatible alone with water-borne system to exhibit the performance as a surface-active agent such as a defoamer. To improve the hydrophilic property of the silicone compounds numerous modifications have been reported from industries,[8–10] as well as academia.[11,12] Generally, polysiloxanes grafted with polyethers,[13] known as silicone surfactants, is the most popular way of making this hydrophile-grafted polysiloxane. The introduction of polyether into polysiloxane backbone is carried out by ethoxylation or propoxylation,[10] which involves the toxic and explosive ethylene oxide or propylene oxide, and cannot be conducted in the laboratories or factories without special equipment and facilities. In this study the di-ethanol amine has been introduced as a hydrophilic moiety onto polysiloxane by a simple *in situ* reaction, where the main polysiloxane chain of this produced polymer can lower the surface tension of the solution and the grafted di-ethanol amino group can enhance the hydrophilic properties. Thus, these hydrophilic-grafted polysiloxane can effectively be self-emulsified in pure water to form stable emulsion, and can also be used as an oil-in-water type emulsifier to emulsify the silicone oil. Both those emulsions can further be used as effective defoamers for water-borne systems without any migration problem. It is worthwhile, therefore, to evaluate their performance as an emulsifier as well as a defoamer. In this study the stability of those emulsions and their ef-

TABLE I
Symbols and Compositions of Hydrophile-Grafted Polysiloxanes with Varying wt % of Hydrophile

Hydrophile-grafted polysiloxanes (symbols)	Wt % of hydrophilic moiety	Wt % of DC-1007	Wt % of D_4	Wt % of DC-2000	EEW of SG polymer	$\bar{M}_n \times 10^{-3}$ of SG polymer
SHE10	10.35	10	85	5	815	—
SHE20	20.53	20	75	5	460	7.72
SHE30	29.85	30	65	5	347	—
SHE40	39.80	40	55	5	286	7.01
SHE50	48.78	50	45	5	252	—
SHE60	59.52	60	35	5	226	6.48
SHE80	78.50	70	25	5	194	6.77

$$\text{Wt \% of Hydrophile} - \frac{\text{Wt of DC-1107}}{\text{Wt of DC-1107 + Wt of D}_4} \times 100$$

$\bar{M}_n$ = Molecular weight of SG copolymer.

ficiency in defoaming has been investigated and correlated with their structures.

EXPERIMENTAL

Synthesis of hydrophilic-grafted polysiloxane

The synthesis of hydrophilic-grafted polysiloxane is a three-step process, and is described in detail elsewhere.[1,14]

Step 1. Synthesis of siloxane copolymer (SH)

Polymethylhydrogensiloxane (DC-1107), octamethyl-cyclotetrasiloxane (D_4), and hexamethylhydrogensiloxane (D-2000) were reacted using sulfuric acid as a catalyst, at a temperature of $\sim 45°C$ under N_2 atmosphere.

Step 2. Synthesis of siloxane copolymer derivative (SG)

Using platinum as a catalyst, siloxane copolymer (SH) was reacted with an overdose of ally1 glycidy1 ether in dry toluene, at a temperature of $\sim75°C$, under N_2 atmosphere.

Step 3. Synthesis of nonionic hydrophilic-grafted polysiloxane surfactant (SHE)

The SG copolymer was reacted further with excess di-ethanol amine in ethanol at a temperature of $\sim70°C$. However, as the hydrophilic group of polysiloxane derives from the DC-1107, the hydrophilic degree increases with increasing the weight percent of the DC-1107. Thus, adjusting the stoichometry of DC-1107 and D_4 in the reaction mixture we can vary the active reaction sites for the entry of hydrophilic moieties.

Characterization of polymers

The characterization technique of all of these polymers have been vividly described elsewhere,[1,14] and are not in the scope of this present research. However, tools like FTIR (Nicolet, Magna II 550) and ^{13}C-NMR (Buckner, Model AMX-400) have been adopted to monitor the syntheses of polymers with right functionality in the different stages of syntheses. Epoxy Equivalent Weight (EEW) of SG copolymers has been determined following the same technique as described in our previous research,[14] and the molecular weight of SG copolymers has been determined by Gel Permeation Chromatography (GPC) using polystyrene as the standard.

Preparation of self-emulsified emulsion

Hydrophilic-grafted polysiloxane surfactant (1.5 g) was homogeneously mixed in 10 mL of distilled water at 1000 rpm for 30 min at room temperature to form the self-emulsified emulsion.

Preparation of silicone oil emulsion

Silicone oil (10 mL) (Dow Corning, 50 cs fluid) was emulsified in 10 mL of distilled water in the presence of 1.5 g of hydrophilic-grafted polysiloxane surfactant under vigorous stirrings at 1000 rpm for 30 min at room temperature.

Stability of the emulsions

The stability of the emulsions system was examined by observing the apparent phase separation of the emulsion upon storing, and also the study of their micromorphology using Photo microscope (Olympus, Japan) and Field Emission Transmission Electron Microscope (TEM) (Hitachi model HF-2000). Two hundred mesh Formvar-covered carbon-coated copper
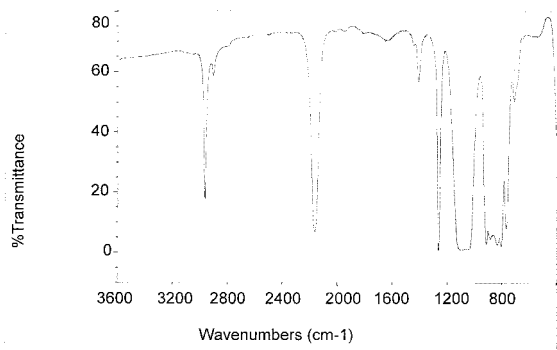
Figure 1 FTIR spectra of siloxane copolymer (SH).

Figure 2 FTIR spectra of the derivative of siloxane copolymer (SG).
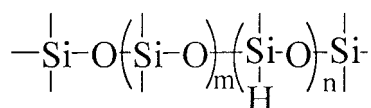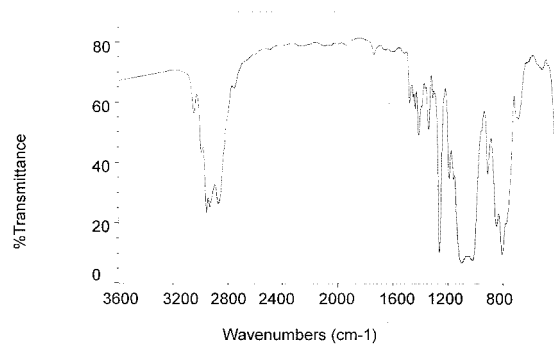
grids were used to carry out TEM. The average sizes of the particles of both the kind of emulsions were measured by MPK Image Map 32 plus.

Examination of defoaming abilities

A solution of SLS (0.5 or 0.25%) (Aldrich) in water was used as a foaming agent.[15] The foams were generated by continuously passing of air through the SLS solution for 3 min using an air supplier pump (SKC Inc. US), with a passing rate of 100 cc/min at the temperature ~40°C. The self-emulsified emulsions and silicone oil emulsions were individually added into the foamy SLS solution, and their defoaming abilities were determined by measuring the foam height reduction with concentration as a function of time.

RESULTS AND DISCUSSION

Table I shows the composition for polysiloxanes used for the synthesis of hydrophile-grafted polysiloxane with varying percentages of hydrophilic groups. The structure of the siloxane copolymer SH has been evaluated by FTIR spectra and shown in Figure 1. The infrared absorption frequencies at 2165 and 1260 cm^{-1} are the characteristic absorption bands of Si—H and Si—CH$_3$, respectively. This suggests that the structure of the siloxane copolymer (SH) is

$$-\underset{|}{\overset{|}{Si}}-O\left(\underset{|}{\overset{|}{Si}}-O\right)_m\left(\underset{\overset{|}{H}}{\overset{|}{Si}}-O\right)_n\underset{|}{\overset{|}{Si}}-$$

The FTIR spectra of the SG copolymer, the resultant product of siloxane copolymer (SH), and allylglycidyl ether reaction (step 2) is shown in Figure 2. It shows that the characteristic absorption bands of Si—H at absorption frequency 2165 cm^{-1} has disappeared, and the absorption at 1161 cm^{-1}, 2860 cm^{-1}, and 840 cm^{-1} indicate the characteristic bands of
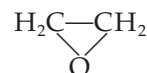
$$\underset{O}{\overset{H_2C-CH_2}{\diagdown\diagup}}$$

Hence, the SG copolymer structure has to be considered, as indicated in Scheme I. Finally, the SG copolymer reacts with diethanolamine (step 3) to produce the hydrophilic-grafted polysiloxane surfactant, and the molecular structure of this hydrophilic-grafted polysiloxane surfactant has been analyzed by ^{13}C-NMR spectroscopy, as shown in Figure 3. The signals at $\delta = 57.39$ and $\delta = 59.56$ are the characteristic absorption peaks for the two methylene carbon of N(C$\underline{H}_2$C$\underline{H}_2$OH)$_2$, the absorption peak of Si—CH$_3$ has appeared at $\delta = 0$ and the signals at $\delta = 72.83$, $\delta = 74.40$ are other two methylene carbon of —C$\underline{H}_2$—O—C$\underline{H}_2$—. Thus, from the above structure
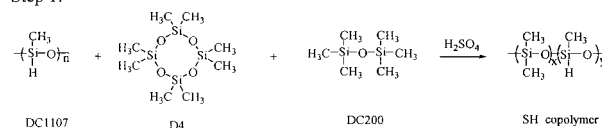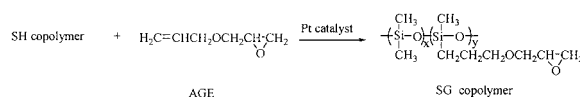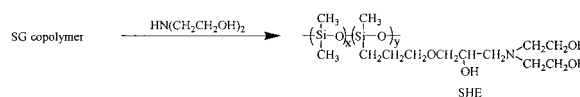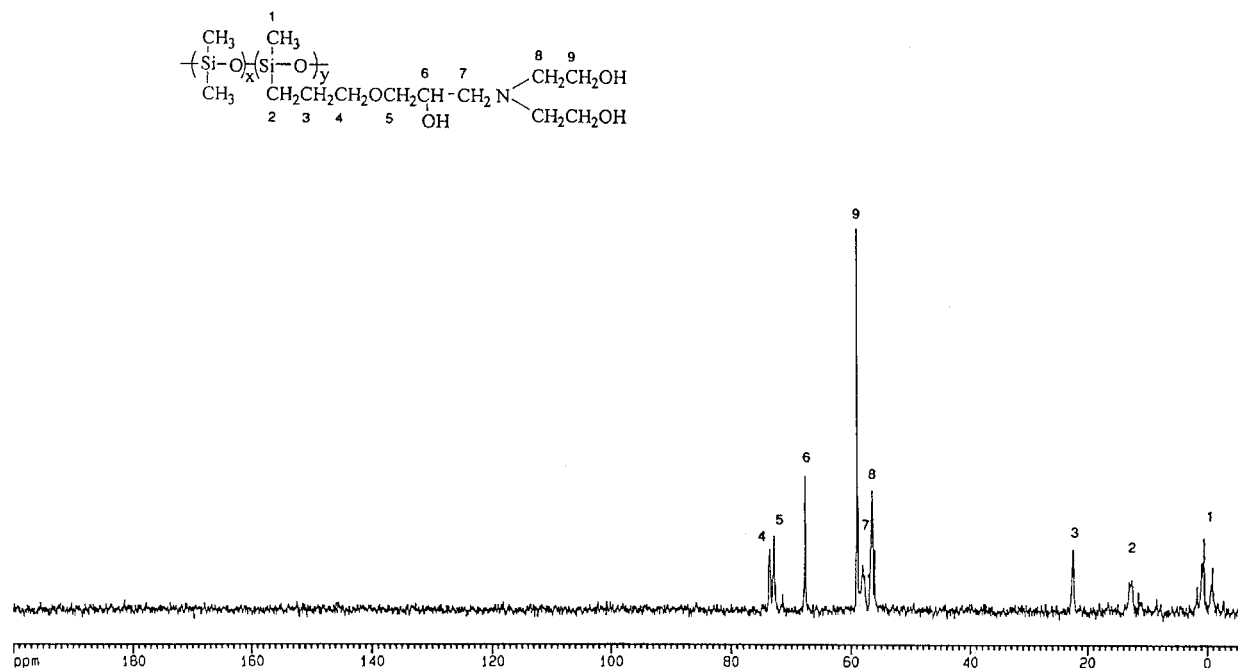

Scheme 1

Figure 3 ^{13}C-NMR spectra of hydrophile-grafted polysiloxane (SHE).

determination data, it can be concluded that the hydrophile-grafted polysiloxanes have been successfully synthesized.

As reported earlier, SHE polymers can transfer to the air/water interface and decrease the surface tension, and the reduced amount is proportional to the surface excess concentration.[1] It has been observed that SHE polymers with varying percentages of hydrophilic groups form a cloudy suspension to clear solution in pure water. The appearance of cloudiness in the aqueous phase indicates that the polymers are self-emulsified to form suspended polymer aggregates. For the self-emulsified emulsions of hydrophile-grafted polysiloxane SHE10 and SHE20 containing 10 wt % and 20 wt % hydrophilic groups, respectively, an obvious phase separation has been observed upon standing only for 1–2 h. The hydrophilicity of these polymers is not enough to form polymer aggregates in the aqueous phase. SHE30, containing 30 wt % hydrophilic groups, shows a better stability, although a distinct phase separation occurs after overnight standing, due to the fact that the hydrophilicity of this polymer is not enough to form stable emulsion. However, the polymer SHE40 containing 40 wt % hydrophilic groups can self-emulsify easily to produce a stable emulsion, of which the wt % of hydrophobic and hydrophilic group is well balanced to form the stable dispersion of polymer aggregates in the aqueous phase. To study the micromorphology of the aggregates produced by the association of this polymer and their change with respect to time, TEM of the emulsions has been recorded and shown in Figure 4. The increase in aggregate size with aging indicates the

slow agglomeration, which ultimately ends up with a phase separation after 30 days. On the other hand, hydrophile-grafted polysiloxanes containing more than 50 wt % hydrophilic groups (SHE50, SHE60, SHE80) are freely dissolved in water to make clear solutions rather than forming emulsions.

Silicon oil has been emulsified as an oil-in-water type emulsion using the titled compounds as emulsifiers. For SHE10 and SHE20, the emulsions have shown a distinct phase separation on storage only after 1–2 h; this poor performance is due to their high hydrophobic nature to cause the emulsifier coming into the silicone oil phase too much. SHE50, SHE60, and SHE80 are also poor emulsifiers to make stable emulsions of silicon oil due to their strong hydrophilic character[16] to cause the emulsifier to get too far into the water phase. However, the silicon oil droplets formed in the emulsion made of SHE30 and SHE40, as the emulsifier respectively has appeared to be quite stable and the phase separations have been noticed after only 30 days of storing. Figures 5 and 6 represent the photomicrographs of silicone oil emulsion with SHE30 and SHE40, respectively. The smaller increase in droplet size with aging of the emulsion with SHE40 than that of SHE30 indicates that the stability of the former emulsion is more than that of the latter one. It is also interesting to compare the average size of the polymer aggregates of SHE40 in the self-emulsified emulsion (Fig. 4) and that of the oil droplets stabilized by the same polymer (Fig. 6). From the image analysis by MPK image map 32, it has been found that the size of the polymer aggregates within the range, dia. 0.3–0.75 μm to
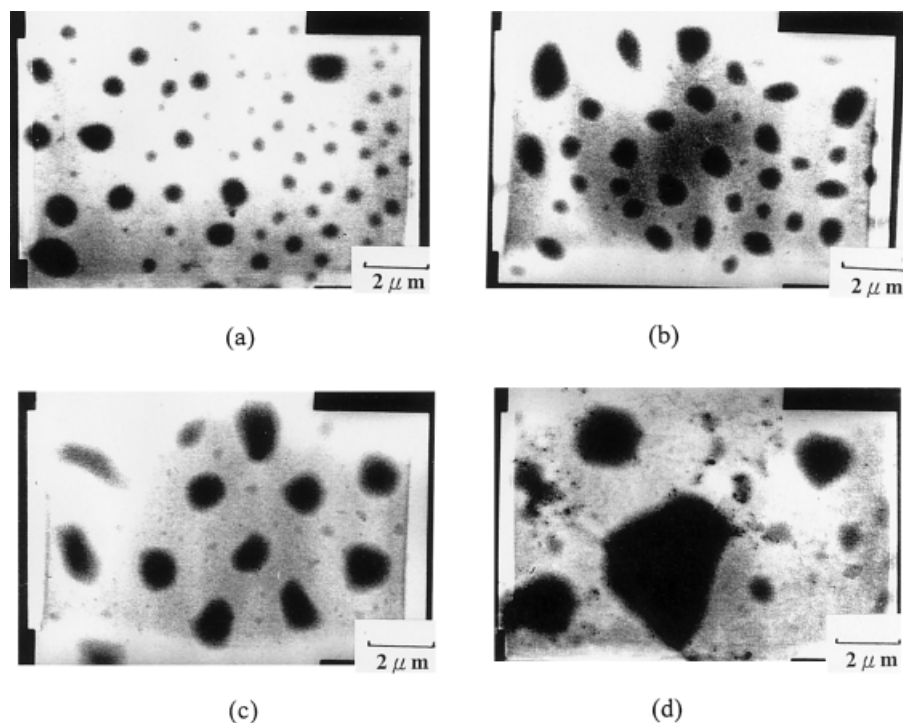
Figure 4 TEM of self-emulsified emulsion of SHE40 in water at various stages of storing: (a) 0 h; (b) 3 days; (c) 7 days; (d) 10 days.

be much smaller than the silicone oil droplet dia. 2.0–5.0 μm, and the former cannot be detected by a simple photomicroscope.

The efficiency of the self-emulsified polymers and the silicone oil emulsions as a defoamer has been determined by measuring the reduced foam height of
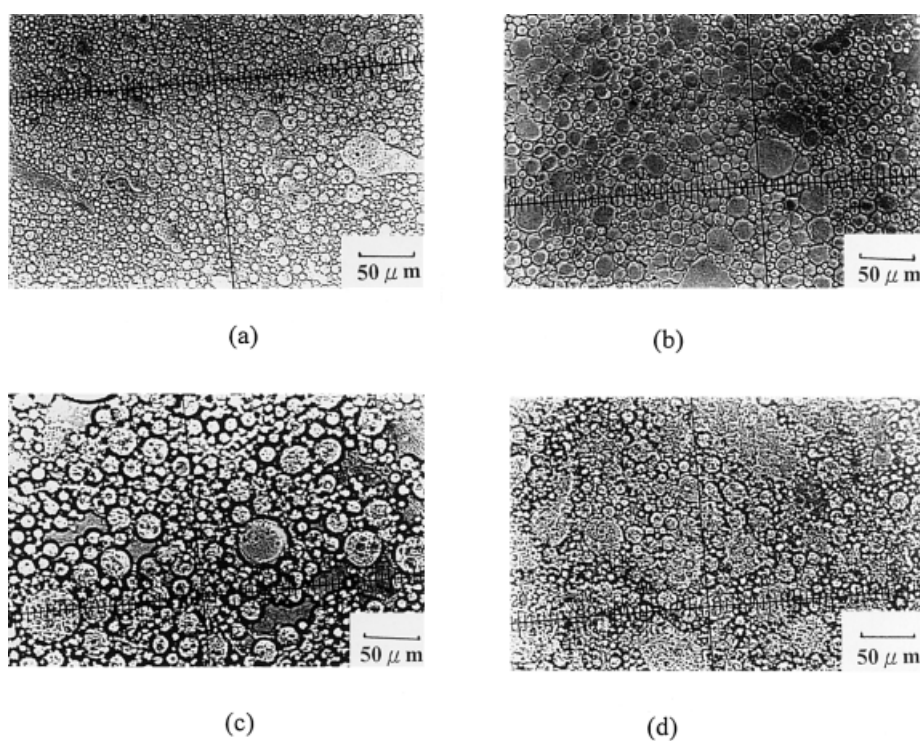

Figure 5 The photomicroscopy of silicon oil emulsion using SHE40 as an emulsifier at various stages of storing: (a) 0 h; (b) 3 days; (c) 5 days; (d) 7 days.
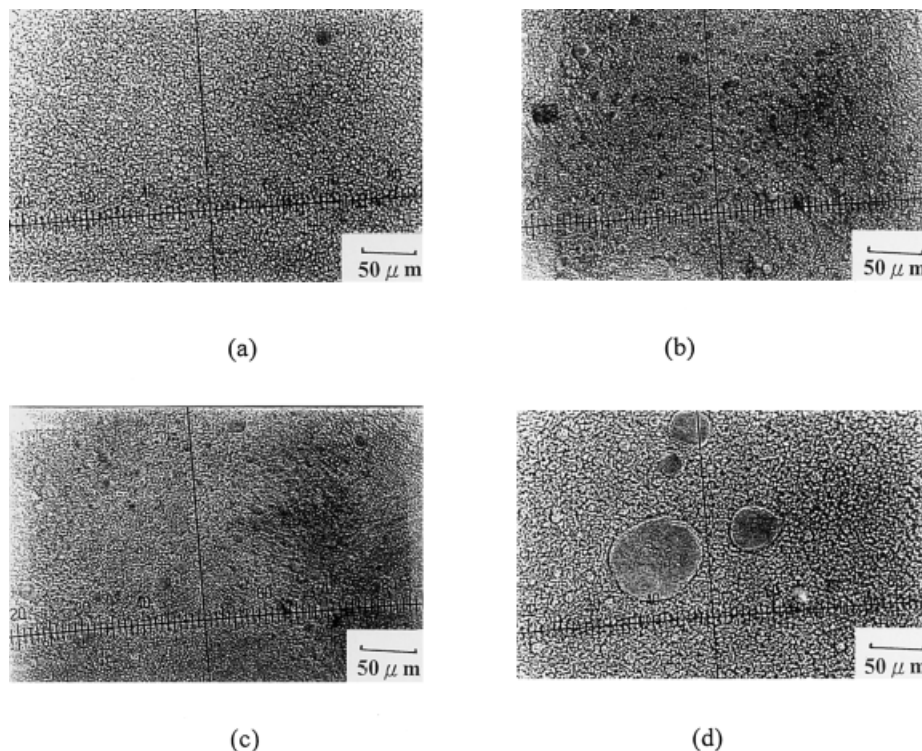
Figure 6 The photomicroscopy of silicon oil emulsion using SHE40 as an emulsifier at various stages of storing: (a) 0 h; (b) 3 dyas; (c) 5 days; (d) 7 days.

the foamy aqueous solution of SLS. The SLS is a popular foaming agent for research and industrial applications. The foam heights have been measured in the absences of emulsions (blank), and the efficiency of defoaming after addition of individual emulsions has been evaluated from the plot of foam height as a function of time. Figure 7 shows the foam height vs.
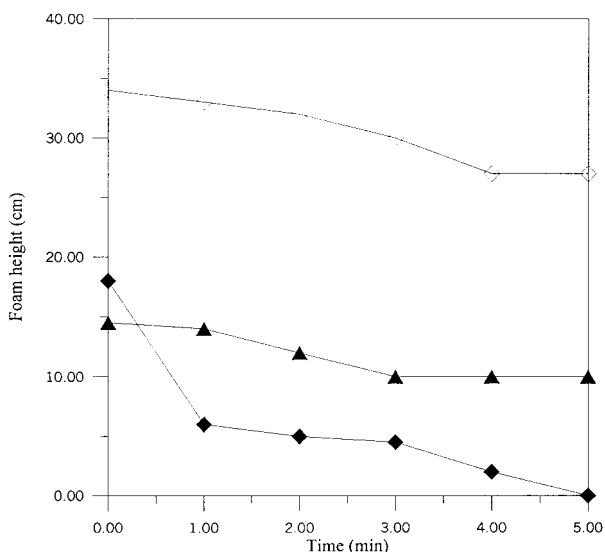

Figure 7 Defoaming abilities of self-emulsified hydrophile-grafted polysiloxane emulsions as a defoamer (SLS = 0.5%, defoamer = 5000 ppm). (◇) blank; (◆) SHE40; (▲) SHE50.

time plots using self-emulsified emulsions as a defoamer. It has been observed from the curves that the defoaming ability decreases with the increase in the hydrophile wt % in the polymer backbone. It indicates that the hydrophile-grafted polysiloxane, having a higher portion of hydrophobic polysiloxane main chain, can lower the surface tension[17] more effectively. Thus, the polymers containing lower hydrophile, i.e., higher hydrophobe wt % in the structure, can break the foams more easily in the aqueous system. Figure 8 represents the foam height vs. time plots for silicone oil emulsions as defoamers, and their ability of defoaming also decreases with the increase in hydrophile wt % in the polymers.

Figures 9 and 10 shows the plot of foam height vs. time using different concentrations of self-emulsified emulsion of SHE40 and of the silicone oil emulsion made of SHE 40 as a defoamer, respectively. It has been observed from the curves that the defoaming ability of the emulsions increases with their increasing concentration. The reason may also be simple; as the hydrophobic portion responsible for the reduction of surface tension has been increased with the concentration of both the emulsions, the defoaming ability also increased.

Besides the above facts, when the defoaming ability of both kinds of emulsions have been compared with respect to their hydrophobe wt % in the system, which is supposed to be responsible for the defoaming per-
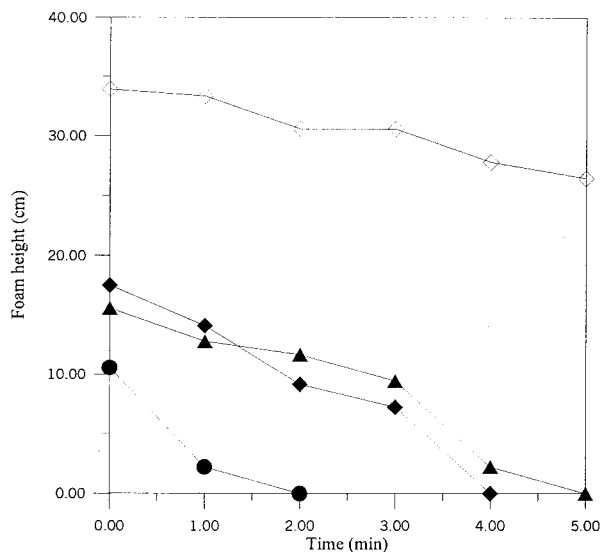
Figure 8 Defoaming abilities of silicon oil emulsions as a defoamer (SLS = 0.5%, defoamer = 5000 ppm).

Figure 10 Defoaming abilities of silicon oil emulsion (SHE40 as an emulsifier) as a function of concentration: (◇) 0 ppm (blank); (△) 1000 ppm; (▲) 2500 ppm; (+) 5000 ppm.

formance of the emulsions, it has been observed from Figure 11 that the self-emulsified emulsion of the SHE40 polymer containing comparatively less hydrophobe (390 ppm) reduces more foam height with respect to time than the silicone oil emulsion made of SHE40 as an oil-in-water emulsifier (hydrophobe contain 500 ppm and 1250 ppm). The hydrophobes content in the emulsion has been calculated on the basis of the wt % of hydrophobic moiety present in the polymeric emulsifier and the wt % of silicone oil used in the individual emulsion formulations. In the self-emulsified emulsion system, the only hydrophobe is the polysiloxane backbone of the dhydrophile-grafted polymer, which forms aggregates above a concentra-
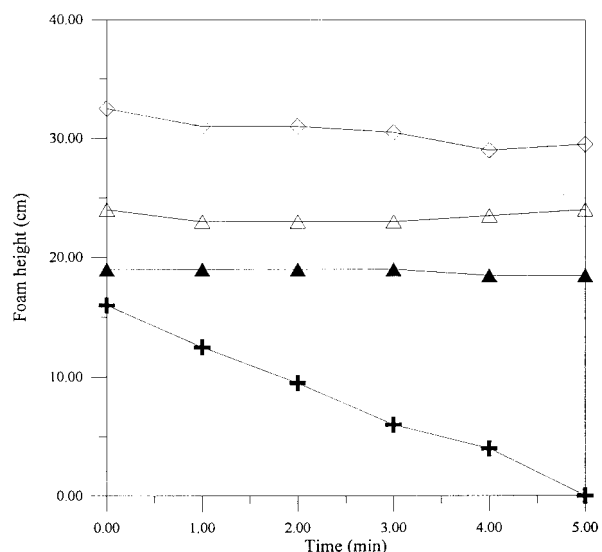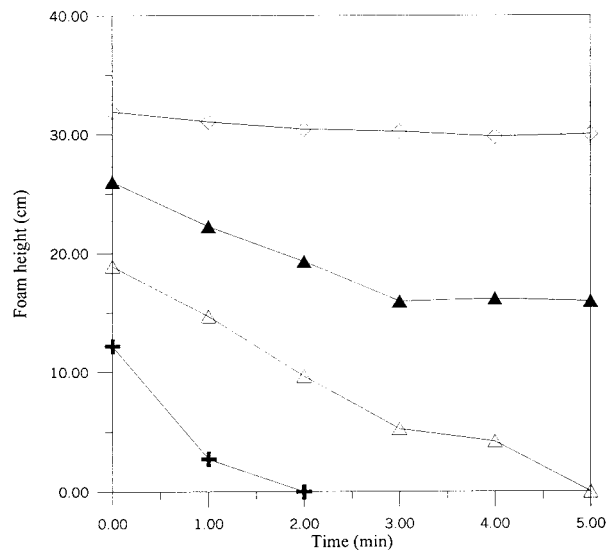
tion called the aggregate forming concentration.[1] On the contrary, in the silicone oil emulsion, the hydrophobic silicone oil forms oil droplets stabilized by the adsorption of dhydrophile-grafted polysiloxane with hydrophobic backbone. However, due to the size difference between the polymer aggregates in self-emulsified emulsion (~0.5 μm) and the oil droplets in silicone oil emulsion (~2.0 μm), the former have the larger surface area to come in contact with the surface of the aqueous foaming system more effectively to reduce the surface tension, and showed better defoaming ability than the latter one at a comparable dosage.
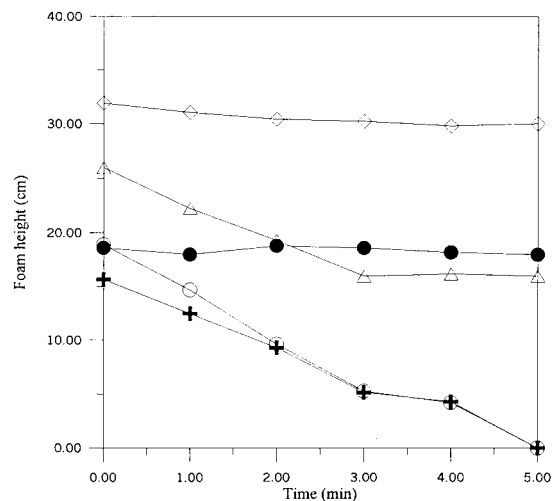

Figure 9 Defoaming abilities of self-emulsified emulsion SHE40 as a function of concentration. (◇) 0 ppm (blank); (△) 1000 ppm; (▲) 2500 ppm; (+) 5000 ppm.

Figure 11 Defoaming abilities of self-emulsfied and silicon oil emulsion as a function of hydrophobe content. (◇) blank; self-emulsified emulsion with hydrophobe (+) 390 ppm and (●) 195 ppm; silicone oil emulsion with hydrophobe (○) 1250 ppm and (△) 500 ppm.

CONCLUSION

The hydrophile-grafted polysiloxanes containing various weight percents of hydrophilic groups have been synthesized. The polymer containing 40 wt % hydrophile, SHE40, forms the most stable self-emulsified emulsion in pure water. The SHE40, as well as SHE30, has also proven to be good oil-in-water emulsifiers to form stable silicone oil emulsion. The size of the polymer aggregates in self–emulsified emulsion is much smaller than that of the silicone oil droplets in silicone oil emulsion.

The defoaming ability of emulsions of both kinds decreases with increasing hydrophile wt % in the polysiloxane backbones, and increases with the increasing dosages of the individual emulsions. However, the self-emulsified emulsion performs as a better defoamer than the silicone oil emulsion at comparable wt % of hydrophobe contents in the emulsions. The former, having polymer aggregates of smaller diameters, i.e., a larger surface area, restrains the foams more effectively.

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