Function and Performance of Silicone Copolymers(II): Syntheses and Interfacial Behavior of Siliconized Acrylic Copolymers

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ABSTRACT: Polysiloxane-containing copolymers were synthesized and characterized by nuclear magnetic resonance and elemental analysis. These copolymers were neutralized by triethylamine. The copolymers could be self-emulsified to form emulsions in water with and without cosolvent PCS and exhibited excellent defoaming abilities. These copolymers were also used as emulsifiers to emulsify silicone oil in water to form stable oil-in-water emulsions. This emulsion again exhibited defoaming properties, more efficiently than that of the self-emulsified emulsion of siliconized acrylic copolymer (SAA). © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 71: 805–811, 1999

Key words: polysiloxane; copolymer; synthesis; self-emuls; defoaming

INTRODUCTION

Polysiloxane[1,2] (or silicone oil) has been widely used as a defoamer[3,4] for many decades. Due to its incompatibility with organic polymer or organic compounds, organo-modified polysiloxane has replaced the normal polysiloxanes in many applications.[5,6] Both polysiloxane and hydrophile-modified polysiloxanes exhibit problems of migration to the surface of plastic or coating film because those molecules are small. If the polysiloxane is immobilized on a polymer, which contains hydrofoils, then this polymer can act as a defoamer with the advantages of having good compatibility, without the migration problem. The types of polymers have the following characteristics:

1. The base polymer provides the polysiloxane moiety, which is compatible with silicone oil.
2. The base polymer should provide sufficient hydrophilicity so that it can migrate to the silicone/water interface and to the air/water interface.
3. The base polymer should provide a layer with strong mechanical attractions at the silicone/water interface by means of polymer backbone groups.

As the polysiloxane and hydrophile components contained in these types of polymer reach an appropriate balance,[6] this copolymer also can be expected to act as an effective emulsifier in the silicone/water system. Acrylic monomers containing special functionality can be easily copolymerized with other acrylic monomers to prepare functional copolymers, which can act as dispersants,[7,8] emulsifiers,[9] and flocculants.[10] A monomer, which contains polysiloxane [siliconized acrylic (SA) monomer], was success-

fully prepared from hydroxyethyl methacrylate (HEMA) and methoxy-functionalized polysiloxane (SY 231) without gelation[7] during condensation. Then, the monomer SA was copolymerized with acrylic acid to form a copolymer [siliconized acrylic (SAA)], which contains both a polysiloxane moiety and hydrophilic groups. As the copolymer SAA was stirred in water, it was self-emulsified[11] to form a colloidal solution, which acted as a defoamer in a solution of a strong foaming surfactant [sodium lauryl sulfate (SLS)[12]]. Also, SAA copolymer was found to be an effective emulsifier in preparing silicone/water emulsions. These emulsions again effectively defoamed a SLS solution.

EXPERIMENTAL

Materials

Methoxy-functionalized polysiloxane, SY 231 (Wacker, Germany), is a commercially available product. It was used without further purification at the step of condensation with HEMA, but was purified after it was incorporated in the copolymer. 2-HEMA (Fluka), silicone oil (Dow Corning), and PCS propylene glycol monomethyl ether (Arco Chemical) are used as supplied. Acrylic acid (Tokyo Kasei), triethylamine (Wako), AIBN (Wako), n-butyl mercaptan (Tokyo Kasei), and SLS (Aldrich) are EP grade. 1,4-Dioxane (Alps), acetone (Alps), and n-hexane (Alps) are UP grade. Water used in these experiments is ion-exchanged and distilled; its pH value is 6.8–7.2 and conductivity is 4.4.

Methods

Synthesis of Polysiloxane-Containing Monomer (SA)

SY 231 (90 g) was poured into the reactor, then the stabilizer (hydroquinone, 0.5% based on SY 231) and HEMA (24 g) were added into the reactor sequentially. After that, the condensation catalyst for silicones tripropyltitarate (TPT, 1%) was added to the reactor.

Reaction components were stirred mechanically (300 rpm, RW20, Ira-Werk), and the reaction temperature was raised from room temperature to 100°C. When the removed methanol amounted to 90% of the theoretically calculated amount then the reaction temperature was raised

to 140°C. Heat was removed from the reactor; however, stirring continued until no more methanol came out.

Synthesis of the SA Copolymer with Acrylic Acid (SAA)

SA (48 g), 1,4-dioxane (200 g), and n-butyl mercaptan (0.64 g; 2 wt % based on the total amount of monomers) were added into the reactor. A mixture of acrylic acid (6 g) initiator (AIBN 0.32 g; 1 wt % based on the total amount of monomers) and 1,4-dioxane (20 g) was added to the reactor under mechanical stirring (300 rpm) at refluxing temperature (105°C) for 2 h.

After the reaction was complete, the solvent was evaporated off, 20% of water was added into the unpurified mixture, and then an excess amount of triethylamine was directly added into the solution gradually while stirring.

The neutralized polymer was purified by reprecipitation from the n-hexane and acetone mixed solvent, and kept in a vacuum oven until further use.

Evaluation of Defoaming Abilities

Because the foaming time of the Ross-Mile method[13] is too short to differentiate the defoaming ability or these copolymers, a continual bubbling system was used to evaluate the defoaming abilities. In this procedure 50 mL of SLS (0.2%) solution containing defoaming agent (or not) was placed in a 2500 mL graduated cylinder, and air was pumped into the cylinder for 3 min. The height of the foam generated was measured for evaluating the various defoaming agents.

RESULTS AND DISCUSSION

SA monomer was obtained from the condensation of HEMA and methoxy-functionalized polysiloxane (SY 231). The unsaturated double bond in HEMA is easily polymerized during the condensation reaction. It is important to determine the appropriate reaction conditions for condensation. The reaction temperature was increased from room temperature to 140°C in the presence of stabilizer (hydroquinone), as well as catalyst to avoid the polymerization of acrylic monomer and the occurrence of gel. The unpurified SA monomer was directly polymerized with acrylic acid and the
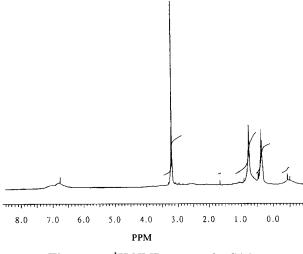
Figure 1   ^{1}H-NMR spectra for SAA.

resulting copolymer (SAA) was purified by precipitation from a mixed solvent of n-hexane and acetone. The structure of the polymer was characterized by nuclear magnetic resonance (NMR)[14] (Fig. 1). From NMR analysis, the methyl group attached to the silicon polysiloxane chain was observed at $\delta = 0$ ppm,[15] and the phenyl group attached to the silicone atom was observed at $\delta = 7.2–7.3$ ppm. The existence of those two groups of peaks indicates that polysiloxane had indeed been introduced into the SA monomer and the SAA copolymer.

For elemental analysis in the liquid state, the sample has to be completely solubilized in water to form a clear solution. The siliconized copolymers prepared in this study could not be completely solubilized in water, thus they are analyzed by solid-state elemental analysis. For the solid-state type of analysis, if the compound cannot be completely burned, the residual solid (SiO_2) retained in the silica column of the elemental analysis unit can cause deviations. In the elemental analysis study, the silicone content measured by a solid-state elemental analysis method was compared with a calculated value. Calculation is based on two assumptions: (1) on the backbone of polysiloxane, the number of silicone atoms is equal the number of oxygen atoms; and (2) after copolymerization, SA monomer and acrylic acid monomer have been completely consumed. This assumption is acceptable due to the yields of those copolymerizations that are in the range of 98–100%.
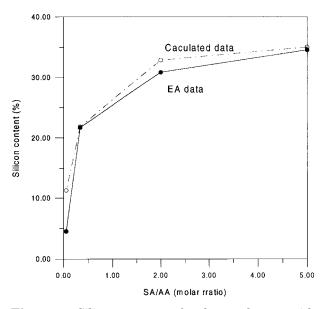
The equivalent weight of SA was calculated to be 320, based on an equivalent weight of SY 231 of 222. The silicone content of SY 231 is 89%; thus, the silicone content in the SAA copolymer, respectively, can be calculated as:
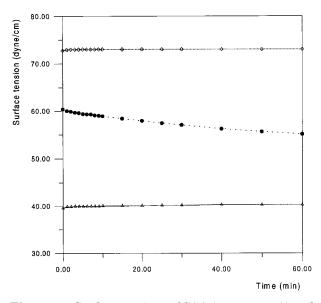
Si (wt %) in SAA

$$= [(207/320)89\%][M/(M + rm)]$$

where M and m are the molecular weight of SA and acrylic acid (320 and 72, g mol^{-1}, respectively), and r is the molar ratio of SA/acrylic acid. The measured (solid line) and calculated (dotted line) silicon contents as a function of different SA/AA ratios are shown in Figure 2. It is seen that the results from elemental analysis measurements agree closely with the calculated values. This demonstrates that two previously described assumptions are reasonable, and that the determination of the silicone content in SAA by solid-state elemental analyses is an appropriate technique.

Surfactants reduce the surface tension[16] (r) of water, because surfactant molecules transfer to the air/water interface and decrease the cohesive force between water molecules. The reduced amount is proportional to the surface excess concentration[17] of surfactant. An important function

Figure 2   Silicone contents for the copolymers with different SA/AA ratios, data from solid-state elemental analysis (EA; solid line), and mathematical calculations (dotted line).

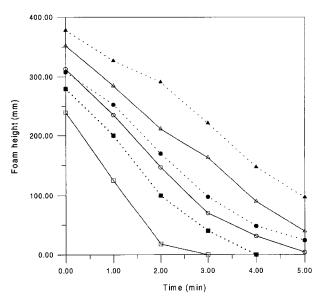**Figure 3** Surface tensions of SAA (1000 ppm, ●) and SLS (1000 ppm, △) and water (◇) as a function of time.

for a surfactant in its role as an emulsifier is that the surfactant can effectively reduce the interface tension at an oil/water interface. Figure 3 shows the surface tension of water as a function of time in the presence of SAA copolymers, compared with normal surfactant (SLS). There are two interesting results that can be observed in Figure 3:

1. For SAA: $\gamma = 61$ dyne cm^{-1} at $t = 0$; the surface tension for SAA (i.e., 61 dyne cm^{-1} at $t = 0$ min) is higher than that of the typical surfactant, SLS (i.e., 39 dyne cm^{-1}).
2. Surface tension of SAA decreases as a function of time, which is different from the phenomena observed for monomeric surfactant (SLS).
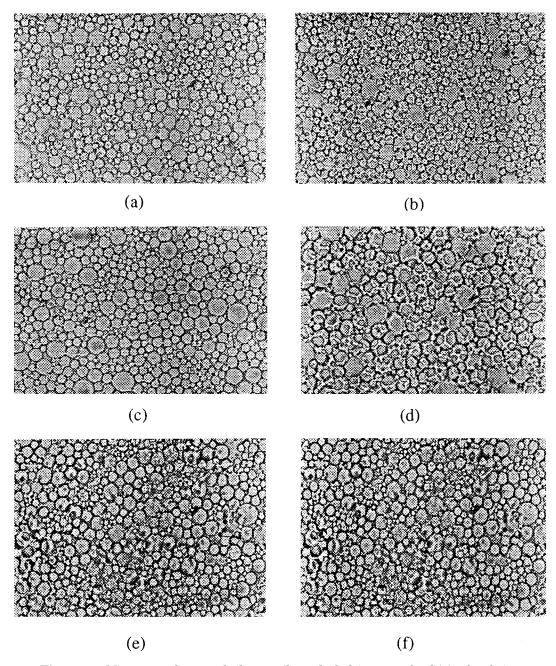
SAA has a silicone moiety that can reduce the surface tension more effectively, compared with conventional surfactant; however, SAA cannot result in a high surface excess concentration due to the difficulty or the exhibit polymer chains to close pack at the air/water interface. On the other hand, SLS is a monomeric surfactant and exhibit, a high surface excess concentration that results in a lower surface tension. This implies that the higher excess surface concentration for SLS is a more important contributor to the reduction of the surface tension than the silicone moiety for SAA. For the SAA copolymer, the decrease in

surface tension as a function of time indicates that the copolymers transfer from the bulk phase to the air/water interface gradually, and the surface tension did not reach equilibrium conditions within a 30-min period for SAA.

The SAA copolymer, with a molar ratio of SA and AA of 1 : 1, was not water-soluble; however, it formed a cloudy suspension in pure water or in 5% PCS aqueous solution, but formed a clear solution in 10% PCS aqueous solution. Because the wavelength of visible light is 400–700 nm, the particles with sizes larger than 50 nm scatter light and result in the formation of a cloudy solution. The particle size of SAA in 5% and 10% PCS aqueous solutions was measured by laser light scattering to be 600 nm in 5% and 50 nm in 10% PCS aqueous solutions. This demonstrates why the solution is cloudy in 5% and clear in 10% PCS aqueous solutions. Cloudiness means that SAA was self-emulsified in the 5% PCS aqueous solution. These results indicate that the addition of 5% PCS helps SAA to be emulsified in water, whereas 10% PCS causes SAA to be soluble in water. The defoaming properties of SAA in aqueous solution and in 5% and 10% PCS aqueous solutions were measured and compared as described.

SLS is a popular foaming agent for research and industrial applications. In the absence of

Figure 4 Defoaming abilities of SAA self-emulsified (1000 ppm) in water and cosolvent (5% or 10% PCS). 0% PCS: ▲, △ (without and with SAA). 5% PCS: ●, ○ (without and with SAA). 10% PCS: ■, □ (without and with SAA).

Figure 5 Microscope figures of silicone oil emulsified in water by SAA after being emulsified at time 0 h, and 1, 3, 7, 14, and 30 days. 500 × original magnification. Define: (a) 0 h (b) 1 day (c) 3 days (d) 7 days (e) 14 days (f) 30 days

SAA (blank), the foam height of an aqueous SLS solution decreases with the increasing time, whereas the SLS solutions containing 5% and 10% PCS show lower foam heights (Fig. 4). The addition of SAA results in a decrease in the foam height after a given time for each SLS solution. Obviously, SAA is able to defoam SLS solutions both in pure water and in 5% or 10% PCS solutions.

SAA was used as an emulsifier to emulsify a silicone oil/water mixture (100 : 50, w/w). The SAA concentration was chosen to be 5%, so that it is within the reasonable range of emulsifier concentrations for usual emulsion applications.
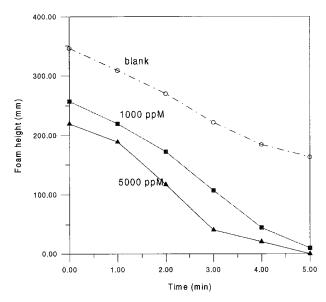
The resulting emulsion was dyed by water-soluble dyes, and the conductivity of that emulsion was found to be close to that of water. This indicates that the emulsion is an oil-in-water system [i.e., the silicone oil droplet is surrounded by water (water is a continuous phase)]. The particle size of this emulsion was measured to be 1–3 μm by a laser-induced light diffraction method.

The stability of this emulsion was not evaluated by measuring the height of separated phase, because the boundary of the phase separation was not obvious. Instead, it was evaluated by an optical microscopy method[18] by observing the change in particle size. Particle size was measured immediately after preparation of the emulsion (0 h) and after 1, 3, 7, 14, and 30 days (shown in Fig. 5). Figure 5 shows that the particle size did not change appreciably after 14 days. After that, the particle size became slightly bigger. No stabilizer was used in this emulsion system to observe the original emulsifying ability of SAA copolymer only. The emulsion system remained stable without large changes in particle size over 30 days, indicating that SAA is an effective emulsifier for emulsifying silicone oil in water.

The previously described emulsion could then be easily diluted by water, because it is an oil-in-water emulsion. The diluted emulsion was added to SLS solution to evaluate the defoaming ability of the silicone droplet emulsified by SAA. As shown in Fig. 6, 1000 ppm of SAA decreases the foam height. As the concentration of SAA was increased to 5000 ppm, the defoaming effect is more remarkable. Obviously, the silicone/water emulsion prepared using SAA as an emulsifier is an effective defoamer. Comparing Figures 4 and 6, it can be concluded that the emulsified silicone oil exhibits better defoaming properties to SLS, compared with the self-emulsion type of SAA (with SA/AA = 1 : 1) at the same level (1000 ppm).

CONCLUSIONS

In this research, copolymers containing polysiloxane side chains were successfully synthesized, as evidenced by the silicon group that was attached to the methyl and phenyl groups as observed by the peaks shown in NMR. Those copolymers were neutralized by triethylamine to have appropriate

Figure 6 Defoaming abilities of the silicone oil emulsified in water by SAA (1000 and 5000 ppm).

hydrophilicity; thus, the SAA copolymer was self-emulsified to form emulsions in aqueous and co-solvent (PCS) solutions; these emulsions exhibited excellent defoaming abilities. The neutralized copolymers were also used as emulsifiers to emulsify silicon oil in water and resulted in a stable oil-in-water emulsions. This emulsion again exhibited defoaming properties and is more efficient than that of self-emulsified emulsions of SAA copolymer.

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