

Preparation and Properties of Water-Soluble Polyester Surfactants. III. Preparation and Wetting Properties of Polyethylene Glycol–Polydimethylsiloxane Polyester Surfactants

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ABSTRACT: A novel series of water-soluble polyethylene glycol–polydimethylsiloxane (PEG–Silicone) polyesters was prepared by reacting organopolysiloxane with hydroxyl-terminated polyester. The polyesters are obtained by the polymerization of maleic anhydride (MA) and PEGs (number-average molecular weights $M_n = 2000$ – $10,000$). FTIR, ¹H-NMR, and elemental analysis were employed to characterize the structures of these compounds. These compounds exhibit good surface activities such as surface tension and low foaming. The influence of the PEG–Silicone

polyester surfactants introduced at various concentrations (0.1–2 wt %) was examined by the contact angle method. The measurements performed with various solid substrates indicated that, at comparable concentrations, the PEG–Silicone polyester surfactants were shown to be more efficient for wetting PET and glass. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 88: 1236–1241, 2003

Key words: polysiloxanes; silicones; surfactants; polyesters; water-soluble polymers

INTRODUCTION

Adhesion of coatings to the substrates they cover is a critical problem that limits, in many instances, the applicability of the thermal or radiative curing of liquid resins. To improve the interactions between the solid substrate and the liquid film, it is of prime importance to ensure good wetting of the surface.

Silicone surfactants are becoming increasingly important in the pharmaceutical and cosmetic industry because of their versatility, low cost, and technology advantages. Silicone oil/water interfaces in the presence of surfactants have been the focus of considerable discussion, and contact angles at these interfaces have been measured. If the polyester fiber is first covered with oil, it is then difficult for water to displace the oil phase and the contact angle measured is greater than 90°. ^{1–3}

Recently, the wetting properties of surfactants on drug surfaces have shown that surfactants vary considerably in their ability to wet surfaces. ^{4–6} Wetting was evaluated through the determination of the surface tension and contact angle of the various solutions using poly(methyl methacrylate) (PMMA) as a surface

have been studied. ⁷ It is concluded that the surfactant solutions tested were significantly better for wetting the surface.

In the present study, a novel series of water-soluble polyester surfactants were prepared by the reaction of a hydroxyl-terminated polyester and an organopolysiloxane. The polyesters used in this study were prepared by the polymerization of maleic anhydride (MA) and polyethylene glycol (PEG). The surface active properties of PEG–Silicone polyesters including surface tension and wetting were investigated. The investigation was performed with organic and inorganic materials exhibiting various surface energies.

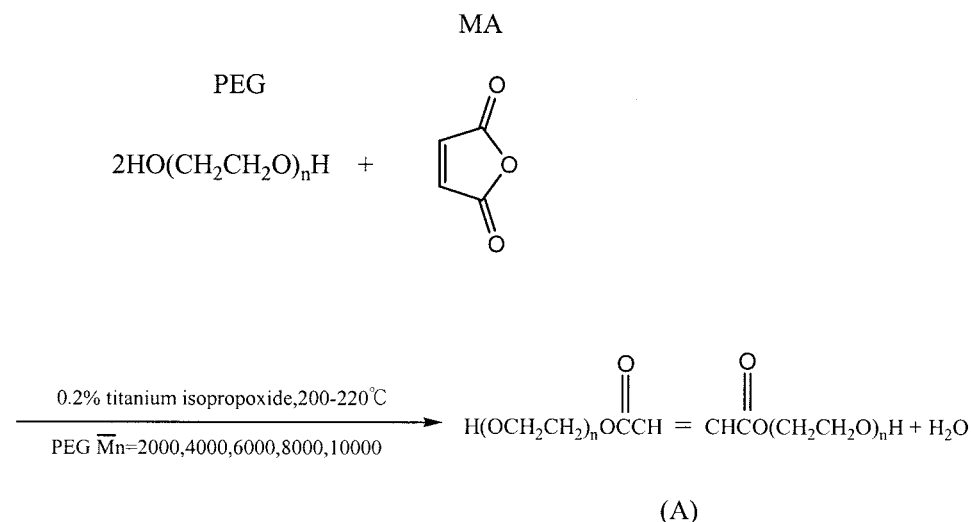
EXPERIMENTAL

Materials

Commercial-grade silanol chain-stopped polydimethylsiloxane (molecular weight 3400) was supplied by Dow Corning (Midland, MI). Reagent-grade titanium isopropoxide, sodium hydrogen sulfite, maleic anhydride, and polyethylene glycol (number-average molecular weight, $M_n = 2000$ – $10,000$) were purchased from Hayashi Pure Chemical Co. (Japan) and used without further purification.

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Step1 :



Step2 :

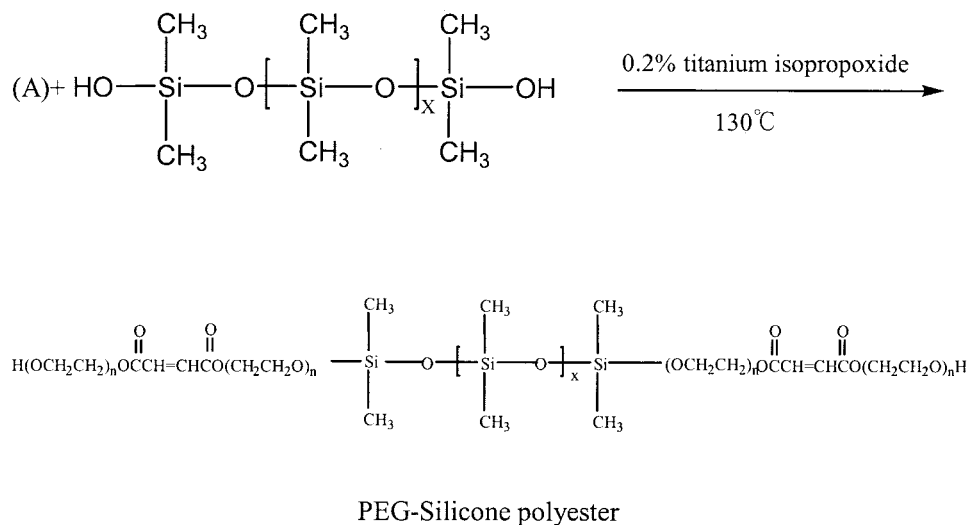


Figure 1 Preparation of PEG-Silicone polyesters.

Preparation of PEG-Silicone polyester surfactants

Figure 1 illustrates that the PEG-Silicone polyesters were prepared in two steps. In the first step, the water-soluble polyesters were prepared by the polymerization of 2 mol PEG and 1 mol MA in the presence of 0.2% catalyst (titanium isopropoxide) at 200–220°C for 6–8 h. In the second step, 2 mol of the polyesters that were obtained from the first step were reacted with 1 mol silanol chain-stopped polysiloxane in the presence of the same catalyst (0.2%) at 125–130°C for 3–5 h.

Analysis

The acid value and hydroxyl values were determined by standard methods described elsewhere, and from these values the molecular weights of polyesters were calculated.⁸ The structure of the final products was confirmed by infrared spectrum (IR), proton nuclear magnetic resonance (¹H-NMR) spectrum, and elemental analysis. IR spectra were obtained with a Perkin-Elmer Spectrum One (Perkin Elmer Cetus Instruments, Norwalk, CT) and ¹H-NMR spectra were obtained with a Varian 360 L NMR (Varian Associates, Palo Alto, CA).

TABLE I
Analysis of PEG–Silicone Polyesters

Compound	Acid value	OH value	\bar{M}_n	Elemental analysis (%) ^a			
				C		H	
				Obs.	Calc.	Obs.	Calc.
PEG 2000–Silicone	5.98	6.14	9258	41.91	39.54	9.09	8.68
PEG 4000–Silicone	3.19	3.00	18116	49.29	45.69	9.03	8.85
PEG 6000–Silicone	2.30	2.11	25432	49.20	48.26	8.90	8.92
PEG 8000–Silicone	1.83	1.43	34424	50.82	49.68	8.97	8.96
PEG 10000–Silicone	1.79	0.87	42120	51.86	50.57	8.96	8.98

^a Obs., observed; Calc., calculated.

Measurements

Surface tension was determined at room temperature with a Japan Kaimenkaguka CBVP-A3 surface tensiometer (Kyowa Interface Science Co., Japan). Foaming properties were determined by the Ross–Miles method. Foam production was measured as the height of the foam initially produced, and foam stability was measured as the height after 3 min. Buffer capacity was determined at room temperature with a Solar pH meter.

The contact angle, which describes the angle formed between the planes tangent to the surfaces of the solid and the liquid at the wetting perimeter, was measured with a FACE CA-5 contact angle meter. The PEG–Silicone surfactants were eventually added (0.15–2 parts); all indicated percentages are expressed in wt %.

RESULTS AND DISCUSSION

Preparation

Table I shows the results of an elemental analysis of the final PEG–Silicone polyesters containing different lengths of a polyoxyethylene chain. The number-average molecular weight (\bar{M}_n) of compounds was calculated according to the following expression:

$$\bar{M}_n = \frac{1}{(\text{Acid value} + \text{Hydroxyl value}) / (2 \times 56.1 \times 1000)}$$

A typical IR spectrum of the synthesized PEG2000–Silicone polyesters, as shown in Figure 2, displayed bands at 2880 cm^{-1} (CH_2), 1260 cm^{-1} (C—O—C), and $830\text{--}1110 \text{ cm}^{-1}$ (Si—O—Si). These bands were characteristic of the desired compounds. The structure of the compounds was further supported by the $^1\text{H-NMR}$ spectrum, as illustrated for PEG2000–Silicone in Figure 3. It gave signals at $\delta = 0.1 \text{ ppm}$ (Si—CH_3) and $3.2\text{--}3.8 \text{ ppm}$ ($\text{—OCH}_2\text{CH}_2\text{O—}$).

Surface tension

Surface tension is one of the most important surface properties of a surfactant solution. The PEG–Silicone

polyesters prepared in this study possess complex amphiphathic structures contributed by the polydimethylsiloxane group. As shown in Figure 4, a decrease in the surface tension of the aqueous solution was observed when the concentration of the PEG–Silicone polyesters in the solution was increased. In addition, the surface activity was sensitive to the length of the polyoxyethylene chain presented in these polyesters. An increase in the chain length resulted in a decrease of the surface activity. These results may be attributed to the fact that an increase of the hydrophilic portion of the PEG–Silicone polyester results in a decrease in its concentration at the surface.

Foaming properties

The low-foaming tendency of surfactants is an important property required in some applications, such as using surfactants as dyeing auxiliaries in the modern textile industry. In some cases, most of the silicone-containing surfactants have been shown to be excellent defoamers in antifoam applications.⁹ As shown in Table II, all of the PEG–Silicone polyesters showed excellent low-foaming properties and low-foam stability. These excellent low-foaming properties are probably attributable to the presence of multihydrophilic groups, which cause a considerable increase in the area per molecule and produce less cohesive forces at the surface. The water-soluble poly-

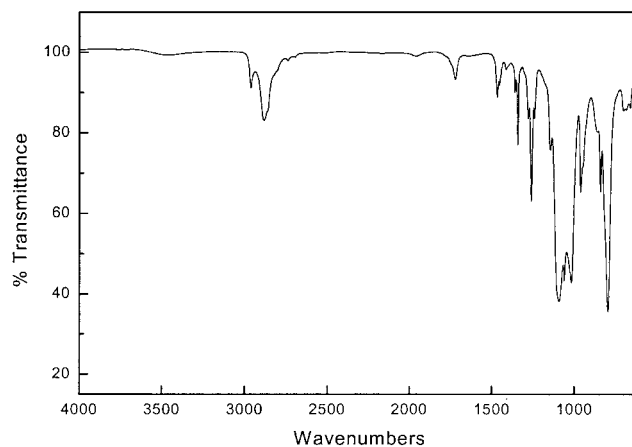


Figure 2 FTIR spectra of PEG2000–Silicone polyester.

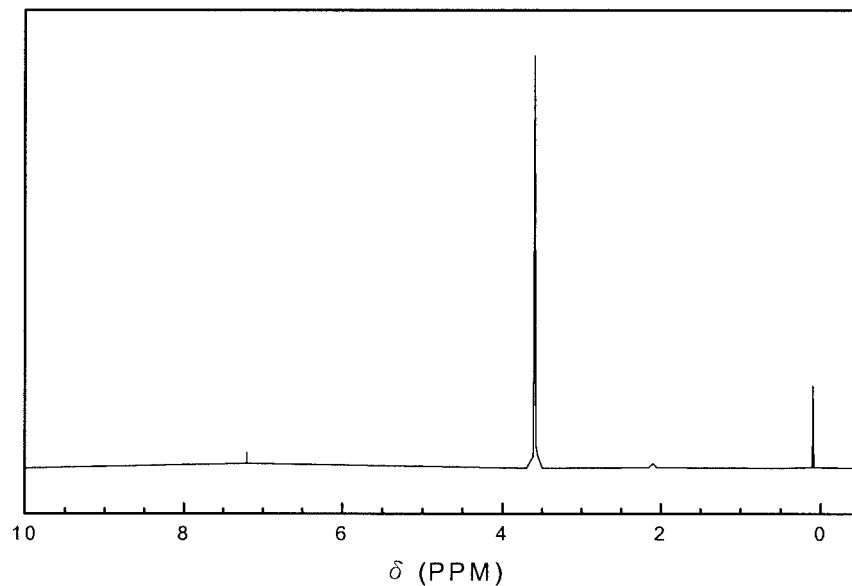


Figure 3 $^1\text{H-NMR}$ spectra of PEG2000-Silicone polyester.

mers, which are believed to coil in the aqueous phase to decrease the cohesive force, are the result of intra- and intermolecular bonding.

Table II shows the foaming properties of the PEG-Silicone polyesters. The initial foam height was low in all cases, giving an indication of the suitability for use where low-foaming properties are required. The compounds can also lower the stability of the existing foams,

as indicated by the decrease in foam height measured after 3 min of initial foam formation. The low-foaming effects are similar to those observed with surfactants prepared in our previous studies.^{10,11} These effects are probably attributable to the presence of multihydrophilic groups, causing a considerable increase in the area per molecule and producing less cohesive forces at the surface.

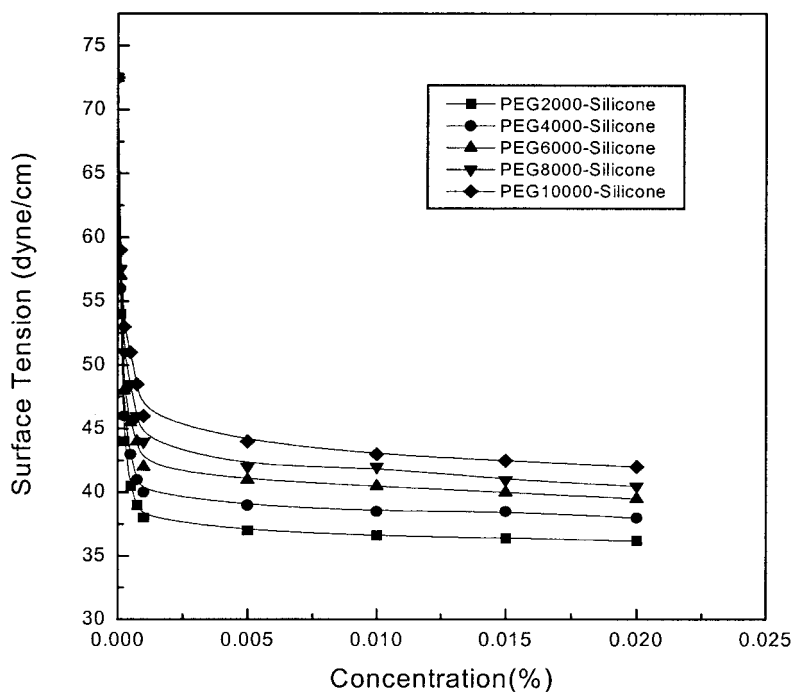


Figure 4 Plots of surface tension against concentration of PEG-Silicone polyesters.

TABLE II
Foaming Properties of PEG-Silicone Polyesters

Compound	Foam height (mm)	
	Initial	After 3 min
PEG 2000-Silicone	3.0	2.0
PEG 4000-Silicone	5.0	2.0
PEG 6000-Silicone	7.0	2.0
PEG 8000-Silicone	10.0	2.0
PEG 10000-Silicone	10.0	2.0

pH buffer capacity

In textile dyeing processes, acid or base agents are usually added to improve the softness, handle, and color properties of the fabrics. However, these auxiliaries cause a pH change effect on dyes. Surfactants are used for improving the pH buffer capacity and providing a better stability under dyeing conditions.

Figure 5 shows the buffer capacity of solutions containing different PEG-Silicone polyester surfactants. In each solution the concentration of the surfactant is 10 g/L. This figure shows that for pure water, the pH changed quickly from 11.0 to 3.0 as the HCl amount was raised from 0 to 1.5 mL by the addition of 0.1N HCl. On the other hand, the results in Figure 5 indicate that the addition of the PEG-Silicone polyester surfactants resulted in solutions that have better buffer capacities than that of pure water. It explained that these PEG-Silicone polyesters possessed multiple ionic

groups and polyoxyethylene chains in the hydrophilic portion.

Wetting power

Wetting power is another important property of dyeing auxiliaries. In the dyeing process, good wetting power of dyeing auxiliaries may accelerate the diffusion or penetration of dyes into the fibers, as well as improvement with leveling. The silicone additives induce better or similar wetting effects than those of conventional surfactants.¹² The outward measure of the degree of wetting is the contact angle: the angle formed between planes tangential to the surfaces of the solid and the liquid at the wetting perimeter.

Figure 6 illustrates the contact angle of solutions containing different PEG-Silicone polyesters. A decrease in the contact angle of the aqueous solution was observed when the wt % of the PEG-Silicone polyesters in the solution was increased. In addition, an increase in the polyoxyethylene chain length of the nonionic segment clearly decreased the contact angle, that is, PEG10000-Silicone, which has the minimum value contact angle, is a better wetting agent than other products. This phenomenon, similar to surface tension, is attributed to the enlargement of the hydrophilic portion of the surfactant molecule, resulting in a decrease in concentration of surfactant at the liquid surface.

Figure 7 shows each type of substrate for which we measured the contact angle without additive and with

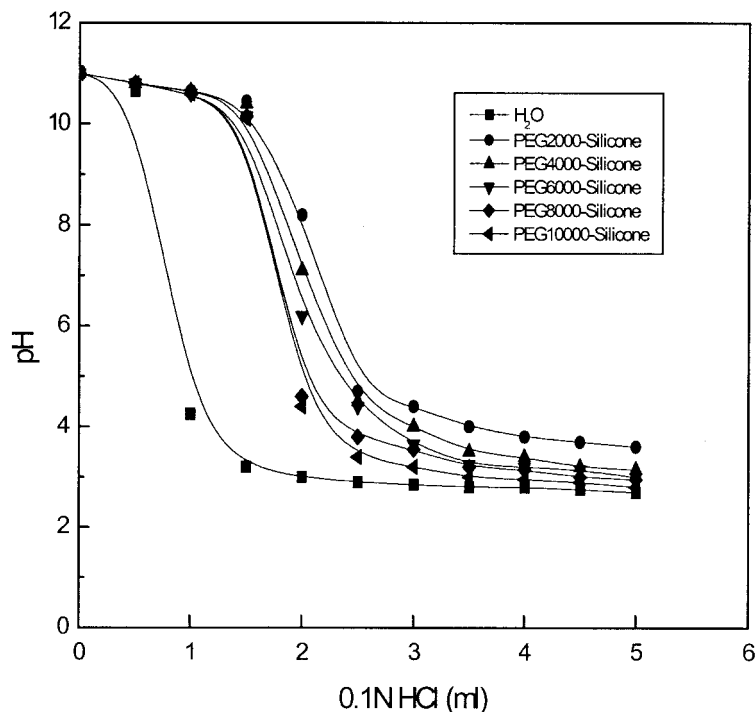


Figure 5 pH buffer capacity of PEG-Silicone polyesters.

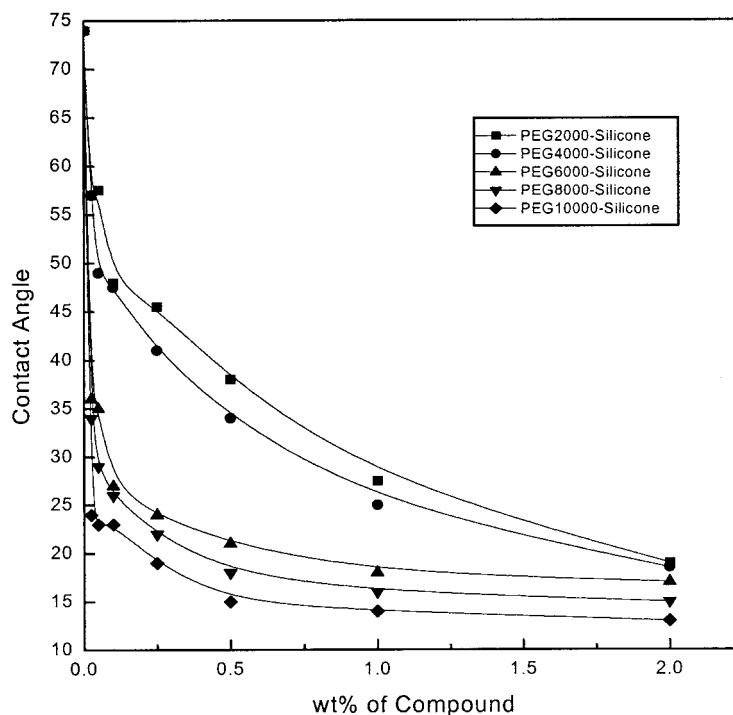


Figure 6 Plots of contact angle against the amount of PEG-Silicone polyester.

0.15, 0.3, 1, and 2% of PEG2000-Silicone surfactants. On Teflon, PVC, PE, and PU, the contact angle was 65–90°, which indicates that the PEG-Silicone polyesters had less efficient wetting properties. Conversely, on polyethylene terephthalate (PET) and on glass, the PEG-Silicone polyesters had better wetting properties than those of other substrates; the contact angle of PET from 74 to 35° and of glass from 47 to 19° was obtained by the addition of PEG-Silicone polyesters up to 2%, respectively. PEG-Silicone polyesters exhibit an excellent wetting effect on glass.

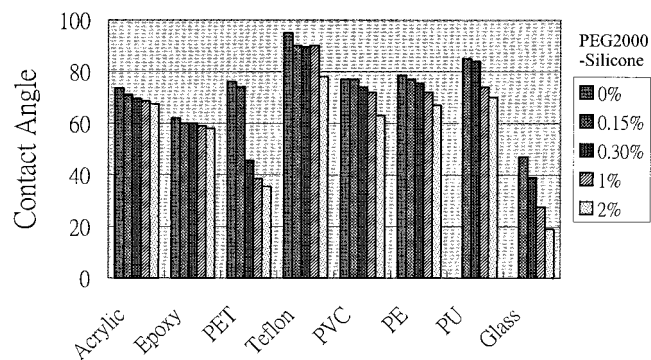


Figure 7 Comparative evolution of contact angle θ on various substrates containing variable amounts of wetting agent (left to right: 0, 0.15, 0.30, 1, and 2 wt %).

CONCLUSIONS

A novel series of PEG-Silicone polyesters with water-soluble properties were prepared by the reaction of organopolysiloxane and hydroxyl-terminated polyesters. The polyesters used in this study were prepared by the polymerization of maleic anhydride and polyethylene glycol. These novel compounds were found to exhibit good surface activities, including surface tension and foaming. The PEG-Silicone polyesters were shown to be more efficient for wetting PET and glass. Increasing the amount of the PEG-Silicone polyesters improved their wetting ability.

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