Rheology of Decamethylceclopentasiloxane (cyclomethicone) W/O Emulsion System

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Abstract: A highly dispersed W/O emulsion of silicone oil (cyclomethicone)/water system was prepared with a nonionic surfactant. The surface and interfacial tension between the oil and water were characterized in terms of the droplet size distribution and viscosity change of the emulsion. When the dispersed phase concentration was relatively high, the viscosity of the emulsion was rapidly increased and the droplet size of the emulsion was decreased. The rheological behavior of the emulsion system showed non-Newtonian and shear thinning phenomena depending upon the content of the dispersed phase. The droplet size of the emulsion was decreased with increasing surfactant content and water concentration. The relative viscosity of the emulsion was better predicted with the Choi-Schowalter model than with the Taylor model. The value of the complex modulus increased with increasing surfactant concentration. The linear viscoelastic region was expanded with a dispersed phase concentration. According to the change in the viscosity, the behavior was classified into three distinct regions: [I] linear viscoelastic, [II] partially viscoelastic, and [III] viscous. The creep/recovery behaviors in each region were characterized.

Keywords: rheology, silicone, W/O emulsion, surfactant, shear thinning.

Introduction

Due to the various unique interfacial, physical, chemical properties such as chemical resistance, temperature resistance, high gas permeability, and insulating properties, silicone compounds composed of alternating silicon and oxygen atoms in the main chain have been widely used in construction, electronics, food, paper-making, personal care products, aerospace, and biomedical applications.[1,2] One of the important applications of silicone oil as one of the silicone compounds is a cosmetic application due to its water-repelling property, anti-foaming, and aesthetic performance. In the cosmetic application, silicone oil is often formulated in a water-in-oil (O/W) emulsion type. Therefore, the understanding the rheological properties of silicone emulsions has been important for their relationship to industrial applications.[3,4]

Silicone oil has several structures such as liner dimethicone, cyclic cyclomethicone. Cyclomethicone has better lubricating properties and chemical affinity with other chemical agents. However, silicone oil significantly destabilizes emulsion due to its low interfacial tension.[5,6] Silicone surfactants show characteristic properties which make their use very attractive to the cosmetic industry.[7] One of the advantages

of silicone surfactants is that the molecular weight can be readily controlled. Siloxanes can have a very high molecular weight which is advantageous for forming W/O emulsions. They improve the aesthetic property by eliminating high melting point waxes.

W/O emulsions are basically obtained by dispersing the aqueous phase into an oil phase.[8,9] They are produced by fragmenting aqueous solution, accompanied with adsorption of the surfactant on the surface of the aqueous droplet phase, leading to an aqueous droplet phase to be stabilized by the surfactant. The persistence of the surfactant is entirely governed by its surface activity to prevent coalescence of the dispersed water phase. Surfactant molecules adsorb on the surface of the dispersed phase and lower interfacial tension between oil and aqueous phases. Finally, they provide emulsion stability against flocculation and coalescence of the dispersed phase. For emulsifying silicone emulsions, nonionic surfactants are generally used, which include polyoxyethylene alkyl ether and polyoxyethylene alkylphenyl ether.[10,11] Despite of their good emulsifying capability, such surfactants are toxic and the biodegradability is low.

In this study, silicone surfactants, which have bio-compatibility and improved affinity with other chemicals, were employed in W/O silicone emulsion systems using a nonionic silicone-based surfactant, PEG/PPG 10/1 demethicone

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(cetyl demethicone copolyol, ABIL EM90, Goldschmidt) in conjunction with a hydrophilic cosurfactant, dimethicone copolyol methyl ether (KF-6011, Shinetsu). The rheological properties of prepared emulsions were characterized in terms of viscoelastic behaviors where the effect of a surfactant and cosurfactant was investigated.

Experimental

Materials. As a continuous oil phase, decamethylcyclo-pentasiloxane (KF995, Shinetsu) was used. A lipophilic non-ionic silicone surfactant, cetyl PEG/PPG 10/1 demethicone (cetyl demethicone copolyol, ABIL EM 90, Goldschmidt) and a hydrophilic cosurfactant, demethicone copolyol methyl ether (KF-6011, Shinetsu) were used. The physical properties of the materials are listed in Table I and their chemical structures are shown in Figure 1. Water was doubly distilled and deionized prior to use.

Sample Preparation. Predetermined amounts of cyclomethicone and surfactants were mixed at 25 °C. While the mixture was stirred with a homogenizer (T.K. Homomixer MARK II, Tokushu Kika Kogyo Co., Japan) at 2,000 rpm, deionized water was charged using a micro tube pump (WHEATON MP-3) at the injection speed of 5.2 mL/min for 50 min. After the addition of water, the emulsion was continuously mixed at 2,000 rpm for 10 min. Aliquot of stock emulsion was withdrawn and water was further added to the parent emulsion to have 60, 70, and 80 vol% (water content) while stirring at 1,000 rpm.

Characterizations. Surface and interfacial tension between the continuous oil phase and water were measured using a digital tensiometer (Kruss GMBH, Germany) employing a Du Noüy ring method at 25 °C. The morphology and the average diameter of the emulsion were measured using a digital camera (Polariod) equipped microscope (Olympus BX60, Japan). The average size was obtained using an image analyzer (SimplePCIp). Rheological properties of the emulsions prepared with various concentrations of silicone oil and surfactants were investigated by means of Stress Tech Rheometer (Reologica Instrument, Sweden) using two different geometries, bob and cup, and cone and plate (plate diameter: 40 mm, cone angle: 4°). The linear and nonlinear viscoelastic regions were determined from the dynamic oscillatory stress sweep mode (1-100 MPa) using a frequency of 1 Hz. The recovery behavior was investigated at the different
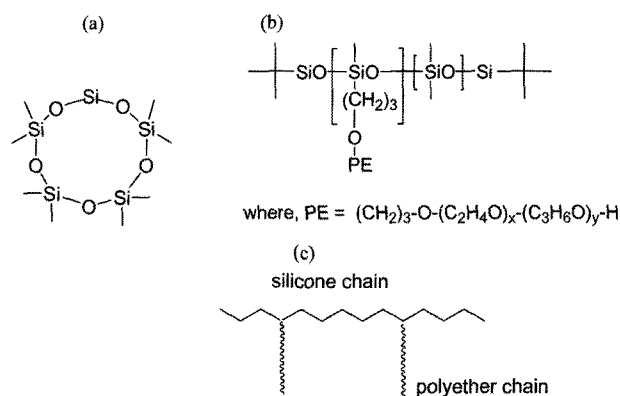

Figure 1. Chemical structure of the materials used: (a) KF-995, (b) ABIL EM 90, and (c) KF-6011.

stress levels at each region. All measurements were carried out at 25 °C.

Results and Discussion

Measurement of Surface and Interface Tension. Generally, the size of the dispersed phase determines the nature of emulsions. If the size of the dispersed phase is large in a micrometer scale, it causes sedimentation and phase separation with time. However, if the dispersed phase is present in a nanometer scale, the emulsion possesses a good colloidal stability.[12-14] According to the size of the dispersed phase, the emulsions are classified into macro-emulsion having the size above 0.4 μm, mini-emulsion with the size ranging 0.1-0.4 μm, and transparent micro-emulsion with the size below 0.1 μm. Currently, industrially used emulsions have the size of the dispersed phase up to 4 μm caused by time-dependent coalescence. So it is of great importance to decrease the size of the dispersed phase as possible.[15] The size of the dispersed phase is strongly influenced by the concentration of surfactants. In order to obtain sufficiently stable emulsions, the properties of the silicone oil and water phases in terms of surface and interface tension should be characterized first.

In Figures 2 and 3, the surface and interfacial tension of oil solution with respect to the concentration of the hydrophilic silicone-based surfactant (KF-6011) at 25 °C are represented. As the concentration of the surfactant increases in the oil phase, the surface and interfacial tension decrease due to the decrease in the surface free energy by the absorp-

Table I. Physical Properties of Materials Used in This System at 25 °C[a]

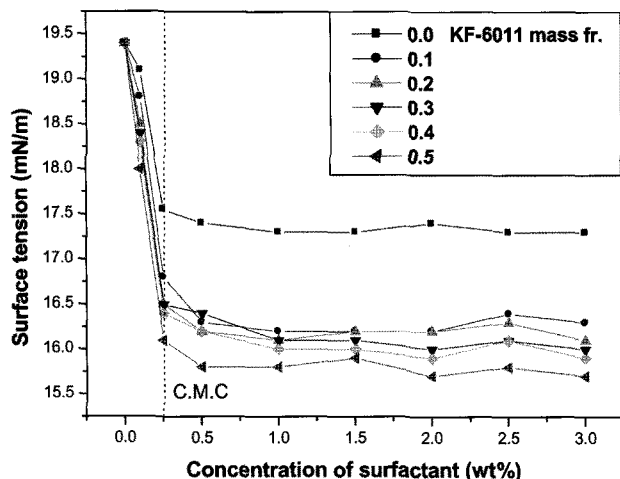| Surfactant	Role	Surface Tension (mN/m)	Specific Gravity	Viscosity (cP)	HLB	MW
KF-995	Continuous Phase	17.8	0.956	4.0	n/a	n/a
ABIL EM 90	Main Surfactant	19.4	0.956	3,720	5	395
KF-6011	Cosurfactant	n/a	1.070	102	14.5	n/a

[a]Given by supplier.

Figure 2. Surface tension of oil solution as a function of surfactant (KF-6011) concentrations at 25 °C.
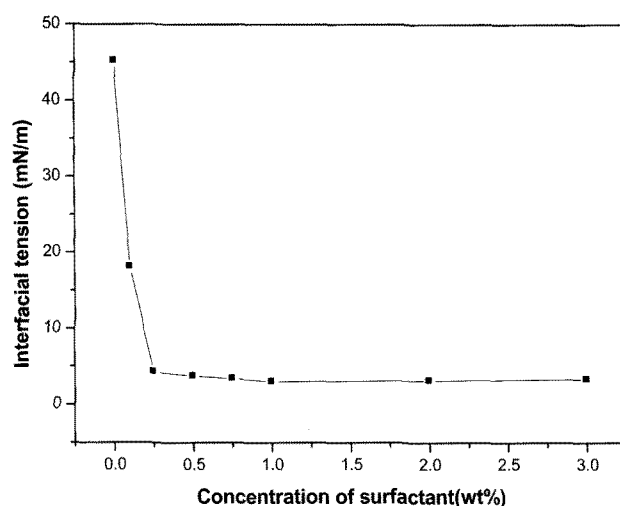

Figure 3. Interfacial tension of oil phase as a function of surfactant (KF-6011) concentrations at 25 °C.

Figure 4. Optical microphotographs of 80% water content emulsions prepared with different concentrations of the surfactant (ABIL EM 90) in the absence of KF-6011: (a) 0.5, (b) 1.0, (c) 1.5, (d) 2.0, (e) 2.5, and (f) 3.0 wt% ABIL EM 90.

Figure 5. Average droplet size of emulsion prepared with different concentrations of the surfactant (ABIL EM 90) in the absence of cosurfactant (KF-6011). The parent W/O emulsions were diluted in 60, 70, and 80% water.

tion of the surfactant molecules at the interface between oil and water.[16] The abrupt decrease in the surface and interfacial tension at 0.25 wt% of the surfactant concentration indicates the critical micelle concentration (cmc). The results imply that the emulsion should contain more than 0.25 wt% KF-6011 to obtain colloidally stable state. Therefore, the emulsions containing the surfactant above cmc were prepared and characterized for further characterizations. Furthermore, the utilization of the controlled concentration of the hydrophilic cosurfactant, KF-6011, sufficiently decreases the interfacial tension by preferential locating at the interface.

Size Distribution of the W/O Emulsion. Considering the aforementioned effect of the size of the dispersed phase on the emulsion stability, the optimum concentrations of surfactant and cosurfactant were determined in order to generate small size of the dispersed phase with narrow size distribution as possible. Herein, the parent W/O emulsion was
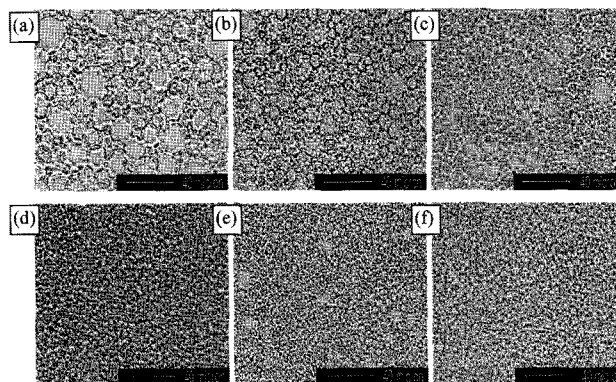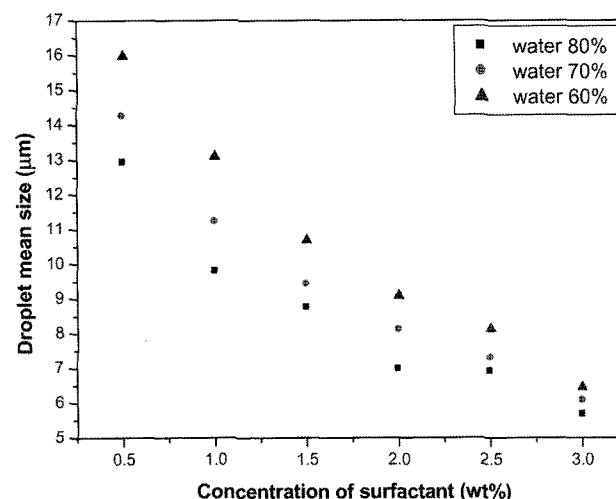
diluted with water to observe the morphology of the emulsion droplets. Figure 4 shows the optical micrographs of the size distribution of W/O emulsion. The parent emulsion was prepared with various concentrations of ABIL EM90 in the absence of cosurfactant, KF-6011. The parent emulsion was diluted in 80% water. The variation of size of the emulsion droplet diluted in 60, 70, and 80 % water is depicted in Figure 5. A crosspacking structure is achieved as the concentration of the dispersed phase increases. The smaller emulsion droplets are obtained at the high amount of water with a fixed concentration of the surfactant. As the concentration of the surfactant increases from 0.5 to 3.0 wt%, the average size of the dispersed phase decreases. When the amount of surfactant is greater, the surfactant molecules absorb on wider interface area, leading to the reduction of the droplet size. The reduction of the droplet size with respect to the

concentration of the dispersed phase can be interpreted by the following equation:[17]

$$a_m = 6R(1-\Psi)/2\Psi \qquad (1)$$

where a_m denotes the mean surface-to-surface distance, R is the droplet radius, and ψ represents the volume fraction of dispersed phase. In eq. (1), as the concentration of dispersed phase increases (i.e. as the concentration of continuous phase decreases), the mean surface-to-surface distance between the droplets becomes closer, finally resulting in the reduction in the average size of the droplets.

In addition to the size issue, the size distribution of emulsion droplets also has a great significance in order to maximize the colloidal stability. It has been known that the use of cosurfactants is a practical strategy to obtain narrowly distributed droplets. The addition of hydrophilic cosurfactants causes close packing of surfactant molecules at the interfaces, which generates smaller droplets with a narrow distribution. In this case, the viscosity of the emulsions increases.[18,19] Figure 6 shows the effect of the presence of cosurfactant, KR-6011, on the droplet mean size of emulsions prepared with 3.0 wt% main surfactant, ABIL EM90. It is noted that the parent emulsions are again diluted in 60, 70, and 80 % water. With the increase in the amount of the cosurfactant, the average size of the droplets decreases up to the 0.3 wt% cosurfactant, then grows with the amount of the cosurfactant since repulsion force among the closely packed hydrophilic surfactant molecules overwhelms the attractive force.

Effects of the Concentrations of Dispersed/Continuous Phases on Viscosity. Rheology of the emulsion has a close relationship with the emulsion stability, i.e. the variation of droplet size. Therefore, rheological properties should be carefully investigated for monitoring the stability of emulsion systems. The rheological behavior of the emulsions depends on size and shape of the dispersed phase, viscosi-
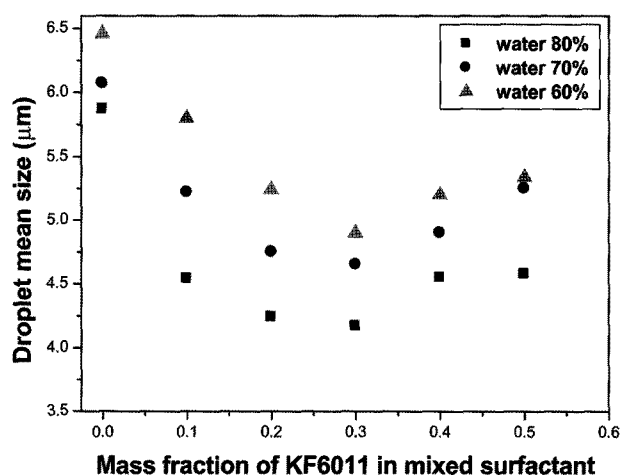
ties of the continuous and dispersed phases, shear rate, temperature, pressure, and so on. Herein, the shape of the droplets is assumed to be perfectly spherical, and the measurements were performed at 25 °C and 1 atm. Therefore, the viscosity of the continuous phase, concentration of surfactants, and viscosity of the dispersed phase were taken into account to characterize viscoelastic properties of the emulsions in this system.

Figure 7 envisages the viscosity change of the emulsion systems containing various concentrations of the surfactant. This result shows the effect of the concentration of a continuous phase, i.e. oil solution, on the rheological behavior. As the shear stress increases, the viscosity of the oil solutions is hardly changed, showing a typical Newtonian behavior due to a complete mixing between the oil phase and surfactant. It is noted that the increase in the viscosity of the medium with the concentration of the surfactant is ascribed to the higher viscosity of the surfactant than that of the oil phase. In Figure 8, the effect of the concentration of the surfactant at different concentrations of the dispersed phase (various water contents) on the viscosity is represented. It is seen that the amount of the surfactant proportionally increases the
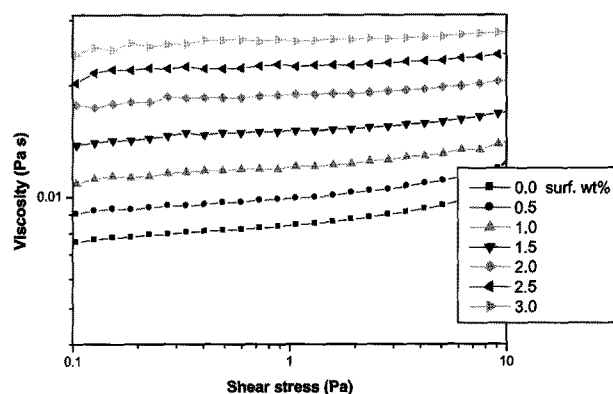

Figure 7. Viscosities as a function of shear stress for different surfactant concentrations of oil solutions.

Figure 6. The effect of the cosurfactant (KF-6011) on the average droplet size of the emulsions prepared with 3.0 wt% surfactant (ABIL EM 90).
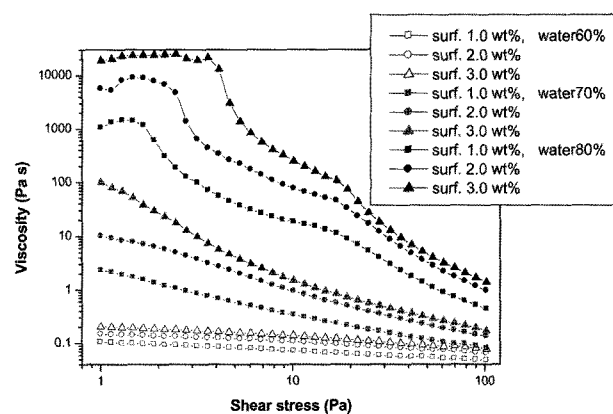

Figure 8. Viscosities as a function of shear stress for 60-80 wt% water contents emulsion systems at different surfactant concentrations.
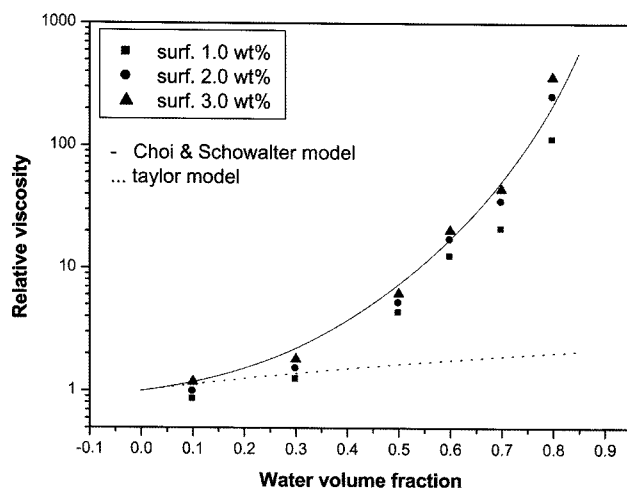
Figure 9. Comparison of relative viscosity data of emulsions with the theoretical emulsion models (solid line: Choi-Schowalter model, dotted line: Taylor model).

viscosity of the emulsions at all water contents. This phenomenon is pronounced at a high concentration of water content, 80%, where the shear thinning behavior is substantially greater.[20] Figure 9 compares the experimentally obtained relative viscosity with well-known Taylor[21] and Choi-Schowalter[22] models.

Taylor model: $\eta_r = \dfrac{\eta_{emul}}{\eta_c} = 1 + \dfrac{(5\kappa + 2)}{2(\kappa + 1)}\varphi$ (2)

where η_r is relative viscosity, κ is a ratio of the viscosity of a disperse to continuous phase, and φ represents the volume fraction of particles.

Choi-Schowalter model: $\eta_r = 1 + I(\lambda)\varphi$ (3)

where $\lambda = \varphi^{1/3}$ and $I(\lambda)$ is determined by the following relationship:

$$I(\lambda) = \frac{2[(5\kappa + 2) - 5(\kappa - 1)\lambda^7]}{[4(\kappa + 1) - 5(5\kappa + 2)\lambda^3 + 42\kappa\lambda^7 + 4(\kappa - 1)\lambda^{10}]}$$ (4)

Since Taylor model does not consider interactions among the particles, it is valid only for diluted systems. So, the experimental data show the best fit with Choi-Schowalter model where the interactions are greatly considered.

Creep/Recovery Behavior. In this section, the viscoelastic properties of the emulsions were investigated where the distinct regions showing different viscoelastic characteristics were identified in a dynamic oscillatory stress sweep mode, then creep/recovery behavior of each region was evaluated.

The elastic property of emulsion is usually witnessed at a emulsion with a high viscosity having a high concentration of dispersed phase. Stress sweep results for the emulsion with 80% water content stabilized with various concentrations of the surfactant is displayed in Figure 10. Below a certain level of shear stress (yield stress), the emulsions possess the constant complex moduli, and then the values are
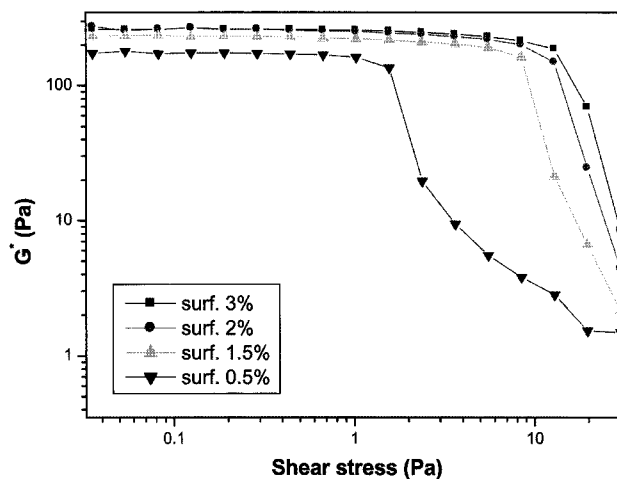

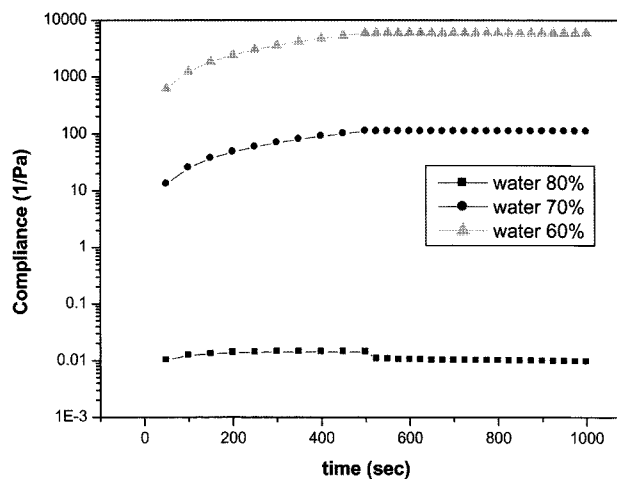**Figure 10.** Complex modulus (G^*) changes for 80% water content emulsions.

Figure 11. Compliance changes for 60-80% water content emulsions at shear stress of 1 Pa.

suddenly reduced above the yield stress. The longer span of linearity of the complex modulus is obtained at a high concentration of the surfactant. For the following creep/recovery experiment, the emulsion containing 3% surfactant was chosen and the stress level was fixed at 1 Pa at which the linear viscoelasticity was retained as shown in Figure 11. For the emulsions with 60 and 70% water, no recovery is observed, whereas relatively good recovery is seen for the emulsion containing 80% water. The emulsions with 60 and 70% water are quite dilute so that they show viscous behavior rather than elastic property. However, the emulsion with 80% water (dispersed phase) is so concentrated to show stronger elastic property than the diluted emulsions.

In Figure 12, the flow curve, viscosity vs. shear stress, for the 80 % water content emulsion with 3.0 surfactant is analyzed. According to the change in the viscosity, the behavior is classified into three distinct regions: [I] linear viscoelastic, [II] partially viscoelastic, and [III] viscous region. In lin-
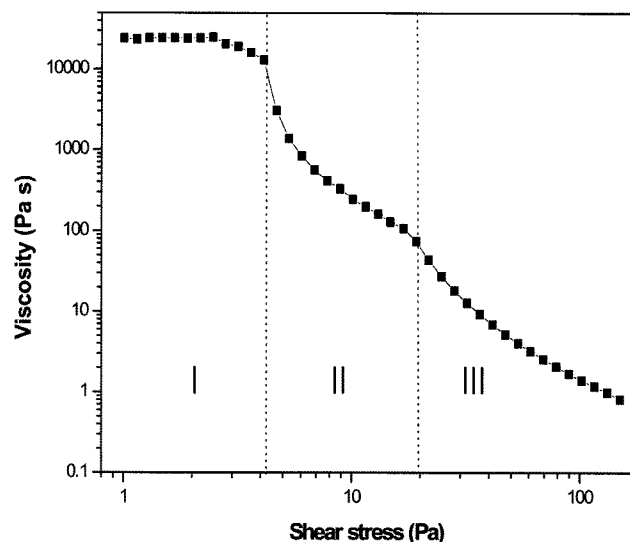
Figure 12. Viscosities as a function of shear stress for 80% water content emulsion with 3.0 wt% surfactant; [I]: linear viscoelastic region, [II]: partially viscoelastic region, and [III]: viscous region.

ear viscoelastic region, the viscosity is independent of the shear stress. At high shear stress (region [III]), the viscosity of the emulsion shows a free-flowing behavior. The creep/recovery behaviors at each region are depicted in Figure 13. In the viscoelastic region [I], typical recovery upon the removal of the applied stress is achieved. In the partially viscoelastic region [II], the partial recovery is obtained at a low applied stress, 3 Pa. However, no recovery is witnessed in the region [III] since the emulsion has a purely viscous property.

Conclusions

A highly dispersed W/O emulsion of silicone oil (cyclomethicone)/water system was prepared with a nonionic surfactant. The surface and interfacial tension between the oil and water were characterized in terms of the droplet size distribution and viscosity change of the emulsion. When the dispersed phase concentration was relatively high, the viscosity of the emulsion was rapidly increased and the droplet size of the emulsion was decreased. The rheological behaviors of the emulsion system showed non-Newtonian and shear thinning phenomena depending upon the content of the dispersed phase. The droplet size of emulsion was decreased with the increase in the surfactant content and water concentration. The relative viscosity of the emulsion was well predicted with the Choi-Schowalter model rather than Taylor model. The value of the complex modulus increased with the surfactant concentration. The linear viscoelastic region was expanded with dispersed phase concentration. According to the change in the viscosity, the behavior was classified into three distinct regions: [I] linear viscoelastic, [II] partially viscoelastic, and [III] viscous region. In linear
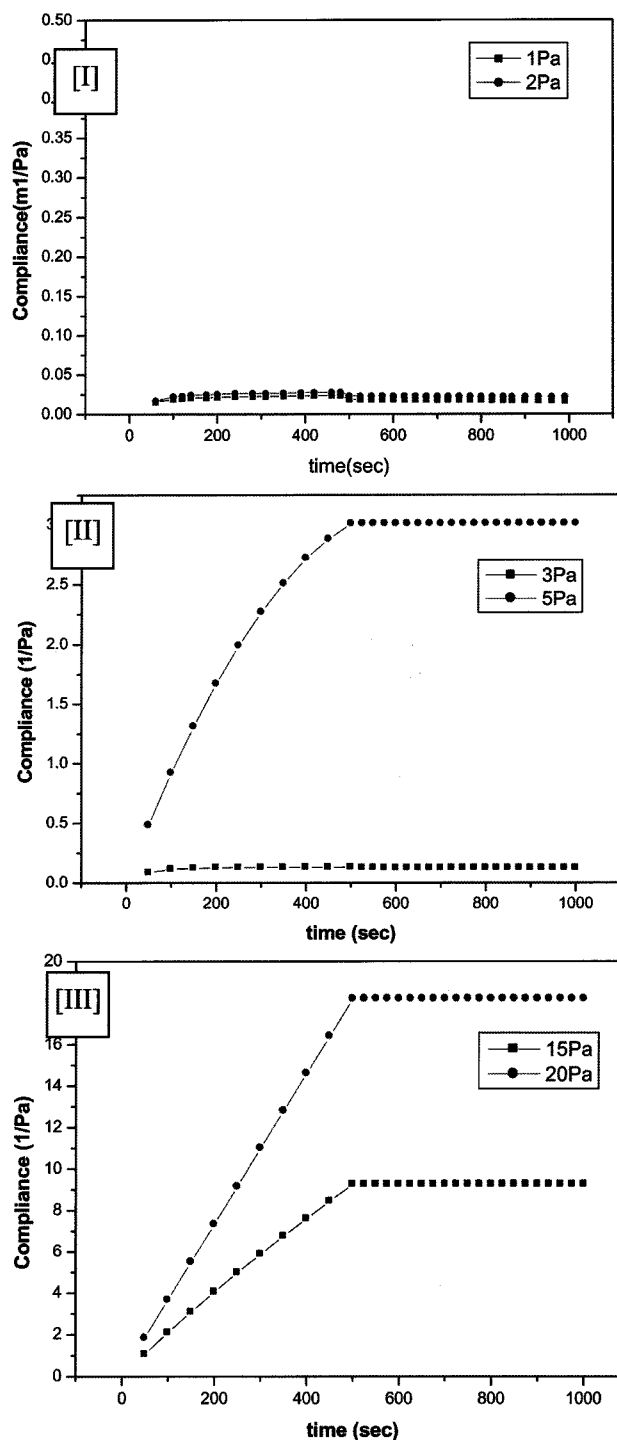

Figure 13. Compliance changes for 80% water content emulsion with 3.0 wt% surfactant; [I]: linear viscoelastic region, [II]: partially viscoelastic region, and [III]: viscous region.

viscoelastic region, the viscosity was independent of the shear stress. At high shear stress (region [III]), the viscosity of the emulsion shows a free-flowing behavior. In the viscoelastic region [I], typical recovery upon the removal of the applied stress was achieved. In the partially viscoelastic

region [II], the partial recovery was obtained at a low applied stress, 3 Pa. However, no recovery was witnessed in the region [III] since the emulsion has a purely viscous property.

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