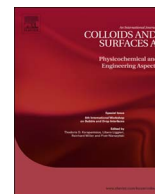




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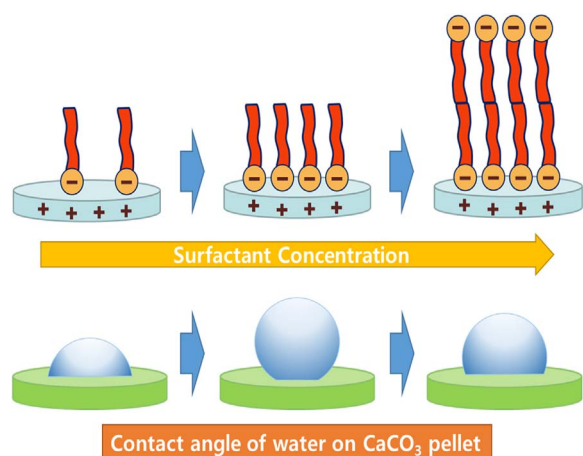
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Surface modification of calcium carbonate nanoparticles by fluorosurfactant

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GRAPHICAL ABSTRACT

Schematic illustration for adsorption behavior of anionic fluorinated surfactant on CaCO₃ substrate

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ABSTRACT

In this study, the effect of adsorption behavior of anionic fluorinated surfactant (Zonyl TBS) on the wetting property of CaCO₃ substrate was investigated. In a low surfactant concentration region, the CaCO₃ surface becomes more hydrophobic with an increase in surfactant concentration due to monolayer adsorption of surfactant molecules on the solid surface. However, further increase in surfactant concentration after the formation of a monolayer saturated with surfactant molecules produced a reverse change from hydrophobic to hydrophilic due to bilayer formation of surfactant molecules on the CaCO₃ surface. Foam stability test for aqueous solutions containing 1 wt% of CaCO₃ nanoparticles indicated that ultrastable foam was observed at 1.70×10^{-1} wt% of Zonyl TBS concentration where the contact angle measured through the aqueous phase was found to be $93.6 \pm 0.3^\circ$. This result indicated that CaCO₃ nanoparticle treated by low concentration of fluorosurfactant Zonyl TBS is a strong candidate for the potential applicability as a foam stabilizer.

1. Introduction

Calcium carbonate (CaCO₃) represents the highest output and probably the lowest cost of commercial materials in the world due to its

widespread applications [1,2]. CaCO₃ is one of the major ingredients used in the industries of plastics, rubber, paint, adhesive, sealant, pigments, coating, toothpaste, cosmetics, thermosetting resins, paper, and food [1–3]. However, one of the most confronting issues for the

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industrial uses of CaCO_3 is the hydrophilic property, and this problem makes CaCO_3 nanoparticles very difficult to be used widely [4,5]. For example, CaCO_3 particles cannot be used as a filler for the preparation of polymeric composites, since the high-energy hydrophilic CaCO_3 particles are not compatible with the low-energy hydrophobic polymers such as polyethylene and polypropylene [6–8].

The modification of CaCO_3 surface by a variety of surface modifiers has been extensively studied [2,5,7–17]. Recently, surface modification of CaCO_3 nanoparticles has been performed by using 2 different kinds of anionic surfactants, such as alkylbenzene sulfonic acid type and laurth sulfonic acid type [16,17]. The maximum contact angles obtained with alkylbenzene sulfonic acid type and laurth sulfonic acid type were found to be 59° and 55° respectively, which are not sufficient to be compatible with low-energy hydrophobic polymers.

Fluorosurfactants, or fluorinated surfactants, are synthetic organofluorine chemical compounds that contain a perfluoroalkyl group. Fluorinated surfactants have low surface tensions compared with typical hydrocarbon surfactants or silicone surfactants because of the strong electronegativity of fluorine relative to hydrogen [18]. Therefore, fluorinated surfactants are reported to reach surface tension as low as 15–20 mN/m and to have lower critical micelle concentration (CMC) values [19]. It is also well known that fluorinated surfactants are far superior to nonfluorinated surfactants in terms of wetting action and both thermal and chemical stabilities in harsh environments [19–21]. Generally, fluorinated surfactants are more compatible than hydrocarbon surfactants in nearly all systems due to excellent surface activity and outstanding stability [18–21].

Obtaining stable aqueous foams is an important issue in many industrial applications such as food products, automatic dishwasher detergents, hand dishwashing detergents, soaps, shampoos, bubble bath, shaving creams, cosmetics, enhanced oil recovery, flotation of minerals, blast mitigation, fire extinguishing agents and so on [22]. Foams can be stabilized in practice by partially hydrophobic nanoparticles, i.e. when the contact angle between particles and water is not too small. Nanoparticles also have the potential to stabilize foam under harsh conditions of temperature, acidity and salinity [22]. Moreover, these nanoparticles can be obtained cost-effectively from cheap raw materials such as fly ash and silica [23]. Many studies have reported the use of colloidal particles with different surface chemistry as sole stabilizers for bulk foam [24–26].

In this study, a quartz crystal microbalance with dissipation monitoring (QCM-D) was used to investigate the structure and properties of the organic layer formed on CaCO_3 surface upon coating with surfactant molecules and to understand the adsorption process and properties of the adsorbed layer on a molecular level by measuring the adsorbed amount at the solid surface as well as the viscoelastic properties of the formed layer [27,28]. Contact angle measurement, surface free energy analysis, and floating test have been conducted to study the effect of surfactant adsorption on the wetting property of CaCO_3 substrate. Foam stability test has been also performed with surface modified CaCO_3 nanoparticles in order to test the potential applicability as a foam stabilizer.

2. Methods

2.1. Materials

CaCO_3 nanoparticles (COLLOID-7000) with a purity of greater than 98.3%, the whiteness of 97.0 L and the average particle size of 78.4 nm were supplied by Dongyang M & M Industry Co., Korea. The average pore size and BET surface area of CaCO_3 , determined by nitrogen adsorption (ASAP 2000, Micromeritics), were found to be 20.0 nm and $22.9 \text{ m}^2/\text{g}$ respectively [16,17].

Zonyl TBS is an anionic sulfonate fluorinated surfactant, whose structure is given by $\text{R}_F\text{CH}_2\text{CH}_2\text{SO}_3\text{Y}$ where R_F is $\text{F}(\text{CF}_2\text{CF}_2)_{1-9}$ and Y is a mixture of hydrogen and ammonium. Zonyl TBS was purchased from

DuPont Company and used without any further purification. Hydrochloric acid solution (1.0 M HCl) and sodium hydroxide solution (0.1 M NaOH) with a purity of greater than 98.0% were purchased from Sigma-Aldrich Co. and used for pH adjustment of aqueous solutions. ELOTANT™ AO 32 (AO32), dimethyl lauryl amine oxide type nonionic surfactant, was obtained from LG Household & Health Care in Korea and used for foam generation purpose in foam stability experiments. Rhodamine B (Sigma-Aldrich Co.) was used to stain CaCO_3 nanoparticles for high resolution fluorescence microscope observation. Water used for sample preparation was ultrapure, which has been double distilled and passed through a Nanopure (Sybron-Brinkman Inc.) ion exchange system.

2.2. Methods

2.2.1. Characterization of fluorinated surfactant zonyl TBS

During this study, the critical micelle concentration (CMC) was determined by measuring the surface tension of a surfactant as a function of concentration. The CMC was considered to reach when there was no further decrease in surface tension with an increase in surfactant concentration. Equilibrium surface tension of an aqueous surfactant solution was measured at 25°C by using a Du Nüoy ring tensiometer with a platinum ring (Kruss K100, Germany). The platinum ring was cleaned several times by distilled water before each measurement to remove any residual deposit. 3 readings were made on each sample to check repeatability and to obtain an average value. The surface tension values were within an error less than or equal to $\pm 1 \text{ mN/m}$.

During migration of surfactant molecules to the liquid surface bordering air, surface tension decreases as a function of time and finally approaches an equilibrium value. Maximum bubble pressure method is commonly used to measure dynamic surface tension for the system containing surfactants or other impurities since it takes more time to obtain a completely formed surface and this means that it is difficult to achieve the static equilibrium as a pure liquid does [16,17]. In this study, dynamic surface tensions for shorter time periods were measured at 25°C by a maximum bubble pressure tensiometer (Kruss BP2, Germany), where the range of bubble life time used was from 10 to 50,000 ms.

2.2.2. Preparation of aqueous dispersions of CaCO_3 nanoparticles for zeta potential measurement

The aqueous paste of CaCO_3 nanoparticles was weighed into a glass bottle of dimensions 6.7 cm (h) by 4.6 cm (d) followed by adding pure water or aqueous surfactant solution of different concentration [16,17]. The mixture was then dispersed for 2 min by an ultrasonic processor (Vibracell, SONICS) operating at an output of 50W. 1.0 wt% of aqueous dispersions of CaCO_3 nanoparticles were dispersed in pure water as described above for measurements of size and zeta potential of CaCO_3 nanoparticles. The particle size of aqueous dispersions of CaCO_3 nanoparticles was measured using a particle size analyzer (SOS1, K-ONE LTD) at 25°C and the zeta potential was measured using an electrophoretic light scattering spectrometer (ELS-8000, OTSUKA) at 25°C . The detailed experimental procedure for zeta potential measurement has been described previously [16,17].

2.2.3. Surface modification of CaCO_3 nanoparticles

1 g of CaCO_3 nanoparticles was weighed into a glass vessel of dimensions 6.7 cm (h) by 4.6 cm (d) followed by adding 50 mL of aqueous surfactant solution of different concentration. The mixture was then dispersed using a stirrer for 25 min, and the dispersion was left at 25°C in a temperature incubator (DF-95B, Duri Science) for 24 h. After separating the suspended particles by using a centrifugal separator (A50S-6 rotor, Mega 17R, HANIL Science Industrial) at 5000 rpm for 10 min, the particles were rinsed 3 times with distilled water to remove remaining foams on the surface [2,16,17]. The final products were

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