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Preparation of water powders by the adsorption of hydrophobic nanoparticles at the surface of hydrated starch particulates

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ABSTRACT

Water powders, aqueous droplets stabilized by the adsorption of hydrophobic nanoparticles at surface, were prepared for the cosmetic applications. The mild shear stress applied to water powders can induce the collapse of powders, and release water to skin. The hydrophobicity of nanoparticles, measured by the contact angle with water, played an important role for the formation of water powders. When the contact angle of nanoparticles with water was between 126 and 138°, the stable water powders were formed. The surfaces of silica or TiO_2 nanoparticles were modified with dimethicone or alumina to control the hydrophobicity of nanoparticles. Also the size of nanoparticles was one of the key factors in forming water powders. When the size of nanoparticles was 1/500–1/750 compared with that of modified starch particulate, the water powders were formed well. The modified starch particulates were swelled with aqueous phase. The optimal amount of aqueous phase in water powder was 75–80% by weight. Even though the content of aqueous phase was very high, the appearance of water powder was powdery. The water powders prepared at various conditions were investigated with SEM and an optical microscope.

1. Introduction

Aqueous droplets coated with hydrophobic nanoparticles, water powders, have been of a great interest for cosmetic scientists [1–3]. The appearance of water powders looks like the aggregates of many hydrophobic inorganic nanoparticles. But lots of water molecules are included inside the water powder. When mild shear forces are applied to these water powders, water powders are disintegrated and aqueous phase can be released outside. The schematic diagram for water powder is shown in Fig. 1.

Since the size of nanoparticles is small (usually less than 100 nm), the surface properties of nanoparticles play a decisive role in determining the characteristics and functionality of particles. The surface modifications become more and more important in the application of nanoparticles. Nanoparticles are adsorbed into liquid/liquid interface to form emulsion called as 'Pickering emulsion' [4,5].

Recently Pickering emulsions are of a great research interest in cosmetic and food industry with the extensive studies of the adsorption of nanoparticles at liquid/liquid interface [6]. But the adsorption of nanoparticles at liquid/gas interface has not been investigated extensively.

The aqueous droplets coated with hydrophobic nanoparticles by physical adsorption at surface can be collapsed by the gentle shear forces (around 100–200 g/cm^2), and release water to skin when used in cosmetics. The use of water powders in cosmetics is the unique formula which can induce the curiosity for consumers by delivering water through the unexpected way, and the hydrophobic nanoparticles can remove the oily components from skin. Also water powders can play a role in delivering water as solid particulates.

When the surfaces of nanoparticles are hydrophilic, the particles can be dispersed easily in water (Fig. 2a). As the hydrophobicity of particle increases, the flocs are formed by aggregation of several nanoparticles and these flocs are dispersed in water (Fig. 2b). When the hydrophobicity at surface of nanoparticles is very strong, all nanoparticles are separated out from the water (Fig. 2d) [7,8]. In the certain range of hydrophobicity of nanoparticles, water droplets coated with nanoparticles can be formed (Fig. 2c). The nanoparticles are adsorbed strongly at liquid/gas interface and large quantity of water is kept inside the aggregate of powder. The hydrophobicity of nanoparticles is the key factor to decide whether the water powder can be formed or not. The hydrophobicity of nanoparticles can be evaluated by measuring the contact angle between water and nanoparticle surface [9].

In this study, water powders were prepared using surface modified silica particles with dimethicone and surface modified titanium dioxide with dimethicone and alumina. The effects of hydrophobicity of nanoparticles on the formation of water

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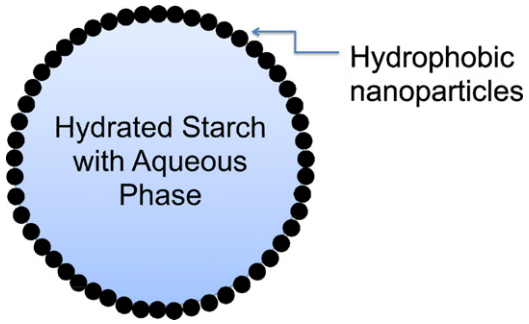

Fig. 1. Schematic diagram for water powder.

powders were studied by measuring the contact angle between water and nanoparticles. Also it was studied how the size of nanoparticles and contents of aqueous phase can influence the formation of water powders. The modified starch was used to stabilize the shape of aqueous droplets. These water powders were characterized using microscope and the efficacy in delivering whitening agent into skin was investigated.

2. Experimental

2.1. Materials

Water powders were made from aqueous phase, surface modified nanoparticles and water absorbing agent (modified starch). Surface modified nanoparticles are called as antiflocking agent. Aqueous phase was composed with water, polyol and whitening agent. The PG (propylene glycol, SK Chemical Company, Korea), glycerine (Palm-Oleo Company), 1,3-butylene glycol (Daicel Chemical, UK) and phenoxy ethanol (Galaxy Surfactants Company) were used as polyol, and niacinamide (Niacinamide PC, manufactured by DSM) was added as a whitening agent for skin.

Water absorbing agent can hold water phase and help to keep particulate form of water phase by increasing the viscosity. Also water absorbing agent interacts with nanoparticles that have hydrophobic surface. The modified starch (trade name: DRY FLO 28-1800, manufactured by National Starch, corn starch modified) of food grade was used as water absorbing agent. Antiflocking agents, surface modified nanoparticles, are adsorbed at the surface of water absorbing agent to prevent the coalescence between the droplets of aqueous phase. The layer of antiflocking agents is formed at the surface of aqueous phase and water powders can be formed. The surface modified silica particles with dimethicone

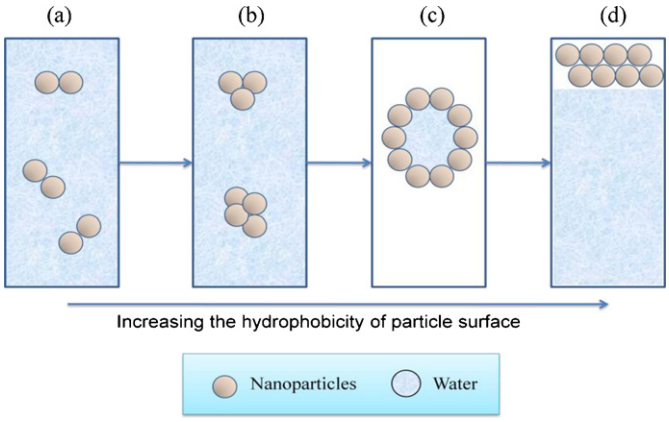

Fig. 2. Changes in the aggregation behavior of nanoparticles in water as the hydrophobicity of nanoparticles increases.

(Aerosil R202, manufactured by Degussa, composed of 95.75% silica and 4.25% dimethicone) and surface modified titanium dioxide (TiO_2) with dimethicone as well as alumina (UV-Titan M170, manufactured by SACHTLEBEN, composed of 81.2% titanium dioxide, 11.5% dimethicone and 7.3% alumina) were used as antiflocking agents. And polymethylsilsesquioxane (TOSPEARL 2000B, manufactured by Toshiba Silicone, methylsiloxane reticular polymer, PMSQ) was added to prevent the coalescence between water powders. The particle size of antiflocking agent was less than 100 nm.

2.2. Preparation of water powders

The solid form of water absorbing agent (modified starch), antiflocking agent (surface modified nanoparticles) and PMSQ were mixed together in the mechanical stirrer with the revolutionary speed of 1000 rpm for 5 min at room temperature. The antiflocking agent was adsorbed at the surface of particulates of modified starch [10]. The layers of surface modified nanoparticles are formed due to the interaction between water absorbing agent and antiflocking nanoparticles. After the formation of the particulates of starch covered with the layer of surface modified nanoparticles, the aqueous phase containing water, polyol and whitening agent was added by spraying into the solid mixtures. The aqueous phase can penetrate into starch through passing the layer of antiflocking agents.

2.3. Measurement of contact angle between water and nanoparticles

The contact angle between nanoparticles and water was measured using Goniometer (Surface and Electro Optics Company). Artificial skin was covered on the surface of the slide glass. Then surface modified nanoparticles were spread on the artificial skin as a tightly packed layer. The water drops were located above the layer of nanoparticles. The contact angle between water and layer of nanoparticles was evaluated through the optical microscope [9].

2.4. Characterizations of powder morphology

Field emission scanning electron microscopy (FE-SEM, JEOL Co. Models JSA 840A and JSM-6700) and an optical microscope were used to investigate the shape and size of the water powders. For the characterization of FE-SEM, the samples were coated with platinum by sputtering at 15 mA for 3 min [11].

3. Results and discussion

The delivery of water to skin can be performed by various formulas such as emulsion, microemulsion, solubilization, etc. in cosmetics. Nowadays, it is emphasized to develop new and efficient methods for delivery of water to skin. Water powder is one of the most interesting formulas for this purpose.

In this study, the starch, PMSQ and hydrophobic nanoparticles were mixed together to prepare water powders. Then the aqueous phase was sprayed into the starch, PMSQ and nanoparticle mixtures. By adding aqueous phase into mixture, the starch is swelled and hydrated.

Due to the hydrophobic interaction between surface modified hydrophobic nanoparticles and starch particulate, the nanoparticles will be adsorbed onto the surface of starch particulates swelled with water and will stabilize the water powders.

When the starch, PMSQ and antiflocking agent were mixed together in the mechanical stirrer, the small particulates of modified starch were formed. Then the surface modified nanoparticles will be adsorbed at the surface of starch particles. PMSQ will be located between these particulates and prevent the coalescence. Fig. 3 shows the surface morphology of starch particulate after