



Original Research Paper

Effect of steric hindrance on surface wettability of fine silica powder modified by *n*- or *t*-butyl alcoholAki Kawamura^a, Shoichi Ueno^b, Chika Takai^a, Takashi Takei^b, Hadi Razavi-Khosroshahi^a, Masayoshi Fuji^{a,*}^aAdvanced Ceramics Research Center, Nagoya Institute of Technology, Honmachi 3-101-1, Tajimi, Gifu 507-0033, Japan^bFaculty of Urban Environmental Sciences, Tokyo Metropolitan University, Minami-Osawa 1-1, Hachioji, Tokyo 192-0397, Japan

ARTICLE INFO

Article history:

Received 1 May 2017

Received in revised form 4 June 2017

Accepted 9 June 2017

Available online 12 July 2017

Keywords:

Silica

Surface modification

FT-IR

Preference dispersion

Butyl alcohol

ABSTRACT

Fumed silica is an important industrial material, which is widely used in medical, cosmetic, and electronic products. One important industrial application of the fumed silica powder is using it as fillers, which are key materials for reinforcing the high-performance/high-functional industrial products. However, the use of fumed silica as filler is limited to micrometer or millimeter sized particles, because nanometer sized silica particles tend to aggregate. In this study, the surface of fine silica powder is modified with *n*- and *t*-butyl alcohols, which exhibit different steric hindrance effects. The surface wettability of each modified silica powders is determined in two ways: macroscopic and microscopic wettability. Macroscopic wettability refers to preference dispersion test and microscopic wettability refers to evaluation of the molecular level by Fourier transform infrared spectroscopy (FT-IR). The modification ratio of each sample is confirmed by thermogravimetry-differential thermal analysis (TG-DTA), and the hydrophobicity of these modified silica powders is evaluated by the preference dispersion test. Molecular level evaluation of surface wettability by FT-IR confirms an obvious structural difference due to the steric hindrance of the *n*- and *t*-butoxy groups on the surface of silica. In addition, a correlation between macroscopic and microscopic evaluation results for the surface wettability of modified silica powders is confirmed.

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1. Introduction

Fumed silica is a unique industrial material, thanks to its extremely small particle size, large surface area, and high purity [1]. Fumed silica is widely used in medical products as glidant [2], in cosmetics as sun protection agent [3], in electronics as chemical-mechanic planarization (CMP) [4,5], in paints and printing inks as thickening agent [6–8], an anticaking agent in the processing of dry materials, and in thermal insulators in high temperatures as high as 1000 °C. Another important industrial use of the fumed silica powder is using it as filler. Silica fillers are key materials for reinforcing the high-performance/high-functional industrial products [9,10] and recently high performance fillers, which can answer divers industrial requirements are desired. Nanosized silica fillers show an advantage over their micrometer or millimeter sized counterparts thanks to their high surface area, which leads to better reactivity and adhesion between filler and matrix particles. However, nanosized silica particles usually suffer from aggregation

[11–13], which is nanosized particles tend to stick to each other due to the high surface area. Therefore, the development of monodisperse silica nanoparticles, which hardly aggregate is of great importance for both industrial and academic applications.

Another factor that causes aggregation in silica particles is hydroxyl groups (–OH), which are present on the surface of fumed silica particles [1]. These hydroxyl groups can be in the form of isolated hydroxyl groups, hydrogen-bonded hydroxyl groups, geminal hydroxyl groups, and siloxane groups, which usually facilitate the aggregation of silica particles. Therefore, the surface of silica particles is usually modified by various functional groups like alcohol [14,15], silane coupling agent [16–18], and silicone oil [19,20] in order to prevent them from aggregation. Determining the amount of modification is also important and evaluation methods like measuring the weight loss by thermogravimetric and differential thermal analysis (TG-DTA) [11,15], examining the wettability by preferential dispersion test [15], measuring total organic carbon content [1], and measuring the contact angle between the silica surface and water [21,22] have been reported. However, to the best of our knowledge a systematic study, which investigates the interaction of water molecules and modifiers present on the surface of

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silica particles is lacking. Molecular level understanding of the surface structure of modified silica particles is also important for improving the performance of silica nanoparticles, i.e., the wettability of a fumed silica surface is dependent on the molecular structure of the functional species on the surface of silica particles [23].

Fourier Transform infrared spectroscopy (FT-IR) has been widely used for observation of fumed silica surfaces and the states of their hydroxyl groups [24]. However, a comparison between macroscopic and microscopic results will help to obtain a better view of the surface wettability of modified fumed silica surfaces. In the present study, the wettability of fumed silica surfaces modified by two different structures of butyl alcohols is measured. Here, preference dispersion test in water is used as macroscopic wettability evaluation method, and water vapor adsorption test determined by FT-IR is used as microscopic wettability evaluation method, and a mechanism for the formation of a water film on the surface of silica is proposed in molecular level.

2. Experimental

2.1. Materials

Fumed silica powder (Aerosil 200, A200) is provided by Nippon Aerosil Co., Ltd. A200 is non-porous and its surface is smooth, it is adequate material to investigate their surface structures macroscopically and microscopically. The specific surface area (200 m²/g) is measured using the Brunauer-Emmett-Teller (BET) method by nitrogen adsorption isotherms [25]. *n*- and *t*-butyl alcohols (special chemical grade, Kanto Chemical Co., Inc.) are used as modifying agents, and *n*-hexane is used as solvent.

2.2. Surface modification

Surface modification of the fumed silica is carried out using the autoclave [26,27]. 2.0 g of A200 sample is dispersed in *n*-hexane containing 0–1.4 ml/g of either *n*- or *t*-butyl alcohol. The samples are dispersed in *n*-hexane and placed in the autoclave system. Autoclave system is purged by N₂ gas for 5 min to completely remove the air. Finally, the system is heated at 260 °C for 1 h at 30 bar.

2.3. Evaluation of the surface structure

The proportion of butoxy groups introduced onto the silica particles is determined by thermogravimetry-differential thermal analysis (TG-DTA; TG/DTA300 SSC 5200H, Seiko Instrument, Inc.). Measurements are conducted in air flow of 250 ml/min at up to 500 °C with a heating ramp of 20 °C/min. The modification ratio of butoxy group θ (%) on the silica surface is calculated using the following equation:

$$\theta(\%) = \frac{(\Delta G/y_3 - w) \times N_A}{mw \times S \times N_{OH}} \times 100 \quad (1)$$

where ΔG is the weight loss of the modified sample measured by TG-DTA, y_3 is the initial weight of the modified sample, w is the weight loss of surface silanol groups from unmodified silica, mw is the molar weight of the species used for modification, S is the BET specific surface area calculated from the nitrogen adsorption isotherm, N_A is Avogadro's number, and N_{OH} is the surface silanol density (–OH/m²) [11,28].

The extent of silica surface modification is also observed using FT-IR (IR 5300, Jasco Corporation; operated at a resolution of 2 cm⁻¹ and with 16 scans per spectrum). The modified samples are molded and placed into a sample cell. The system is depressurized to 10⁻¹ Pa, and the sample is pretreated by degassing at 160 °C. FT-IR spectra are quantitatively analyzed. Absorbance at

1864 cm⁻¹ is used as the standard peak because it is reported to be proportional to the thickness of the sample pellet [29]. The absorbance of the modifiers is examined in the range of 2800–3000 cm⁻¹.

2.4. Determination of the amount of water vapor adsorption by FT-IR

The microscopic wettability of modified silica is determined by measuring water vapor adsorption using FT-IR [30]. 0.02 g of modified silica pellet is prepared with a diameter of 13 mm at 0.7 kPa using die set for compaction. The pellet is placed in a sample cell, and the system is evacuated for 4 h at 160 °C. The sample chamber is cooled to room temperature and the IR spectrum is obtained. Subsequently, water vapor is introduced into the sample chamber until the relative pressure is about 0.1. After adsorption reached equilibrium, the FT-IR spectrum is recorded. These steps are repeated with increasing vapor pressure until the maximum relative pressure is reached. The amount of water vapor (S_{OH}) is calculated from the areas of the silanol peaks as follows:

$$S_{OH} = \frac{S_A - S_{CH}}{I(1864 \text{ cm}^{-1}) - I(2450 \text{ cm}^{-1})} \quad (2)$$

where S_A is the area of the peaks in the 2450–4000 cm⁻¹ region, S_{CH} is the area of the peaks in the 2750–3000 cm⁻¹ region which indicated the C–H stretching region, and $I(1864 \text{ cm}^{-1})$ and $I(2450 \text{ cm}^{-1})$ are the absorbance at the respective wavelengths.

2.5. Preference dispersion test

The macroscopic wettability of the modified silica samples is determined by a preference dispersion test. Fumed silica sample is dried at 160 °C for 4 h. The sample is then stirred in distilled water, and the wettability is determined by visual observation it is noted that hydrophilic samples are dispersed in the water, while hydrophobic samples are floated on the water surface. The samples are slowly placed in a thermostatic tank at 30 °C, and observed for 6 h with an additional dispersion every 30 min [15,30].

3. Results and discussion

3.1. Characteristics of modified fumed silica surface

Degree of surface modification ratio, θ %, as a function of alcohol content is shown in Fig. 1. Here, the modification ratio is the fraction of modified hydroxyl groups, relative to the total hydroxyl groups on the surface of unmodified silica. It is shown that modification ratio increases more drastically for *n*-modified silica when butyl alcohol content increases, as compared to *t*-modified silica. The modification ratios of *n*- and *t*-silica are 30% and 20% when 0.1 ml/g of *n*- and *t*-butyl alcohol are used, respectively. As the alcohol concentration increases to >0.1 ml/g, the modification ratio increases at a slower rate than that at lower concentrations. Decrease of modification rate at butyl alcohol concentrations higher than 0.1 ml/g is due to the steric hindrance of those modification agents that are already present on the surface of silica particles. The highest modification ratios obtained for *n*- is 49% and *t*-silica is 39%, when the adding amount of alcohols are 0.5 ml and 1.5 ml, respectively.

The surface modification by butyl alcohols proceeds via a dehydration reaction between hydroxyl groups on the silica surface and R–OH groups in the alcohol. As a result, Si–OH is replaced by Si–O–R, where R is either *n*- or *t*-butoxy groups. The differences in the modification ratios of *n*- and *t*-modified silica are attributed to the chemical structure of the butyl alcohols. The *n*-butoxy group is relatively narrow and their conformation is changeable (flexible), while the *t*-butoxy group is very bulky and their conformation

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