NMR as a Tool to Characterize the Aggregation Structure of Silica Nanoparticles in a Liquid[†]

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Abstract

The NMR-based solvent relaxation technique, a non-invasive tool to characterize the surface of particles, which are dispersed in a liquid, was applied to characterize the nanoparticles' aggregation structure. The liquid molecules in a dispersion undergo a rapid exchange between the bound states at the interface and highly mobile free states in a bulk liquid. The relaxation time of the liquid molecules bound on the particle surface is shorter than that of the free states liquid. By detecting how much liquid is bound on the particle surface, the wetted specific surface area (S_{NMR}) can be determined. In this study, it was clarified that the water adsorbed at more than a 1.138 layer from the silica surface can be detected by the NMR and the maximum limitation ranged from 2.160 and 3.336 layers. The model aggregates with an artificial solid neck among the particles were mixed with the silica nanoparticle dispersion. Although the determined S_{NMR} was underestimated compared to S_{BET} from gas adsorption, even a low ratio (5 mass%) of the model aggregates in the dispersion can be detected.

Keywords: aggregation structure, wetted specific surface area, solvent relaxation NMR, adsorbed water, silica

1. Introduction

It is well known that nano-sized particles easily aggregate due to many active sites on their surface compared to micron-sized particles. It is also common knowledge that the excellent properties of the nanoparticles, such as mechanical, thermal, magnetic, electrical, etc., are strongly affected by the structure of their aggregation in addition to their dispersion.

The three-dimensional silica nanoparticles network in rubber, linked by their secondary aggregates, encourages the wet grip performance of car tires on ice. These important particle network structures were characterized by small-angle X-ray scattering (SAXS) in combination with transmission electron microscopy (TEM) (Baeza et al., 2013; Stauch et al., 2019). Song et al. (2019) proved that aggregation in a heat-transfer fluid called a nanofluid, which was obtained by suspending metallic nanoparticles in a conventional liquid, can increase the thermal conductivity due to the formation of an “efficient heat channel,” using the Monte Carlo simulation considering phonon

transport. Yang et al. (2019) developed a self-healing system of a thermoplastic polymer in which the superparamagnetic nanoparticle aggregations were embedded. Under the application of an oscillating magnetic field, the migrated nanoparticles generate a high local temperature which heals the electrical tree channels in the polymer. Ajmal et al. (2019) produced that a highly-conductive silver/polyvinyl alcohol nanocomposite fibers by adding silver ions to prevent aggregation of the originally dispersed silver nanoparticles. The gaseous byproduct from the precursors dramatically increased the flexibility of the nanocomposite's tensile strength.

Thus, understanding the aggregation structures, which are directly connected to the nanoparticles' performance, is highly recommended. There have been several techniques to characterize them via microscopic observations, scattering of electromagnetic waves, sedimentation tests, rheological behaviors (Wang et al., 2012), differential scanning calorimetry (DSC) (Korobov et al., 2010), nitrogen gas adsorption (Yoshida et al., 2016), etc. Some of the data were analyzed in combination with theoretical models including fractal dimensions.

The interparticle bond energies can range from weak van der Waals forces (agglomerates) to stronger solid state necks (aggregates). Teleki et al. (2008) distinguished those of “as-prepared” flame-made TiO_2 nanoparticles by the TEM observations before/after a high-pressure-dispersion, in combination with the particle size distributions

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measured by dynamic light scattering (DLS) and the specific surface area calculated from the N_2 adsorption isotherm by applying the Brunauer–Emmett–Teller equation. When considering deformation of the aggregation structure under vacuum during observation, some techniques to fix the aggregation structures of particles such as carbon coating on the freeze-dried-thinned-samples called cryo-replica TEM (Tiarks F. et al., 2008) and direct visualization technique through polymerization of medium-soluble-monomers (Takahashi M. et al., 2004), were developed. These visualization techniques are indeed effective for understanding, however, at the same time, they are time-consuming when manually obtained 100–1000 particles need to be counted for reliable determination of the particle size distribution (Tsantilis S. et al., 2002).

The ultrasmall-angle X-ray scattering (USAXS) and the small-angle neutron scattering (SANS), as the scattering techniques, detect a structure of 1000 nanometers at most which reflects the nanoparticles' aggregation. The scattering profile as a function of the scattering vector q ($q = 4\pi \sin(\theta)/\lambda$, where 2θ and λ are the angle between the incident beam and the detector, and wavelength of the radiation) can be fitted with intensities calculated from different model shapes when the size distribution is known (Kammler et al., 2004; Hurd et al., 1987). Gilbert B. et al. (2009) reported that low-aggregation (i.e., higher porosity) of iron oxyhydroxide nanoparticles improved the metal uptake performance due to physical loss of the accessible surface area, by a synchrotron SAXS analysis considering the fractal dimensions. Bharti et al. (2011) determined the lysozyme as a protein induced compact and a loose flocculated silica nanoparticles network at low and high pHs, respectively, by the laboratory SAXS and proved by cryo-TEM and a sedimentation test which will be described later.

Korobov et al. (2010) estimated the aggregation structure from the DSC traces by observing the melting behaviors of water in the particles' gap by means of the nanophase of water's non-freezing property. Yoshida et al. (2016) combined N_2 gas adsorption with a He gas pycnometer and DLS to characterize the primary and secondary aggregation of carbon black, as an alternative to conventional ways such as the incorporation of chemicals (e.g., cetyl trimethyl ammonium bromide, di-butyl phthalate) into the particles' gap. They warned that the pressure during the Hg intrusion into the particles' gap probably deformed the aggregation structure.

The particle size distribution from the sedimentation test was determined by Stokes law. The sedimentation time is inversely proportional to the particle size to the second power. For the nanoparticles, of course, centrifugal force is required to reduce the time (Allain et al., 1995). Lerche et al. (2007, 2014 and 2019) proposed an

analytical centrifuge (AC) system for determination of the characteristic material properties related to the sedimentation and consolidation behavior of the dispersions. The STEPTM-Technology (Space and Time resolved Extinction Profiles) allows one to simultaneously measure the intensity of the transmitted light as a function of time and position over the entire sample length. The data are displayed as a function of the radial position as the distance from the center of rotation. The progression of the transmission profiles contains information on the kinetics of the separation process and allows particle characterization. They also showed that this technique was very effective for dispersions of hard and soft micro- and nanoparticles (e.g., titania or lysozyme coated silica), sterical, electrosterical, and rheological stabilization (polyelectrolyte coated nanoparticles), mixtures of different particle types (silica and iron oxide nanoparticles), at any pH value and ionic strength. Walter et al. (2015) developed a new data evaluation technique by applying analytical ultracentrifugation (AUC) which can detect particles less than one nanometer in size with Ångström resolution. They showed a very good correlation with an error of 10.65 % between atomic force microscopy AFM and AUC for the mean lateral diameter of the fully delaminated graphene oxide (GO) sheet, which was achieved using one single AUC measurement and hydrodynamic modeling based on an assumed sheet height and density.

Meanwhile, Nelson A. et al. (2002) monitored the individual adsorption of two different polyelectrolytes (PEO and PVP) on silica particles as well as the polymeric displacement of one polymer (PEO) by another (PVP) using nuclear magnetic resonance (NMR) at 200 MHz. This relies on the fact that mobile (liquid-like) and immobile (solid-like) protons have very different relaxation times. They also investigated the effect of electrolytes on adsorbed polymer layers on PEO adsorbed silica (Flood and Cosgrove, 2006), determined how many polymers per particles (Flood and Cosgrove, 2008) using NMR at 300 and 400 MHz.

According to Fairhurst et al. (2016), a portable benchtop NMR spectrometer operating at 13 MHz could possibly determine the particle size, wetted surface area, and porosity of the nanoparticles (nanocarbon) due to the fact that solvent molecules in a dispersion undergo a rapid exchange between the bound states at the interface and highly mobile free states in the bulk solvent. The relaxation time of the solvent molecules bound on the particle surface is shorter than that of the free states solvent. The observed single relaxation time, T_{av} , is determined from the reciprocal of the spin relaxation rate, R_{av} . As Eqn. 1 indicates, the relaxation rate is an average of the relaxation rates of the molecules on the particle surface, R_s , and free solvent, R_b , weighted by their relative populations as P_s and P_b .

$$R_{av} = P_s R_s + P_b R_b \quad (1)$$

The wetted specific surface area, S_w , of the particles can be expressed as follows. Considering the particle volume concentration, ϕ_p , thickness of the bound liquid layer, L , the particle density, ρ_p , the Eqn. 1 was transformed into 2.

$$R_{av} = \phi_p S_w L \rho_p (R_s - R_b) + R_b \quad (2)$$

Using standard reference materials, the constant (called the specific surface relaxivity) $k_A (= L \rho_p [R_s - R_b])$ was defined. It clearly depends on both the particle type and dispersing solvent. Using this parameter, Eqn. 2 reduces to the following Eqn. 3.

$$R_{av} = k_A S_w \phi_p + R_b \quad (3)$$

Here, $R_{sp} = [R_{av}/R_b] - 1$, which indicates the affinity of the particle surface to the solvent, is defined. R_{sp} increases with an increase in their affinity with the same specific surface area. Using Eqn. 4, the wetted specific surface area (S_{NMR}) can be determined.

$$S_{NMR} = \frac{R_{sp} R_b}{k_A \phi_p} \quad (4)$$

The NMR based solvent relaxation technique has advantage of being non-destructive with minimal temperature control requirements and minimal sample pretreatment in addition to a rapid analysis for highly-concentrated and opaque samples which are sensitive to aggregation. Various particles have already been characterized using the solvent relaxation NMR to investigate the exfoliation behavior of Laponite clay (Karpovich et al., 2016), the hydrophilicity and hydrophobicity of superparamagnetic Fe_3O_4 nanoparticles (Ali et al., 2018), the reactivity of CuO, ZnO, and SiO_2 (Paruthi and Misra, 2017), the wetted specific surface areas of ZnO and Ag/ZnO as photocatalysts (Saoud K. et al., 2015), etc. Fairhurst et al. (2016) provided information regarding the selection of the solvent in which porous particles (e.g., porous graphene) were dispersed. In the case of using ethanol, which has a strong interaction with the graphene, a much more mobile bound layer provided shorter decay times than the water samples. Depending on which of the relaxation times was used for the calculation, the wetted specific surface area significantly changed. Elliott and co-workers (2018) investigated the effect of a high electrolyte concentration on the particle surfaces by solvent relaxation NMR. TiO_2 nanoparticles were unaffected by the solvent conditions, while the R_{sp} values of the SiO_2 and $CaCO_3$ nanoparticles were substantially enhanced in the presence of the KCl electrolyte. They concluded that the

difference in R_{sp} between TiO_2 and $CaCO_3$ is attributed to a counterion effect. Hossain et al. (2018) characterized aqueous dispersions of hollow amorphous nanoparticles with a 50-nm outer size that have two liquid accessible surfaces (i.e., inner and outer surfaces) using solvent relaxation NMR. A higher wetted surface area was observed in the hollow nanoparticles than in the dense nanoparticles. The solvent relaxation NMR has been utilized to investigate various kinds (metal oxides, metals, and ionic crystals) and shapes (spheres and clays) of particles which are dispersed in both aqueous and nonaqueous solvents. This has a great potential for particle characterization, however, there is still some challenging concerns regarding the understanding of the obtained relaxation time.

In this study, we focused on applying the NMR based solvent relaxation technique to understand the aggregation structure of nanoparticles. There is solvent (water, in this study) which penetrates into the particle's gap during the aggregation. By counting the adsorbed amount of the solvent, the density and porosity of the aggregation can be estimated. However, the problem is how many adsorbed layers can be detected and how many are unclear. According to Hossain et al. (2018), the water captured in approximately 30-nm-hollow interior (Lee et al., 2014) had probably been detected by the solvent relaxation NMR. The ability of the solvent relaxation NMR to characterize the nanoparticle aggregation structure was investigated in combination with water vapor adsorption. Based on the results, characterization of model aggregates in the silica nanoparticle dispersions was attempted. The model aggregates were prepared with different loads by uniaxial pressing.

2. Experimental section

2.1 Sample preparations

Silica nanoparticles (Aerosil 200 (12 nm), Aerosil 130 (16 nm), and Aerosil OX50 (40 nm), all kindly provided by Nippon Aerosil Co., Ltd.) or silica sub-micron particles (SO-C1 (0.2–0.4 μm), kindly provided by Admatechs Company Limited) were dispersed in distilled water or an organic solvent (hexane, purchased from Fujifilm Wako Pure Chemical Corporation) by a 1-h stirring. Unless otherwise noted, the particle concentration of the dispersions was kept at 10 mass%.

For the experiment to compare the dispersion states, an ultrasonication (HSR-301, Honda Electronics Co., Ltd.) was additionally conducted at 1 MHz, 40 W for 180 seconds.

For the experiment to investigate the effect of the adsorption amount of water, particles were exposed to water

vapor for 24 h whose humidity was controlled by saturated salt solutions of 60, 70, 80, 86, and 92 % by NaBr·2aq, Ca(NO₃)₂·4aq, KBr, KI, and KNO₃, respectively (Kawamura et al., 2014). The adsorbed weight of water was determined by weighing before and after the 24-h exposure.

The model aggregates were prepared using silica nanoparticles (Aerosil 130) as follows. The pellets with 10-mm diameter were prepared by uniaxial pressing (TB-50H-D, NPa System Co., Ltd.) with the average load of 1, 5, and 10 kN (13, 64, and 127 MPa). The porosity of the pellets were 78.4, 69.5, and 62.1 %, respectively, measured by their volume and weight. The as-prepared pellets were heat treated at 400 °C for 2 h to intentionally create solid-state necks among the nanoparticles. The heated pellets were then milled and sieved using 100-μm stainless steel mesh. The fragments of the pellets over 100 μm were used as the model aggregates. The model aggregates, after vacuum deairing for more than 1 h, were dispersed in distilled water by a magnetic stirrer for 24 h as a 10 mass% dispersion.

To investigate the effect of the ratio between the model aggregates and the as-received silica nanoparticles (Aerosil 130, after vacuum deairing), the 5 kN load model aggregates were mixed with the silica nanoparticles using a magnetic stirrer for 24 h to form a 10 mass% dispersion. The concentrations of the model aggregates were 0, 5, 10, 40, and 100 %.

2.2 Characterizations

The dispersion state was also characterized by a laser diffraction instrument for particle size analysis (MT3200II, MicrotracBEL Corp.). The water vapor adsorption isotherm and nitrogen gas adsorption isotherm were created using a high precision gas/vapor adsorption measurement instrument (BELSORP-max II, MicrotracBEL Corp.).

Regarding the NMR based relaxation technique, 1.0 ml of the dispersion was placed in a sample tube and inserted it into the Acorn area (Xigo Nanotools, Inc.). The sample resides within a coil located between two permanent magnets. A static, uniform magnetic field causes the protons within the solvent to align with the magnetic field. This process typically takes a few seconds. At the start of the measurement, a short radio frequency (RF) pulse excites the coil at a frequency of approximately 13 MHz. This pulse produces a large magnetic field inducing a temporary shift in the magnetic orientation of the sample protons. When this induced field stops, the protons of the sample dispersion then realign with the static field. This realignment induces a decaying voltage in the coil (XiGo Nanotools, 2015). By using specific RF pulse sequences, the sample's T_1 (longitudinal, spin-lattice relaxation) and

Fig. 1 Typical graph obtained from the NMR based solvent relaxation technique.

T_2 (transverse, spin-spin relaxation) relaxation times are measured. T_1 and T_2 depend on the rotational and translational motion of the molecules. The magnitude of the shift in relaxation (from bulk to surface) is different for T_1 and T_2 . Typically, the shift in T_2 is greater than for T_1 . The T_2 measurement uses the Carr-Purcell-Meiboom-Gill (CPMG) pulse sequence method. **Fig. 1** shows the typical T_2 data of the silica nanoparticle dispersion and distilled water as the dispersing medium.

The 37 % reduced points from the initial magnetization is defined as T_2 . The T_2 value of the dispersion was more than twice as high as that of water. It can be said that there is a large amount of water molecules trapped on the silica nanoparticle surface. The k_A , that appeared in Eqn. 3, was determined using the specific surface area of the silica particles calculated from the nitrogen gas adsorption isotherm applying the BET equation.

3. Results and discussion

3.1 Effects of particle sizes, concentrations, and adsorbed water layer on the relaxation time

As shown in **Fig. 2**, the effects of the particle sizes and concentrations on the relaxation time were investigated using Aerosil 200, Aerosil OX50, and SO-C1, whose nominal primary particle sizes were 12 nm, 40 nm, and 0.2–0.4 μm, respectively. The T_2 values are listed in **Table 1**. Regarding the particle concentrations (1, 3, 5, and 10 mass%), there was a decreasing tendency in the relaxation time independent of the particle size. This is consistent with **Fig. 1** that the amount of the water molecules trapped on the particles increased with the increasing particle concentration. It is well known that the

Fig. 2 Effects of primary particle sizes and particle concentrations on the relaxation time; (a) Aerosil 200, (b) Aerosil OX50, and (c) SO-C1.

Table 1 The T_2 values of silica particle dispersions with different solid contents.

Solid content [mass%]	T_2 [ms]		
	Aerosil 200 (12 nm ^a)	Aerosil OX50 (40 nm ^a)	SO-C1 (0.2–0.4 μm ^a)
1	1035.7	1766.9	1945.4
3	607.1	1174.6	1340.9
5	344.7	930.7	965.3
10	188.6	599.8	643.9

^a Nominal primary particle size.

specific surface area increases with a decrease in the particle size. When comparing the particle sizes, the relaxation time decreased with the decreasing particle size. This can also be explained by the increasing amount of the water molecules trapped on the particle surface.

Fig. 3 shows (a) the particle size distributions and (b) the magnetization vs relaxation time of the SO-C1 dispersions before and after ultrasonication. In **Fig. 3(a)**, before the ultrasonic treatment (i.e., after magnetically stirring for 24 hours), the main peak of the suspension was over 10 μm and it was reduced to less than 0.2 μm after the treatment. Due to the ultrasonication, the sub-micron particles were so dispersed as to have a particle diameter close to that of primary particles. The relaxation time decreased after the treatment although the change was small (before treatment T_2 was 643.9 ms and after, 584.6 ms.) as shown in **Fig. 3(b)**. It seems that the sub-micron particles formed weak agglomerates which easily disperse by the ultrasonication (Higashitani et al., 1993).

The NMR relaxation defines two liquid phases, i.e., the surface liquid at the particle surface and bulk liquid far from particle. Then how many adsorbed water layers on the particle surface are the surface liquid?

The silica surface exhibits hydrophilic property due to

Fig. 3 Changes in (a) the particle size distributions and (b) relaxation times of the silica particle dispersions before and after ultrasonic (US) treatment.

lots of silanol (SiOH) groups which are categorized into three types in accordance with the number of OH group bonds to the Si atom, i.e., isolated OH, geminal OH, and triple OH. According to Fuji and Chikazawa et al. (2000), the number of total silanol groups on the fumed silica nanoparticles was 2.8 per nm² and decreased with the

heat treatment; $2.3/\text{nm}^2$ at $200\text{ }^\circ\text{C}$, $1.9/\text{nm}^2$ at $300\text{ }^\circ\text{C}$, $1.4/\text{nm}^2$ at $400\text{ }^\circ\text{C}$, and $1.3/\text{nm}^2$ at $500\text{ }^\circ\text{C}$, determined by the Grignard method.

With a decrease in the silanols, siloxane (Si-O-Si) bonds are created and the hydrophilicity decreases. With an increase in the relative humidity where the particles have been stored, the adsorbed amount of water on the particles increases and the degree of particle aggregation is changed (Kawamura et al., 2014).

Fig. 4 shows typical water vapor adsorption isotherm of the silica nanoparticles (Aerosil 200). The adsorption isotherm is IUPAC classification type III. In general, because the interaction between the silica surface and water molecules is strong, the water adsorption isotherm is described as type II. When the interaction between the adsorbate and a solid surface is weak, the adsorption isotherm is listed as type III. In this case, it is thought that the number of silanols on the Aerosil 200 surface is low in comparison to the silica gel. The reason why is re-

Fig. 4 Water vapor adsorption isotherm of Aerosil 200 with adsorbed amount of water measured by weight difference before/after humidity control.

garded as follows. Aerosil 200 is synthesized at a high temperature by a dry process. The surface silanols are eliminated in that process. During the initial stage of water adsorption as shown in **Fig. 4**, the localized adsorption of water molecules occurs on the silanols. This localized adsorption then grew into an island-state adsorption by cooperative adsorption. Furthermore, the adsorbed amount increased at a high relative humidity due to the occurrence of a multilayer adsorption on the continuous two-dimensional water layer which is constructed by contact among the water islands (Fuji et al., 2000).

The plots as black circle in **Fig. 4** represent amount of water adsorbed on the humidity-controlled-silica nanoparticles measured by the weight difference before and after water vapor exposure. The adsorbed water amount also increased with the relative humidity although there are errors which are probably due to measurement principle differences.

Table 2 lists (a), (b) the amount of adsorbed water, (c) the number of adsorbed water molecules, (d) adsorbed water molecules per one silanol groups, and (e) estimated adsorbed water layer when the humidity is controlled from 60 to 92 %. The number of adsorbed water layers rapidly increased especially at the higher relative humidity.

Fig. 5 shows the relaxation time constant ($1/T_2$) as a function of the number of adsorbed water layers which was estimated from the water vapor adsorption isotherm as shown in **Table 2**. These solvent relaxation data were measured as silica nanoparticle, n-hexane dispersions to prevent adsorbed water layer diffusion into the solvent and to only detect the bound water. The $1/T_2$ increased with an increase in the adsorbed water layer. It is noted that gradual increases were observed near the first layer. The first inflection point after the first layer indicated that the adsorbed water at more than a 1.138 layer from the silica surface can be detected by the NMR. The second inflection point indicated that the layer between 2.160 and

Table 2 Estimation of adsorbed water layer on silica nanoparticles calculated from the water vapor adsorption isotherm.

Relative humidity [%]	Amount of adsorbed water [mg/g]		(c) Number of adsorbed water molecules ($\times 10^9$) ^a	(d) Number of adsorbed water molecules per one silanol group ^a	(e) Estimated adsorbed water layer per one particle ^b
	(a) weight difference before/after humidity control	(b) amount of water vapor adsorption ^c			
60	18.0	25.3	8.47	1.51	0.847
70	30.0	34.0	11.38	2.03	1.138
80	57.5	53.1	17.76	3.17	1.776
86	71.3	78.0	26.10	4.66	2.610
92	77.7	99.8	33.36	5.96	3.336

^{a,b} Calculated from c.

^b Calculated using the specific surface area of AEROSIL 200.

Fig. 5 Relaxation time constant as a function of number of adsorbed water layers calculated from water vapor adsorption isotherm.

Fig. 6 Relationship between R_{sp} and total surface area of Aerosil130.

Fig. 7 Particle size distributions (left) and optical microscopic observations (right) of the model aggregates prepared with (a) 1 kN, (b) 5 kN, and (c) 10 kN.

3.336 seems to be the maximum limitation which can be detected as bound water on the silica surface. At least the range between the 1.138 and 2.610 layers can be detected as the bound water.

3.2 Characterization of nanoparticle aggregation by NMR

We now focus on applying the NMR solvent relaxation to investigate the silica nanoparticle (Aerosil 130) aggregation. The nanoparticle aggregates have small pores among the nanoparticle gaps where solvent (water in this case) is included in. How can the NMR detect the bound water in the small pores? To investigate this, the relaxation time of the artificially-prepared model aggregates with different sized pores was determined. The preparation of the aggregates was described in the experimental section. The pore sizes were adjusted by load (i.e., 1, 5,

and 10 kN, which correspond to 13, 64, and 127 MPa, respectively) when preparing the pellets of Aerosil 130. The pellets were used as the model aggregates after being fractured and sieved.

Before starting, the relationship between R_{sp} ($= [R_{av}/R_b] - 1$) and the total surface area of Aerosil 130 was evaluated as shown in **Fig. 6**. The R_{av} , that appeared in the Eqn. 1, is expressed by the sum of the relaxation time constants ($1/T_2$) of the bound water on the particle (R_s) and free water (R_b) which is being multiplied by each concentration. The particle concentrations were changed between 0.15 and 10 mass%. The total surface areas at each solid concentration were calculated using the specific surface area (calculated using BET theory from the gas adsorption isotherm data). The R_{sp} value and the total surface area showed an approximate proportional relationship. Therefore, it can be said that the relative evaluation of the wetted surface area of Aerosil 130 is possible

Fig. 8 (a) Nitrogen gas adsorption (ADS) and desorption (DES) isotherm and (b) BJH pore size distributions ((c) enlarged) of model aggregates.

using the R_{sp} value. The model aggregates were then characterized by their size distribution, microscopic observations, and pore size distribution. **Fig. 7** show the size distributions by the laser diffraction technique and optical microscopic observations of the model aggregates prepared with 1, 5, and 10 kN after being milled and sieved ($> 100 \mu\text{m}$). Their median diameters (D_{50}) were 360.0 (1 kN), 343.9 (5 kN), and 388.9 μm (10 kN), respectively. It can be said that they have similar size distributions. The optical microscopic observations showed us that similar fractured shapes were obtained and small-sized aggregates with less than 100 μm were eliminated. **Fig. 8** shows the nitrogen gas adsorption desorption isotherms and pore size distributions calculated using the BJH method from the isotherms of the model aggregates. The specific surface area (S_{BET} from BET theory) from the isotherms, average pore size, and pore volume (BJH theory) are listed in **Table 3**. With an increase in the load, they decreased. **Fig. 9** shows SEM images of the fractured surface of the model aggregates. The rough surface can be clearly observed in the 1 kN model aggregates. The large pores of more than 100 nm were also observed in the SEM images, which are more than 46.13 nm calculated from the BJH. A pore size more than 50 nm is out-of-detection when using the gas adsorption isotherm. In combination with a mercury porosimetry, the micron-ordered large pores of the pellets disappeared over 60 MPa (5 kN, here) (Our unpublished results). With an increase in the load, the roughness clearly decreased.

Fig. 10(a) shows typical relaxation time curves of the model aggregates at 1, 5, and 10 kN load. Each standard deviation of ten measurements was in the range between 0.5 and 0.7. **Fig. 10(b)** shows the relationship between the wet specific surface area (S_{NMR}) and S_{BET} . The decreasing tendency of the S_{NMR} with an increase in the load was similar to that of the S_{BET} . Since the sizes of the model aggregates are similar as shown in **Fig. 7**, these changes can be affected by the aggregation structure. The reason why S_{NMR} is smaller than S_{BET} is probably due to unde-

Table 3 Fundamental data of the model aggregates prepared at 1, 5, and 10 kN.

Load [kN]	D_{50} [μm] ^a	S_{BET} [m^2/g] ^b	Average pore size [nm] ^c	Pore volume [cm^3/g] ^c
1	360.0	137.6	46.13	1.81
5	343.9	133.7	29.50	1.09
10	388.9	124.2	22.07	0.84

^a Average size from DLS.

^b BET specific surface area.

^c BJH theory.

Fig. 9 SEM micrographs of the model aggregates prepared with (a) 1 kN, (b) 5 kN, and (c) 10 kN.

tectable bound water on the very top surface of the particle. Can the NMR detect the model aggregates which are mixed in the slurry? **Fig. 11** shows the S_{NMR} of the 10 mass% slurry with different ratios of the model aggregate (5 kN). The S_{NMR} , represented as blackened triangles, decreased with an increase in the model aggregate ratio and approached the value of the 5 kN model aggregate. The broken line appeared as the theoretical S_{NMR} calculated using S_{NMR} considering ratio of the as-received AEROSIL 130 and 5 kN model aggregates. The measured

Fig. 10 Typical results of model aggregates and wet specific surface area (S_{NMR}) calculated using Eqn. 4. The break line in (b) means $S_{\text{NMR}} = S_{\text{BET}}$.

Fig. 11 S_{NMR} of the 10 mass% slurry with different ratios of model aggregate (5 kN). The bold and broken lines are theoretical S_{BET} and S_{NMR} , respectively, which are calculated considering the model aggregate ratio.

S_{NMR} became smaller than the theoretical value, especially for the higher ratio of the model aggregate (i.e., 0.4 in this case). This is probably due to the as-received AEROSIL 130 gathering together with the model aggregates. Note that even a low ratio (i.e., 0.05) of the model aggregate can be detected by the solvent relaxation NMR.

4. Conclusion

The effectiveness of the solvent relaxation NMR as a tool to characterize the nanoparticle aggregation structure was verified. The most important finding in this study is that the adsorbed water layer on the silica nanoparticles ranging between 1.138 and 2.610 can be detected as bound water to determine the wet specific surface area (S_{NMR}). The S_{NMR} of the artificially prepared model aggregates was underestimated compared to S_{BET} due to undetectable water which was strongly bound on the particle surface. The S_{NMR} could even show low ratio of the model aggregates in the silica nanoparticle dispersion. The required amount for the NMR experiment is only 1 mL and the measuring time is just few minutes regardless of the particle concentration. In addition, not only the aqueous dispersion, but also a nonaqueous dispersion can be measured. Indeed, there are still difficulties in understanding the results, however, the proposed technique could be a simple and versatile tool to characterize the nanoparticle aggregation structure.

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