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Determination of complex permittivity of surfactant treated powders using an open-ended coaxial cavity resonator

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ABSTRACT

An indirectly coupled open-ended coaxial cavity resonator was used to detect the effect of stearic acid surface treatments on the dielectric properties of powders in the frequency range 2.17–3.79 GHz. The Bruggeman symmetric and Looyenga classical mixing rules and a general mixing model were used to determine changes in permittivity and loss tangent of the inclusions. Surfactant processed powders with stearic acid 0.05–1.36 vol.% induced only a small change in inclusion permittivity but caused a notable change in dielectric losses. The dielectric loss tangents of SiO_2 and Al_2O_3 increased from 2×10^{-4} to 4×10^{-4} and 5×10^{-3} to 6.1×10^{-3}, respectively. However, a significant decrease in dielectric loss tangent, from 6.2×10^{-3} to 3.8×10^{-3}, was noted with surfactant treated ZrO_2. The investigated novel characterization method proved to be able to detect even very slight changes in dielectric properties to be utilized in various types of powdery material characterization, e.g., in composite applications and material quality monitoring.

1. Introduction

Processability of powdery ingredients and stable properties of the final product is the priority in several industrial and research processes. In order to improve the processability, the powders used may be modified with additives and surfactants, which can influence the properties of the final product. Surfactants can be utilized for certain process phases only or they may be retained as a part of the final product. Trunec et al. have reported significant improvements in injection molded and sintered components after the rheological properties of yttria-stabilized zirconia were modified by surface treatment [1]. Insufficient coverage of the surfactant coating can increase the size and quantity of agglomerates. This changes the flowability of the injected material and consequently the properties of the molded components can differ from the desired properties [1–3]. Surfactants can also affect the hygroscopicity of the powders, which has been reported to influence, e.g., the compressibility of pharmaceutical powders and the mechanical properties of composites used in the process and electronics industries, respectively [3–8]. In addition, the dielectric properties of composites can be controlled with surfactants. This has also been reported as decreased dielectric losses of fiber-polyethylene and high-k nanoparticle-polymer composites by Augustine P. et al. and Lu and Wong, respectively [9,10]. Both electrical and mechanical properties can be affected by the surface treatment process. This creates a need for accurate characterization of surface modified powders.

In this paper we characterized the dielectric properties of surfactant treated oxide powders using an indirectly coupled open-ended coaxial cavity resonator. Measurement results were compared with the results for untreated powders and theoretical calculations. Also, coating coverage of the surfactant processed particles was studied by thermal analysis and energy filtered transmission electron microscopy (EFTEM).

2. Experimental

The dielectric properties of untreated and stearic acid coated oxides were measured with an indirectly coupled coaxial cavity resonator operating at 4.5 GHz in transverse electromagnetic mode. This novel characterization method is presented in detail elsewhere [11].

2.1. Characterized materials

The powders used were SiO_2 (Strem Chemicals, 99.8%, 100 mesh), α-Al_2O_3 (Teknofokus, 30 μm) and ZrO_2 (Sigma-Aldrich, 99%, <5 μm). Specific surface areas (SSAs) of the powders were determined based on the nitrogen gas adsorption on powder particles at the temperature of liquid nitrogen and the BET method (ASAP™ 2020, Micromeritics Instrument Corporation, U.S.A.). The SSA values were 0.30 m^2/g, 0.45 m^2/g and 5.05 m^2/g for SiO_2, Al_2O_3 and ZrO_2, respectively. All the powders were dried in a desiccator with 3% relative humidity for a week. The densities of dry untreated particles were measured by the Archimedes method using de-ionized water and a 10.115 cm^3 pycnometer (Gay-Lussac BlauBrand®, Brand GmbH + Co KG, Germany). Stearic acid (Fluka, ≥97%, boiling point 361 °C, 284.49 g/mol) was used as a surfactant for coating the particles. The density of the stearic acid was

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calculated by weighing a solid sample with a precision balance (XB 620 M, Precisa Gravimetrics AG, Switzerland) and measuring the dimensions with a micrometer screw (Series 293, Mitutoyo, U.S.A.). The dielectric properties of the stearic acid particles were measured to allow a theoretical comparison with the corresponding experimental results obtained with the previously presented method at 3.5 GHz [11].

2.2. Coating of powders

The amount of surfactant required to create an extensive monolayer of stearic acid molecules on the particles was calculated based on the measured SSA values of the powders and the area of the stearic acid molecule (~0.21 nm^2) [12]. The surfactant was dissolved in ethanol (Altia Plc., ETAX, Aa, 99.5 wt.%) with a concentration of 2 mg/ml. The powders were dosed with the solution by means of a microliter pipette (BRAND GMBH + CO KG, Germany) to form master samples for subsequent investigations. The amount of stearic acid per master sample was 3.6 mg/5.5 g, 8 mg/8 g and 120 mg/10.5 g for SiO_2, Al_2O_3 and ZrO_2 powders, respectively. The mixture of oxide powder and stearic acid–ethanol solution was ball mixed at room temperature and humidity for 6 h using agate grinding balls and polyethylene jars. After mixing the surfactant treated powders were separated from the solution by a centrifuge and dried in a desiccator for a week. The amount of adsorbed stearic acid was measured from a 50 mg sample by the simultaneous thermal analysis method using thermogravimetry, differential scanning calorimetry and mass spectrometry (STA–TG–DSC–MS, Netzsch QMS 403 C + STA 449 F3 Jupiter®, Germany). The coating coverage of several particles was inspected with an energy filtered transmission electron microscope (LEO 912 Omega, Carl Zeiss AG, Germany) minimizing the effect of miss-focus, i.e., an even, thin corona covering the particles, and using the highest resolution 500,000:1.

2.3. Dielectric properties measurements

The characterization of untreated and stearic acid coated oxides was performed at room temperature in 15–20% relative humidity with six different volume fractions of powders in a homogeneously fully filled 1.092 cm^3 sample cavity. A vector network analyzer (Rohde and Schwarz ZVB 20 GHz) was used to measure the transmission coefficient (S_{21}) and to determine the frequency response of the resonator. The resonance frequency and Q-value, i.e., the ratio of how much energy was stored and dissipated in the resonator during one cycle at resonance frequency, were measured with an empty cavity before the characterization of each powder. All samples were measured at −35 dB coupling strength where the effect of the coupling probes was negligible [11].

2.3.1. Determining dielectric constant

The effective (air-particle mixture) permittivities were calculated based on the measured resonance frequency and resonator dimensions [11]. In the determination of the relative permittivity of inclusions two classical mixing rules, the Bruggeman symmetric (Eq. (1)) and Looyenga (Eq. (2)), were used.

$$\frac{\varepsilon_i-\varepsilon_{\text{eff}}}{\varepsilon_i+2\varepsilon_{\text{eff}}}f+\frac{\varepsilon_e-\varepsilon_{\text{eff}}}{\varepsilon_e+2\varepsilon_{\text{eff}}}(1-f)=0 \tag{1}$$

$$\varepsilon_{\text{eff}}{}^{1/3}=(1-f)\varepsilon_e{}^{1/3}+f\varepsilon_i{}^{1/3}, \tag{2}$$

where ε_{eff}, ε_e, and ε_i are the effective permittivity of medium, permittivity of matrix (e.g., air, $\varepsilon_r = 1.00059$) and inclusion respectively, and f is the volume fraction of the dielectric powder with and without surfactant. These rules had previously been found to correlate best with the particular characterization method [11]. Inclusion permittivity was determined at volume fraction ~0.43 when the effective permittivities of both mixing rules correlated with the measured effective permittivity. The measured effective permittivities and determined relative permittivities of inclusions were compared between untreated and stearic acid coated oxides.

2.3.2. Determining loss tangent

In determination of the dielectric losses, the changes in the Q-value between an empty and a filled resonator were used. The effective loss tangent ($\tan\delta_{\text{eff}}$) of the dielectric sample filling the cavity is defined by Eq. (3).

$$\tan\delta_{\text{eff}}=\frac{1}{Q_{\text{filled}}}-\frac{1}{Q_{\text{empty}}}. \tag{3}$$

Measured effective loss tangents of the surfactant treated powders were compared to the calculated values with theoretical (dosed and optimally adsorbed) amounts of surfactant and measured (STA–TG–DSC–MS) amounts of surfactant with the influence of water. The method was found to correlate with the theory in reference [13] where the influence of water with high dielectric loss (0.157 at 3 GHz) [14] was analyzed. The relations between dielectric loss tangents of composites can be described by the general mixing model, Eq. (4).

$$(\tan\delta_{\text{eff}})^{\alpha}=\sum f_i(\tan\delta_i)^{\alpha} \tag{4}$$

where $\tan\delta_i$ and f_i are the loss tangents and volume fractions of the ith material, respectively. Constant α determines the mixing model, i.e. −1 = serial, 0 = logarithmic and 1 = parallel [15–17].

With high concentrations and parallel mixing Eq. (4) results in $\tan\delta_{\text{eff}} = f_{d1}\tan\delta_{d1} + f_s\tan\delta_s + f_w\tan\delta_w + f_a\tan\delta_a = f_d\tan\delta_d + f_a\tan\delta_a$, where subscripts d1, s, w, a and d refer to untreated dielectric material, stearic acid, water, air and treated dielectric material, respectively. Approximating the loss tangent of air to zero, the equation for the dielectric loss tangent ($\tan\delta_d$) reduces to (Eq. (5)):

$$\tan\delta_d=\frac{\tan\delta_{\text{eff}}}{f_d}. \tag{5}$$

In the calculation of effective loss tangent of the treated powder, the dielectric losses of dry untreated particles and stearic acid at 3.5 GHz were used. The theoretical volume fraction of stearic acid (f_s) was calculated based on the added stearic acid volume in a prepared master sample and assuming that all added surfactants were adsorbed optimally on the particles. In addition, the theoretical losses were recalculated utilizing the results of thermogravimetry and mass spectrometry analysis. The amount of water and stearic acid in the powder was determined after reaching temperatures of 250 °C and 600 °C, respectively.

In determination of the dielectric properties with volume fraction based mixing models, the effect of changes in the density (ρ), due to adsorbed surfactant and water, was taken into account and recalculated with the measured amounts. The volume fraction of dielectric material in the resonator was defined as $f = (m_{\text{filled\_resonator}} - m_{\text{empty\_resonator}}) / (\rho \times V)$, where m represents mass and V is the volume of the cavity. With stearic acid treated dry powders the $m_{\text{filled\_resonator}} = m_{\text{empty\_resonator}} + m_{\text{powder}} + m_{\text{stearic\_acid}}$.

3. Results and discussion

3.1. Resonator measurements

Using the high accuracy of the vector network analyzer, i.e., 6000 measurement points, for the 3 dB bandwidth and an average of the last ten measurements of the transmission coefficient, the measured resonance frequencies and Q-values were stable and the determined dielectric properties were repeatable.