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Rheology of concentrated SiC particles in silicon alkoxide sols

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Abstract

Silicon carbide (SiC) particles were mixed with silicon alkoxide precursors at the sol level, and their rheological behaviors were examined under various solids concentrations ($\phi = 0.10–0.22$ in volumetric ratios) and shear rates ($\dot{\gamma} = 1-1000\ \mathrm{s}^{-1}$). The alkoxide precursors were mixtures of tetraethyl orthosilicate (TEOS, $Si(OC_2H_5)_4$), ethyl alcohol (C_2H_5OH), H_2O and HCl in a constant $[H_2O]/[TEOS]$ ratio of 11. The powdered mixtures all exhibited a shear-thinning flow behavior over most of the shear-rate range examined. This indicates that the concentrated suspensions were flocculated in character. Relative viscosity of the suspensions increased markedly as ϕ increased, suggesting that the particle interaction becomes more pronounced with the increased ϕ. No evidence was seen found for possible particle–precursor interactions at the sol level that might catalyze gelation of the sols. A theoretical maximum solids concentration (ϕ_m) of the suspensions was determined as $\phi_m = 0.26–0.28$ over a shear-rate range $\dot{\gamma} = 10-100\ \mathrm{s}^{-1}$. This reduced ϕ_m value partially confirmed the dominance of attractive interparticle van der Waals forces in the particle–precursor mixtures.

Keywords: D. SiC; Rheology; Aggregation; Sol–gel; Ceramic matrix composite

1. Introduction

Fabrication of ceramic matrix composites via sol–gel synthesis has received much attention over the years, due mainly to the possible attainment of a high degree of dispersion homogeneity between matrix and reinforcement phases that is considered not easily achievable by conventional dry-powder processing routes [1,2]. The sol–gel process usually involves a preparation of metal alkoxide solution as a precursor. An aqueous solution of a metal salt is then added into the precursor followed then by drying and sintering at elevated temperatures for the fabrication of ceramic composites. Hydrolysis and condensation of the precursor mixtures occur when the metal salt is introduced, which result in a formation of ceramic gels at or near the molecular level. This process is relatively simple and is extremely flexible in terms of the capability in tuning desired chemical composition and doping level of the composites. Various ceramic and metal matrix composites have thus been fabricated by the sol–gel route [3–6].

Rodeghiero et al. [1] recently suggest that an incorporation of sol–gel technique into a broader synthesis scheme can be highly beneficial in attaining composites with designed functional structure and hierarchical order. Composites with desirable properties are then fabricated which are otherwise difficult to make. For example, Colomban [7] used various polymeric precursors to mix with fine powders in order for a better control of the composite structure. Functionally graded composites with tailored structural variation and microwave absorption became attainable in a near-net-shape form. Liu [8] and Liu and Parvizi-Majidi [9] fabricated two- and three-dimensional ceramic matrix composites by invoking a pressure-infiltration process which involves a use of powdered suspensions consisting of silica sol and silica/

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alumina particles to infiltrate into woven fiber matrices with a desired architecture. The addition of particles in the slurry was reported to decrease the stresses induced from the sol-to-gel transition, leading to an improved particle-packing characteristic of the formed compact with a reduced risk of matrix cracking. Although the success of the infiltration process depends critically on the flow property of powder–sol mixtures, reports addressing this issue are scarce in the literature. In this study, we intend to examine the rheological behavior of a model silicon alkoxide sol when nanostructured SiC particles were introduced into the precursor solvents at the sol level. A uniform dispersion of SiC particles in the silica sol was aimed so that a composite thin-film with a homogeneous distribution of particulate SiC reinforcement in silica glass matrix may become attainable. This operation is anticipated to render an improved erosion resistance for the fabricated composite silica glass [10,11].

2. Experimental procedure

Silicon carbide powder (CPL-SiC-n01, Titanex Corp., Taiwan) with a main crystalline phase of α-phase and purity >98.5% was used as the raw material. The powder is about polygonal in shape and is heavily agglomerated with some SiC ''nano-wires'' also apparent. As shown in Fig. 1, the agglomerate size often exceeds 100 nm in diameter.

Reagent-grade tetraethyl orthosilicate (TEOS, $Si(OC_2H_5)_4$), ethyl alcohol (C_2H_5OH), H_2O and HCl (all from Aldrich Chemicals) in a constant $[H_2O]/[TEOS]$ ratio of 11 were used as the precursor sol and were mixed with the powder in various solids concentrations ($\phi = 0.10$–0.22 in volumetric ratio). The powdered mixtures were ball-mixed in polyethylene bottles using high purity silicon carbide balls as the mixing media for 24 h. Their viscosity (η_s) was determined by a strain-controlled concentric viscometer (VT550, Gebruder HAAKE Gmbh, Germany) equipped with a sensor system (MV-DIN 53019, HAAKE, Germany) of a cone-cup geometry operated at a constant temperature (25 °C). The measurement was performed with a steady increment of shear rate ($\dot{\gamma}$); to which, the rate was increased in every 1 s^{-1} over the shear-rate range of 1–10 s^{-1}, every 10 s^{-1} over 10–100 s^{-1} and every 100 s^{-1} over 100–1000 s^{-1}. Interfacial interaction that might occur between the alkoxide sol and the SiC surface was examined using an infrared spectroscopy (FTIR, Spectrum RX I, Perkin-Elmer, U.S.A.) over a wavenumber range of 400–4000 cm^{-1}. Repeatedly centrifuged and dried SiC granules were mixed with KBr powders, and the IR spectrums were then measured by using a diffuse reflectance.

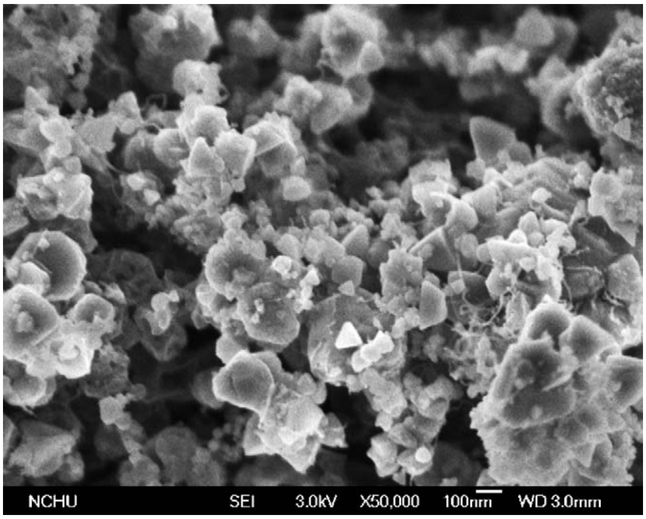

Fig. 1. Particle morphology of the SiC nanoparticles used in the study.

3. Results and discussion

Fig. 2 shows η_s–$\dot{\gamma}$ dependence of the SiC–silica sol mixtures over the shear-rate range examined. All the suspensions exhibited a shear-thinning flow character as $\dot{\gamma}$ increased, indicating that SiC agglomerates existed in the liquid carrier even after the prolonged ball-mixing operation (24 h). The agglomerates were broken down into smaller flow units as the shear rate increased, hence resulted in a reduced flow resistance. It may be interesting to note that the flow behavior of the powdered mixtures appeared to change from shear thinning toward shear thickening as $\dot{\gamma}$ exceeds a critical rate level when the solids concentration was held at less-concentrated levels ($\phi \leq 0.18$). Hoffman [12] has vindicated that powders in given liquid carrier would adapt to become more of an ordered structure with particles arranging themselves toward a uniform, denser packing configuration as shear forces increases for a reduction in the overall potential energy of the suspensions. When shear rate is raised beyond a critical level, any inhomogeneity exists in suspension would perturb the intricate balance among particles in carrier liquid and result in an immediate

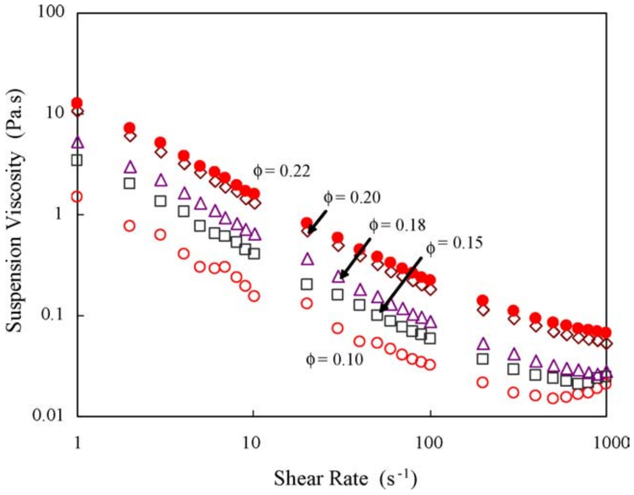

Fig. 2. Suspension viscosity of the SiC–silica sol mixtures at various solids concentrations ($\phi = 0.15$–0.22) over a shear-rate range $\dot{\gamma} = 1-1000$ s^{-1}.

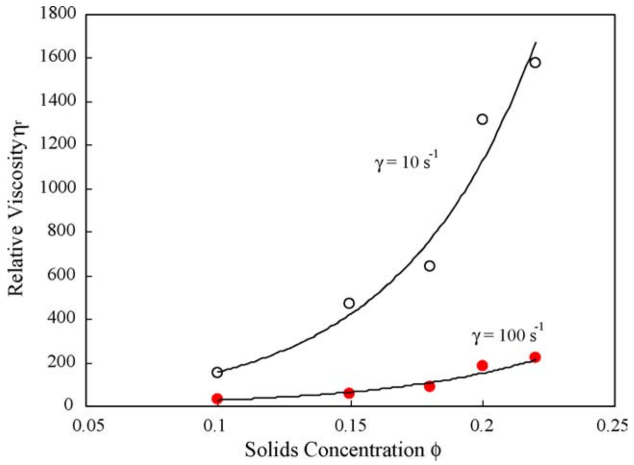

Fig. 3. Relative viscosity as a function of solids concentration for the SiC–silica sol mixtures.

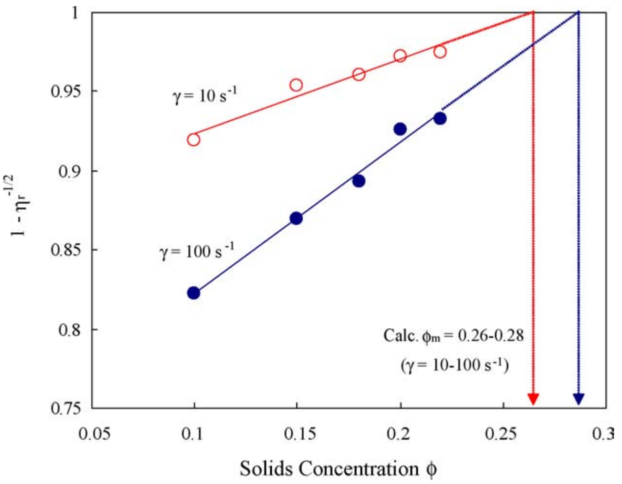

Fig. 4. The $(1 - \eta_r^{-1/2})$–ϕ dependence for the determination of the maximum solids concentration (ϕ_m) for the SiC–silica sol mixtures.

destruction of the regularly arrayed structure. A less ordered structure hence results, and this relatively voluminous configuration requires an increased energy for flow to proceed due presumably to particle ‘‘jamming’’ in liquid [13], which in turn lead to an increase in the suspension viscosity.

Relative viscosity of the suspension (η_r) defined as the ratio of suspension viscosity (η_s) over the viscosity of carrier medium (η_o) appears to be a non-linear function of the solids concentration (Fig. 3). This non-linearity becomes more pronounced at a reduced shear rate (e.g., $\dot{\gamma} = 10\ \mathrm{s}^{-1}$). A theoretical, maximum solids fraction (ϕ_m) of the SiC–sol suspensions can be estimated from the viscosity results. Among many empirical models proposed, a recent report [14] has found that a derivative of η_r, i.e., $1 - \eta_r^{1/2}$, often shows a linear dependence with ϕ over a wide range of solids concentrations, particle sizes and suspension chemistries. ϕ_m can then be determined from an extrapolation of the $1 - \eta_r^{1/2}$ value to unity, at which η_r approaches infinity. For the model suspension examined, the experimentally determined $1 - \eta_r^{1/2}$ values do appear linearly proportional to ϕ with reasonable correlation factors $R^2 > 0.95$ (Fig. 4). The ϕ_m values determined are $\phi_m = 0.26$ and 0.28 at $\dot{\gamma}$ of 10 and $100\ \mathrm{s}^{-1}$, respectively. Note that the ϕ_m values seem to increase moderately with $\dot{\gamma}$. This is not too surprising since an increased ϕ_m often results for powdered suspensions to change to a solid-like ‘‘bulk’’ from a liquid-like ‘‘fluid’’ at an increased external stress so that the ϕ_m determined is indeed shear-rate dependent. Even though the absolute value of the estimated ϕ_m may not be truly meaningful, the ϕ_m values determined are far much lower than that of the random close-packing of monosized spheres ($\phi_m \sim 0.64$). The apparent agglomeration found in the starting powder (Fig. 1), which persistently existed after the high-shear ball mixing, are suspected to contribute at least partially to the reduced ϕ_m attainable. The rheological properties of the SiC–sol mixtures (Figs. 2–4) are possibly governed by the surface potential and the interfacial characteristics existing between the SiC particles in the carrier liquid.

The concentrated SiC–silica sol suspensions showed a plastic behavior with yield stress (σ_y), and the flow curve above the yield stress appeared to follow the Herschel–Buckley model in a form:

$$\sigma = \sigma_y + k\dot{\gamma}^n \tag{1}$$

where k and n are constants that can be determined experimentally. Fig. 5 shows the σ_y–ϕ dependence, and a power-law fit yields a satisfactory correlation with $R^2 = 0.95$. Shih et al. [15] have recently proposed that the self-similar structure of an attractive, interconnected particulate network in liquid and the geometry of powdered aggregates in a flocculated suspension can be characterized by fractal geometry. The suspension σ_y values then scale with ϕ in a simplified form:

$$\sigma_y = G\phi^m \tag{2}$$

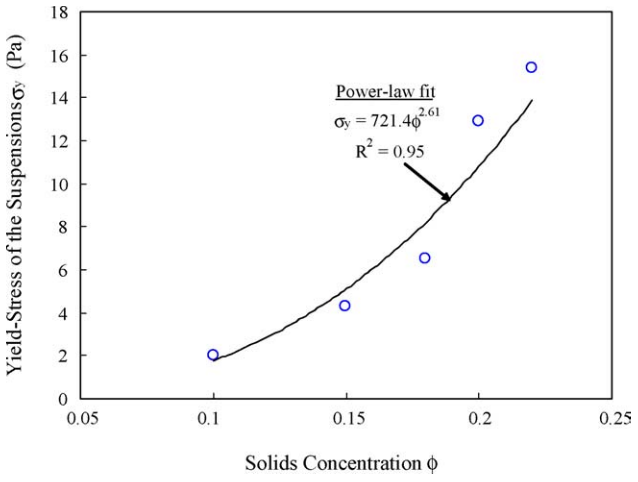

Fig. 5. The σ_y–ϕ dependence of the SiC–silica sol mixtures. The solid curve represents the power-law fit of the experimentally determined σ_y values.

where G is a constant mainly associated with interparticle spacing and zeta potential involved between particle surfaces in liquid. The exponent m can be evaluated from the suspension σ_y–ϕ relationship and is further related to the fractal dimension (D_f) of the flocculated network by equation:

$$m = (d + X)/(d - D_f) \tag{3}$$

where d and X are the Euclidean dimension and the backbone of the clusters, respectively. Considering the fractal geometry in three dimensions and hence the Euclidean dimension $d = 3$, D_f is then determined from the slope m by assuming X equals unity [15]. This gives D_f of 1.47 for the given SiC–sol mixtures examined.

Bergström [13] has pointed out that the lower the value of D_f, the more open is the agglomerate structure in the carrier liquid, i.e., the agglomerate structure with a larger ‘‘intra-agglomerate’’ void space. The calculated D_f, $D_f = 1.47$, approaches that of the diffusion-limited cluster–cluster aggregation (DLCA) model of which $D_f = 1.78$ in three dimensions. This reveals that the van der Waals attraction dominated the interparticle potential of the suspensions, so that the SiC particles were energetically favorable to form agglomerated clusters and eventually interconnected particulate networks in the liquid, when collisions of the particles were made possible by the Brownian motion. The formation of the disordered fractal structures is then solely determined by the diffusion distance involved between the particles in the sol liquid.

The above fractal analysis of the model suspension is carried out by fitting of the experimentally determined viscosity data and some uncertainty (or ‘‘error’’) in determining the fractal dimension may exist. The above analysis nonetheless provides ‘‘clues’’ that an attractive interparticle potential do play a critical role in determining the mixture rheology and hence the subsequent infiltration process for composite fabrication via the sol–gel–powder route. In this regard, an addition of organic surfactant in the SiC–sol mixture may be beneficial in terms of the reduction in mixture viscosity, provided that a possible sol–surfactant reaction can be prohibited. A stable dispersion may be inferred by an electrostatic repulsion of charged particle surface or by a preferential adsorption of surfactant molecules onto the particle surface to avoid a direct contact of the particles (i.e., the steric hindrance mechanism). In a preliminary experiment, a resin-based polymeric surfactant (1040 s, Deuchem Co., U.S.A.) was found useful in the dispersion of the SiC–sol mixtures. A notable reduction in the mixture viscosity results, ~60% reduction at $\dot{\gamma} = 100\ \mathrm{s}^{-1}$ for the $\phi = 0.1$ suspensions. A reduced flow resistance is believed to be beneficial for a successful infiltration process in the fabrication of SiC–SiO_2 composites.

4. Conclusions

Rheology, suspension structure and the determination of maximum solids concentration allowable for a SiC particle–silica sol mixture have been examined over a range of solids concentrations ($\phi = 0.10$–0.22) and shear rates ($\dot{\gamma} = 1$–$1000\ \mathrm{s}^{-1}$). A shear-thinning flow behavior resulted over most of the shear-rate range investigated. This indicates an existence of powder agglomerations in the carrier liquid. The powdered agglomerates were suspected to form porous flocs of low density, eventually resulted in a formation of interconnected particulate networks of disordered structures in carrier liquid. This proposition was confirmed by a fractal analysis determined from the rheological data, and a fractal dimension (D_f) of 1.47 was calculated, approaching that of the diffusion-limited cluster–cluster aggregation ($D_f = 1.78$). The maximum solids concentration (ϕ_m) of the model suspension is determined as $\phi_m = 0.26$ and 0.28 at $\dot{\gamma}$ of 10 and $100\ \mathrm{s}^{-1}$, respectively. This reveals that the rheological response was mainly dominated by the interparticle attractions. Addition of a resin-based organic surfactant appeared to reduce viscosity of the powdered precursor mixtures, which should be beneficial for composite fabrication via the powder–sol–gel route.

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