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Effect of blend ratio on rheological properties of aqueous SiC suspensions

Qiang Huang*, Wei Li, Mingyuan Gu, Ping Chen,
Hongxiang Zhang, Yanpin Jin

*State Key Laboratory of Metal Matrix Composites, Shanghai Jiaotong University,
Shanghai 200030, PR China*

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Abstract

The relationship between blend ratio and rheological properties of concentrated suspensions is of great importance since it is the key to get high solid suspensions. The rheological properties of bidisperse aqueous suspensions made of two SiC powders with different particle size [$d_{(0.5)}=1.63$ and 18.43 μm, respectively] has been studied as a function of blend ratio ξ (the volume fraction of larger particle size). The results showed that the value of critical blend ratio ξ, at which the viscosity is minimized, is in close relation to the shear rate applied. At shear rates below 10 S^{-1}, the critical ξ was greater than 70%. But at shear rates from 10 to 500 S^{-1}, ξ turned to be 50%. The change of shear region from shear-thinning behavior to shear-thickening behavior may be used to account for the variation of critical ξ. Dynamic oscillatory tests showed that the moduli and the linear viscoelastic region of suspensions with higher ξ are smaller than those with low ξ and the increment of blend ratio ξ leads to the change of suspension from nearly an elastic response to a liquid like response.

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1. Introduction

As a covalent material, silicon carbide (SiC) is recognized as an important candidate in a wide range of industrial applications due to its special set of physicochemical properties such as high hardness and strength retention at elevated temperature, good thermal stress resistance and excellent wear, erosion, and oxidation resistance.[1] Furthermore, its excellent combination of thermal properties (low coefficient of thermal expansion, high thermal conductivity), availability and cost have also made it an arresting class of candidates as reinforcements for high volume fraction metal matrix composites (MMCs), which are now being exploited on an industrial scale in electronic packaging.[2,3] However, regardless of the potential use for ceramic components and MMCs, attainment of a well mixed, uniform green body with a high density, minimum density variation and homogenous pore size distribution is the most important aspect in its production.

Colloidal processing including slip casting, gelcasting and direct coagulation casting (DCC) have been suggested as a preferred way to produce high quality SiC green body.[4–6] The physical or chemical processes responsible for the formation of a solid green body differ greatly, but all the methods require a well-dispersed suspension of high solids loading with reasonably low viscosity to facilitate the mold-filling process. So the rheological properties of the concentrated suspensions play a key role in controlling the shape forming behavior and optimizing properties of the green body. Adapting the surface properties of SiC particles by modifying pH value of SiC slurry,[7] choosing approximate dispersant[8] and calcinating SiC powders[9] offers a route to reduce viscosity and hence aid processing. Optimizing particle size distribution (PSD) is also an effective way to obtain high solids loading suspensions with low viscosity.[10] Unfortunately, available reports regarding the influence of SiC PSD on rheological

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* Corresponding author.
E-mail address: qhuang0715@eyou.com (Q. Huang).

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bahavior of aqueous SiC suspensions are limited in the open literature.[11]

To ensure high reliability and good sinterability, the ceramic powders used possess dimension mostly in the size range of 10^{-2}–1 μm. With particles in the colloidal size range, surface modification is an effective way to change the range and magnitude of the interparticle forces, which have a profound influence on the rheological behavior.[12] But for MMCs, because of the existence of interfacial reaction zone, which has negative effect on thermal properties, especially thermal conductivity (TC),[13] ceramic reinforcements are often in the range of 10 μm. Under this condition, optimizing the PSD turns to be a practical and effective way to control the rheological behavior of a dense suspension. In the present work a systematic study on the rheological properties of bidisperse aqueous suspensions made of SiC particles of two different diameters, 1.63 and 18.43 μm, was performed. The effect of the blend ratio on the rheological properties of suspensions are presented and discussed.

2. Experimental procedure

The starting raw materials were two commercial SiC powders A and B (Sanxin Industries). The special surface areas of SiC A and B were measured by a single point BET method (Masteriserzer 2000, Malvern Intrument Ltd., UK) to be 6.55 and 0.39 m^2/g respectively. $d_{(0.1)}$, $d_{(0.5)}$ and $d_{(0.9)}$ for SiC A are 0.36, 1.63 and 3.90 μm, and for SiC B 9.63, 18.43 and 33.34 μm, respectively. SEM study showed that there was no distinct disparity in aspect ratio between SiC A and B, so it was reasonable to assume that the average aspect ratio of SiC A and B are identical. Fig. 1 shows the particle size distribution of the two starting SiC powders. It is seen that the size of SiC A powder is within 0.1–10 μm. Further, the PSD of SiC A exhibits bimodal to a certain extent. The as-received powders were first leached with base solution and were repeatedly rinsed with deionized water.

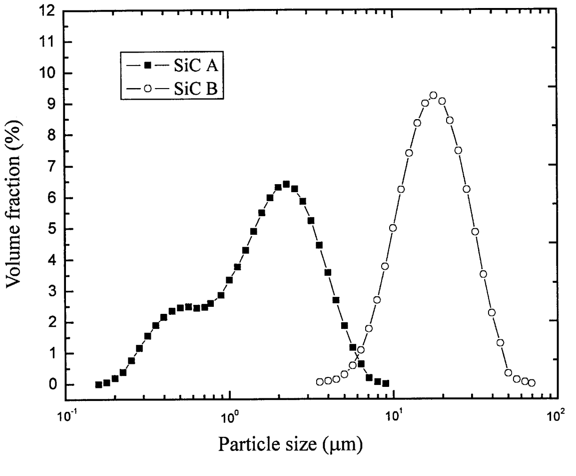

Fig. 1. Particle size distribution of the two starting SiC powders.

The effects of the PSD on rheological behavior of SiC suspensions were investigated by blending the two SiC powders in five different proportions. Aqueous suspensions with a total content of SiC powders (Φ) $45_{\mathrm{vol}}\%$, in which SiC B varied between 30 and 70%, were prepared. Since addition of more SiC B will eventually destabilize the suspension, leading to sedimentation of the solid particles, the volume fraction of SiC B is kept below 70%. The suspensions were then blended thoroughly by ball milling for 10 h using SiC spherical grinding media. The pH value of the suspensions was adjusted to 10.0 by the addition of 20% tetrapropyl ammonium hydroxides (TMAH Shanghai Chemical Plant, China).

The rheological behavior of the SiC suspensions was investigated with a strain-controlled rheometer (4ARES-9a, Rheometric Scientific Inc. USA) at room temperature. Couette (cup diameter: 36.8 mm; bob diameter: 35.0 mm; bob length: 37.3 mm) was used for all these measurements. A small amount of silicone oil was placed above the samples to prevent the evaporation of water. In order to avoid undesired influence from different mechanical histories, all samples were preconditioned at a shear rate of 50 S^{-1} for 1 min and left standing for additional 1 min before collecting the data. Three types of rheological measurements were carried out. Steady rate sweep measurements were used to characterize the general flow behavior with shear rate ranging from 10^{-2} to 500 S^{-1}. The other two kinds of oscillatory measurements—a strain sweep measurement from 10^{-4} to 0.2 at 1 Hz and a frequency sweep measurement from 0.1 to 100 Hz—were also used to obtain information on the viscoelastic behavior of suspensions. Because the measurements taken with different samples of a given composition showed variation on the order of 5% or less, the results presented for each composition are only from single run of one specimen.

3. Results and discussion

3.1. Steady rate sweep tests

Fig. 2 illustrate the effect of the blend ratio of SiC powders on the equilibrium viscosity of the suspensions with a constant solids loading of 45 vol.%. The abscissa and ordinate represent shear rate γ and viscosity η, respectively. It can be seen that all of these suspensions are initially shear-thinning, reaching a minimum viscosity at a critical value of shear rate (γ_c) and then exhibit a shear-thickening behavior at higher shear rates. Neither a high nor a low shear plateau was observed. Further,

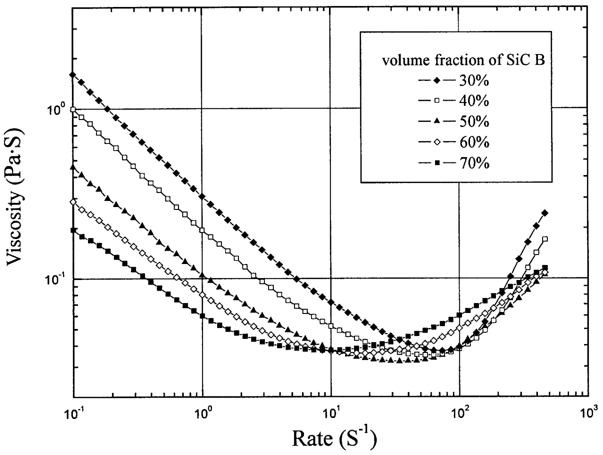

Fig. 2. Steady shear viscosity for two-component SiC suspensions with different blend ratio.

Fig. 2 indicates that the suspensions containing high proportion of coarser powder show lower viscosity value at shear rates below 10 S^{-1}. The viscosity values gradually increased as more SiC A were replaced by SiC B, reaching a maximum when the volume fraction of SiC B reached 70%. But at shear rates greater than 10 S^{-1}, suspension with equal proportion of SiC A and B shows the lowest viscosity. It is also noteworthy to point out that the γ_c and the severity of the shear-thickening behavior decreases as the volume fraction of SiC B changes from 30 to 70%. The shear-thickening behavior of the viscosity as a function of shear rate can be fitted by the Ostwald-de Weale model with the following equation

$$\eta = K(\gamma)^{n-1}$$

where K is the consistency index and n is the shear flow exponent which indicates the departure from Newtonian behavior. The fitting parameters are given in Table 1.

The PSD will influence the packing ability of the powders within a suspension by modifying the arrangement of the particles with the finer particles filling the void space between the larger one and hence, determine the rheological properties of the suspension. The use of bidispere suspensions can provide two advantages. One is that, at a given solid volume fraction, the viscosity of a bidisperse suspension is generally lower than that of a monodisperse suspension. The other is that, for a desirable viscosity value, the use of a bidisperse suspension can attain a higher solid volume fraction than the use of a monodisperse suspension. The main factors which influence the viscosity of bidisperse suspensions are the diameter ratio of large to small particle, $\lambda = d_\lambda / d_\sigma$, and the volume fraction of large particle, which is defined as blend ratio ξ. In our experiments, the size ratio λ was kept constant at 11.3 and the blend ratio varied from 30 to 70%.

Table 1
The critical shear rate γ_c and fitting parameters using Ostwald–de Weale model for shear-thickening behavior in Fig. 1

	Blend ratio of SiC $B_{(18.43\ \mu m)}/A_{(1.63\ \mu m)}$				
	3:7	4:6	5:5	6:4	7:3
$\gamma_c(S^{-1})$	85.7	54.1	34.2	15.8	10.0
K	4.31E-5	1.86E-4	0.0020	0.0051	0.011
N	2.49	2.16	1.64	1.51	1.37

Many experimental and theoretical finding[10,11,14–16] showed that, when Φ and λ are fixed, there exists a critical value of ξ at which the viscosity is minimized. Dames[14] and He[15] found that the viscosity is minimized at $\xi = 70$–80%, depending on the value of λ used. Zaman[10] observed a minimum in the viscosity was between 50% and 55%. Logus[16] agreed that the critical value of ξ is 40%. As demonstrated in Fig. 2, the critical value of ξ must be greater than 70% at shear rates below 10S^{-1}, which is exactly the γ_c of the suspension with blend ratio 70% (see Table 1). But at shear rates from 10–500 S^{-1}, the critical ξ turns to be 50%. So it can be drawn from the above steady sweep tests that shear rate has great influence on the value of critical ξ because of the emergence of shear-thickening. It is especially important for suspensions containing solid particles with diameter greater than 10 μm. This is just because γ_c, which corresponds to the onset of shear thickening, indicates an inverse quadratic dependence on the particle size.[17] The difference of aspect ratio of raw materials used must also be taken into account. The raw materials most investigators used were in the colloidal size range and appeared to be nearly spherical, which formed a sharp contrast with the SiC powders we used in the experiment. It can be seen from Fig. 2 that the shear rate range corresponding to shear-thickening behavior expanded as the increase of ξ. For example, the shear-thickening behavior is seen to exist over more than one and half decade of shear rate for the suspension with blend ratio of 70% (Fig. 2), that is rarely seen in colloidal suspensions.[18] It is suggested that a possible reason for the disperse of the critical value of ξ among the earlier literature may be attributed to the difference in the shear rate used (200 S^{-1} for He[15] *vs* 1000 S^{-1} for Zaman[10]). It should also be noted that typical shear rates during manufacturing and application of ceramic suspensions are in the range of 10–100 S^{-1}. From this point of view, the critical blend ratio ξ is 50% for the bidisperse suspensions.

3.2. Dynamic oscillatory tests

Dynamic oscillatory were also performed to better characterize the rheological behavior, in particular the effect of blend ratio. From these measurements, the storage modulus, G', which is a measure of the elastic properties of the sample, and the loss modulus, G'', which is a measure of the viscous properties, can be obtained. Fig. 3 shows the effect of strain amplitude γ on the storage modulus G' of SiC suspensions with different ξ. At small amplitude, the suspensions are in the linear region where G' is constant with respect to γ indicating the onset of the liquid-like behavior at higher strain amplitude. The storage modulus in the linear region may be extrapolated from the constant G' value at small strain amplitudes, which is designated as G_0'. The largest strain amplitude, below which the suspensions show a linear viscoelastic response as the limit of linearity, is called γ_0. From Fig. 3 we can see that the more SiC B the suspensions contained, the less G_0' and γ_0. For example, suspension with ξ 30% has G_0' and γ_0 4.3 Pa and 1.0%, respectively. However, when the ξ increases to 60%, G_0' and γ_0 decrease to 2.8 Pa and 0.5% instead, and no linear viscoelastic region can even be found for suspension with ξ 70%.

Fig. 4 shows the frequency sweep of the different suspensions. In order to obtain the moduli without destroying the samples, all measurements were performed inside the linear viscoelastic region ($\gamma < \gamma_0$), where the viscoelastic response is linear (the strain is proportional to the stress) and the moduli can be obtained directly. Because suspension with ξ 70% does not exhibit obvious linear viscoelastic region, frequency sweep test was not performed on the suspension. Some structural information can be acquired by conducting this kind of test. As shown in Fig. 4, the magnitude of the viscoelastic response decreases and the slope coefficient of each curve increases with increasing ξ. So the increment of ξ leads to the change of suspension from nearly an elastic response to a liquidlike response.

Fundamentally, the rheological properties of concentrated suspensions are determined by the interactions between particles. This means that there exists an intimate relation between the particle interactions, the suspension structure (i.e. the spatial particle distribution in the liquid), and the rheological response. The dominating forces between particles in aqueous media include long-ranged electrostatic forces, short-ranged attractive van der Waals forces, inertia and the externally imposed shear forces.[19] Besides, the interparticle forces and the local entropy drive the system to an ordered structure. It should be noted that particle size has great influence on the magnitude of these forces. With particles in the colloidal size range, Brownian, electrostatic and Van der Waals forces dominate. Inertia is somewhat negligible due to the small size of the particles. Strong colloidal forces are favorable to the formation of more structured suspensions and the strength of them increased accordingly. In addition, at a given volume fraction, the interparticle interaction becomes stronger for smaller particle suspension due to the closer interparticle distance. So it is not surprising to find that the moduli and the linear viscoelastic region of those two-component SiC suspensions with high ξ will be smaller than those with low ξ (Figs. 3 and 4). The shear-thinning behavior is also associated with the suspension structure. When the imposed flow becomes strong, the three-dimensional structure transforms into a two-layered structure that permits continuous deformation. Then the viscosity drops drastically. At higher shear rates, however, the enhanced hydrodynamic force prevents them from sustaining their ordered state. Coarse particles increase the viscosity of the suspension through the hydrodynamic interactions. This flow instability caused the particles to break out their ordered structure at some critical

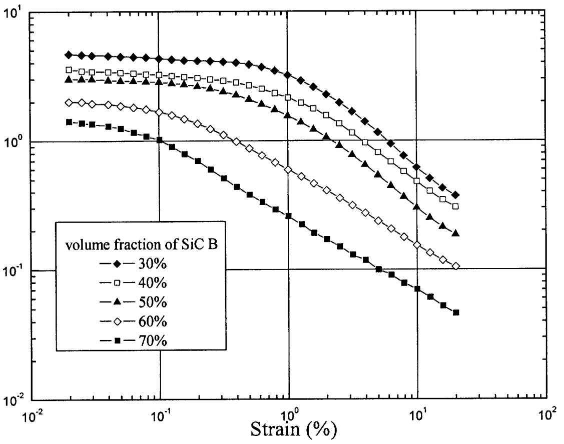

Fig. 3. Storage modulus as a function of strain amplitude for two-component SiC suspensions with different blend ratio.

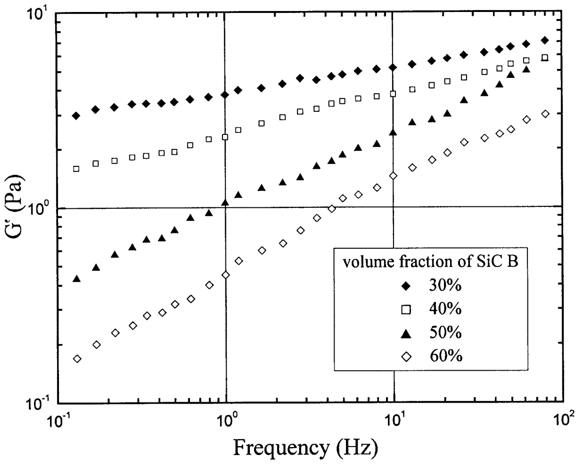

Fig. 4. Storage modulus as a function of radian frequency for two-component SiC suspensions with different blend ratio.

shear rate (γ_c) and jam into one another, thereby causing the shear-thickening.

4. Conclusions

In this paper, two sets of SiC powders (1.63 and 18.43 μm) were selected to study the effect of blend ratio ξ on rheological properties of SiC suspensions. The results showed that shear rate applied has great influence on the value of critical ξ because of the emergence of shear-thickening. At shear rates below 10 S^{-1}, the critical ξ was greater than 70%. But at shear rates from 10 to 500 S^{-1}, the suspension with ξ 50% was found to exhibit the lowest viscosity. Dynamic oscillatory tests showed that the moduli and the linear viscoelastic region of suspensions with higher ξ are smaller than those with low ξ. The increment of blend ratio leads to the change of suspension from nearly an elastic response to a liquid like response. Results of this work can be used to obtain concentrated SiC suspensions of higher solid content without significant increase in viscosity by controlling the value of ξ.

References

1. Takada, Y., Development of high-thermal-conductive SiC ceramics. *J. Am. Ceram. Soc. Bull*, 1998, **67**, 1961–1963.
2. Balch, D. K., Fizgerald, T. J., Michaud, V. J., Mortensen, A., Shen, Y. L. and Suresh, S., Thermal expansion of metals reinforced with ceramic particles and microcellular foams. *Metall. Mater. Trans*, 1996, **27A**, 3700–3717.
3. Zweben, C., Advances in composite materials for thermal management in electronic packaging. *JOM*, 1998, **June**, 47–51.
4. Götze, St., Schulle, W. and Henniche, H. W., Investigation of the deflocculation and cast-forming behavior of SiC slips. *cfi/Ber DKG*, 1992, **69**, 82–87.
5. Zhou, L. J., Huang, Y. and Xie, Z. P., Gelcasting of concentrated aqueous silicon carbide suspension. *J. Eur. Ceram. Soc.*, 2000, **20**, 85–95.
6. Si, W. J., Graule, T. J., Baader, F. H. and Gauckler, L. J., Direct coagulation casting of silicon carbide components. *J. Am. Ceram. Soc.*, 1999, **82**, 1129–1136.
7. Ramachandra Rao, R., Roopa, H. N. and Kannan, T. S., Effect of pH on the dispersability of Silicon carbide powders in aqueous media. *Ceramics International*, 1999, **25**, 223–230.
8. Liu, D. M. and Fu, C. T., Effect of rheological bahavior on properties of cast and sintered silicon carbide. *Ceramics International*, 1996, **22**, 101–106.
9. Huang, Q., Gu, M. Y., Sun, K. and Jin, Y. P., Effect of calcinations on rheological behavior of silicon carbide aqueous suspension. *J. Mater. Sci. Lett.*, 2002, **21**, 569–571.
10. Zaman, A. A. and Moudgil, B. M., Rheology of bidisperse aqueous silica suspensions: a new scaling method for the bidisperse viscosity. *J. Rheol.*, 1998, **42**, 21–39.
11. Ferreira, J. M. F. and Diz, H. M. M., Pressure slip casting of bimodal silicon carbide powder suspension. *Ceramics International*, 1999, **25**, 491–495.
12. Sigmund, W. M., Bell, N. S. and Bergström, L., Novel power-processing methods for advanced ceramics. *J. Am. Ceram. Soc.*, 2000, **83**, 2557–2574.
13. Reeves, A. J., Taylor, R. and Clyne, T. W., The effect of interfacial reaction on thermal properties of titanium reinforced with particulate SiC. *Mat. Sci. and Eng.*, 1991, **141**, 129–138.
14. Dames, B., Morrison, B. R. and Willenbacher, N., An empirical model predicting the viscosity of highly concentrated, bimodal dispersions with colloidal interactions. *Rheol. Acta*, 2001, **40**, 434–440.
15. He, D. and Ekere, N. H., Viscosity of concentrated noncolloidal bidisperse suspensions. *Rheol. Acta*, 2001, **40**, 591–598.
16. Logos, C. and Nguyen, Q. D., Effect of particle size on the flow properties of a south Australian coal–water slurry. *Powder Techno.*, 1996, **88**, 55–58.
17. Hoffman, R. L., Explanation for the cause of shear thickening in concentrated colloidal suspensions. *J. Rheol.*, 1998, **42**, 111–123.
18. Barnes, H. A., Shear-thickening ("Dilatancy") in suspensions of nonaggregating solid particles dispersed in Newtonian liquids. *J. Rheol.*, 1989, **33**, 329–366.
19. Horn, R. G., Surface forces and their action in ceramic materials. *J. Am. Ceram. Soc.*, 1990, **73**, 1117–1135.