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Processing of highly concentrated polyacrylamide-coated silicon carbide suspensions

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Abstract

By using a polyacrylamide (PAAM)-coated silicon carbide (SiC) powder, at pH = 5, homogeneous and stable suspensions of proper rheological property and low viscosity, containing 55 vol.% solids, were prepared. Stability, Zeta-potential and the rheological property of suspensions were studied. To further improve the solids content, two sizes of powders were mixed and graded. When 52 wt.% coarse and 48 wt.% PAAM-coated SiC powder were mixed, the solids content of suspensions was 65–70 vol.%, and the suspensions were of proper rheological property, homogeneity and stability. The results showed that rheological property of suspensions containing coarse particles were shear thinning at a low shear rate and thickening at a high shear rate when the solids content was between 60 and 65 vol.%.

Keywords: D. SiC; Ceramics; Highly concentrated suspensions; Coated rheological property

1. Introduction

Silicon carbide (SiC) is one of the most important ceramics materials, due not only to its excellent mechanical properties at room temperature, such as high flexure strength, high oxidation and corrosion resistance, high resistance to wear and low abrasion coefficient, but also to its high temperature mechanical properties, which is the optimum in all the ceramics materials we know (strength, resistance to creep), and the latter will be an important growing point of ceramics materials of high properties [1,2]. Colloidal processing has been one of the ways to obtain high property SiC ceramics materials because it can control effectively the microstructure of green body, reduce the inside defects of materials and improve the reliance of ceramics materials [3,4].

The prerequisite to the application of colloidal processing is the preparation of homogeneous and stable ceramics suspensions of low viscosity, high solids content (> 50 vol.%) and proper rheological property. In recent years, there have been two methods to prepare the highly concentrated SiC ceramics suspensions [5,6]. One is to select proper dispersants to deal with powders [7–11]. The electrostatic, steric and electrosteric effect has been caused by the dispersants reacting with the surface of powders and then the highly concentrated ceramics suspensions are obtained. The other is to coat the surface of SiC powder with aluminum oxide (Al_2O_3) so that SiC own the similar surface characteristics to that of Al_2O_3 [12]. The above methods have been studied in detail. A different method has been proposed in our investigation. 3-Aminopropyltriethoxysilane (APS) silane coupling agent has been coated on the surface of SiC powder by chemical methods, and then acrylamide (AAM) has been grafted on the surface of APS-coated powder by use of a redox system consisting of ceric ion (Ce^{4+}) and reducing groups on the surface. Finally, the PAAM coating layer is obtained [13–17]. This organic compound has changed the surface characteristics of SiC powder, improved the dispersion state in the water and realized the preparation of the homogeneous and stable ceramics suspensions with lower viscosity, high solids content and proper rheological property.

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Some experiments and some theories have shown the highest solids content of suspensions prepared only by single particle size ceramics powder is difficult to exceed 60 vol.%; however, the broadening particle size distribution of the ceramics powder is beneficial for improving the solids content [18]. So the grading is one of the effective ways to increase the solids content.

2. Experimental

2.1. Raw material

Two SiC powders were used in the investigation. One of them was the fine SiC powder (Rs07, HuaMei Grinding Material and Apparatus Company, China) on the surface of which PAAM was coated; the other was the coarse SiC powder (Rs100, HuaMei Grinding Material and Apparatus Company, China) which was used as grading. The physical and chemical characteristics of the two SiC powders are listed in Table 1. The water was distilled and analytical-grade AAM was supplied by Tianjin Da Mao Chemical Instrument Company (China); APS supplied by Wuhan University Chemical & New Material Company Limited (China) was also analytical grade. The pH was adjusted with standardized analytical-grade HCL and NaOH solution (1 mol/ml).

2.2. Process

In a flask, SiC powder and APS coupling agent with toluene as solvent were mixed and stirred. The mixture was refluxed in a stream of nitrogen for 5 h. After the reaction, the product was extracted and dried in vacuo at 110 °C. Mix the dried APS-coated SiC powder and AAM. Under the initiation of Ce^{4+}, AAM was grafted and formed the coating layer PAAM. After being dried in vacuo, the PAAM-coated SiC powder can be used to prepare the highly concentrated SiC ceramics suspensions.

2.3. Testing methods

2.3.1. Measurement of Zeta potential

ZetaPals instrument (Brookfield, Britain) was used for measuring the Zeta potential of powder surface. Taking the distilled water as solvent, 0.4 mg/ml SiC suspensions were prepared then ultrasonicated and stirred the suspensions for 15 min before the measurement so as to make sure that only the single particles were measured; pH value was adjusted by using analytical-grade HCl, NaOH and was demarcated by using PXS-5 digital acidity indicator at 25 °C. Then recorded the average value of three points in each measurement.

2.3.2. Measurement of stability

Stability was measured by sediment experiment which was performed by dispersing 16.89 g SiC powder in 100 ml distilled water, using calibrated glass cylinders with scale. The upper of cylinder was sealed with a plastic film to ensure minimum evaporation, and the suspensions were ultrasonicated and stirred for 30 min and allowed to stand undisturbed for several days. Time and sediment height were recorded. The stability was judged by the relative sediment height percent which was the ratio of the height of opacitus suspensions to the total height of suspensions. The greater the height value was, the better the stability was.

2.3.3. Measurement of viscosity and rheological property

The viscosity and rheological property were examined by NXS-11A rotation viscometer at a constant temperature (25 °C). The shear rate increased from 5.6 to 360 rpm. Each shear rate was kept for 1 min and the viscosity as recorded; then the shear rate was decreased from 360 to 5.6 rpm, still kept each shear rate for 1 min, and recorded the viscosity.

2.3.4. Measurement of solids content

10 g distilled water was balanced exactly and then SiC powder was added into the water gradually. According to the different amounts of powders, the suspensions with different solids content were obtained, and the equation is

$$\text{vol.\%} = (m_{\text{powder}}/\rho_{\text{powder}}) \times 100\%/(m_{\text{powder}}/\rho_{\text{powder}} + m_{\text{water}}/\rho_{\text{water}}).$$

In this paper, the highest solids content of suspensions refers to the value in the time from adding powders into the distilled water till the formed suspensions can not flow.

3. Result and discussion

3.1. Zeta potential of coated SiC powder

Zeta potential of uncoated and coated SiC powders are shown in Fig. 1. As shown in the chart, Zeta poten-

Table 1
The physical and chemical characteristics of SiC powder

Raw material	d_{50}/μm	Special area/$m^2 \cdot g^{-1}$	SiC/wt.%	Free Si/wt.%	O/wt.%	Free C/wt.%	Fe_2O_3/wt.%
Fine SiC powder	1.2	4.19	>98	0.45	0.49	0.66	<0.5
Coarse SiC powder	118	0.032	–	–	–	–	–

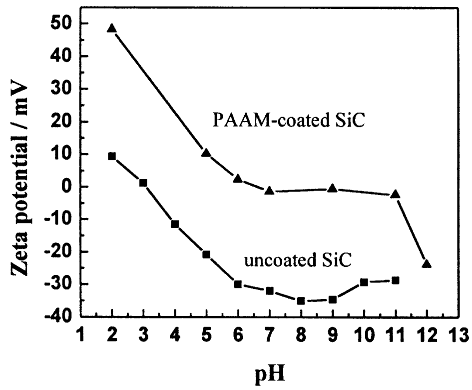

Fig. 1. The relationship curve of pH vs. Zeta potential.

tial of the two SiC powders are different, which indicate that each powder has different surface characteristics. The isoelectric point (IEP) of the uncoated powder is close to pH = 3, basically, the higher the Zeta potential is, the higher the absolute value of Zeta potential is. At pH = 5, Zeta potential is −35 mV. Considering electrostatic, the uncoated SiC powder can be dispersed easily under the basic condition. IEP of the coated powder is shifted, IEP of the PAAM-coated SiC powder is close to pH = 7 and the higher Zeta-potential is under the acid condition; at pH = 2, Zeta potential is about 50 mV. Therefore, the surface characteristics of coated SiC powder are different from that of uncoated SiC powder and all the shown properties are affected by the coating layer.

3.2. Stability of SiC suspensions

The pH value has an effect on the stability of two SiC powder suspensions. By selecting the aqueous solution with different pH value, the optimum pH value is confirmed and the stability of suspensions is judged. Thus to study the suspensions stability, the influence of pH value needs to be taken into consideration first. The relative sediment height of the two suspensions with different pH value standing for 5 h are shown in Figs. 2 and 3. For the uncoated SiC powders, the highest relative sediment height appears at pH = 8, which indicates the powder can be stable under the basic condition. However, for the PAAM-coated SiC powders, the highest relative sediment height appears at pH = 5, when pH < 5, the stability becomes slightly poor; whereas when pH > 7, the stability of suspensions decreases sharply and the suspensions form serious flocculation.

The curve of sediment experiment is shown in Figs. 4 and 5. For these two suspensions, under the optimum condition of stability, the sediment velocity of uncoated powder is fast, the relative sediment height percent was lower than 80% within 1 h then the velocity of the sediment decreases and sediment was completed basically within a day, whereas the PAAM-coated SiC powder is very stable and the velocity of sediment is

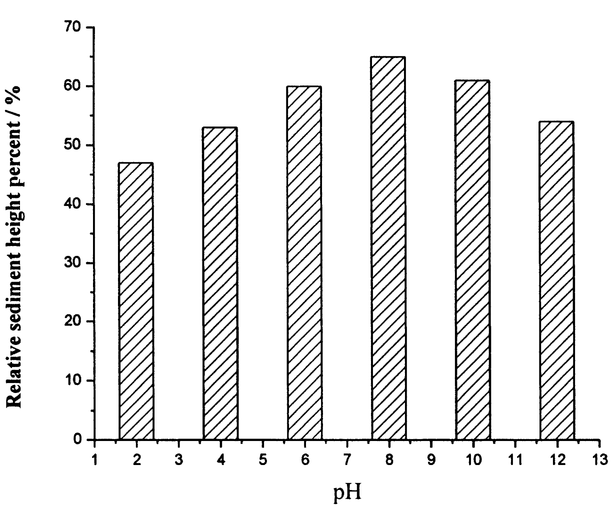

Fig. 2. The influence of pH value on the stability of uncoated SiC powder.

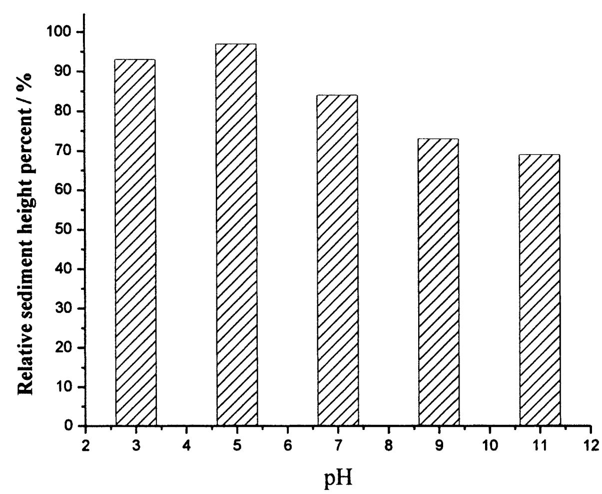

Fig. 3. The influence of pH value on the stability of PAAM-coated SiC powder.

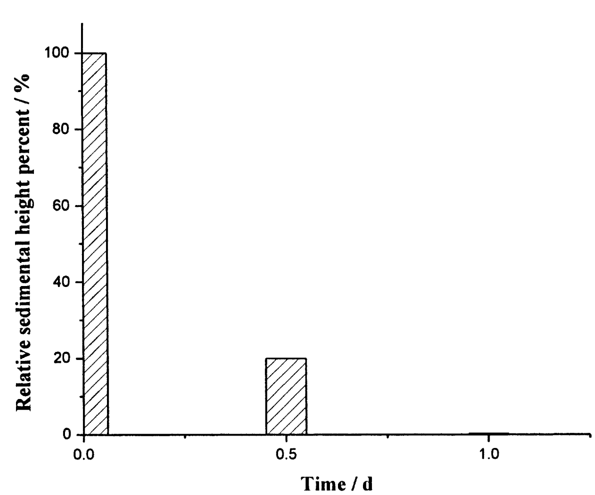

Fig. 4. Stability of uncoated SiC powder.

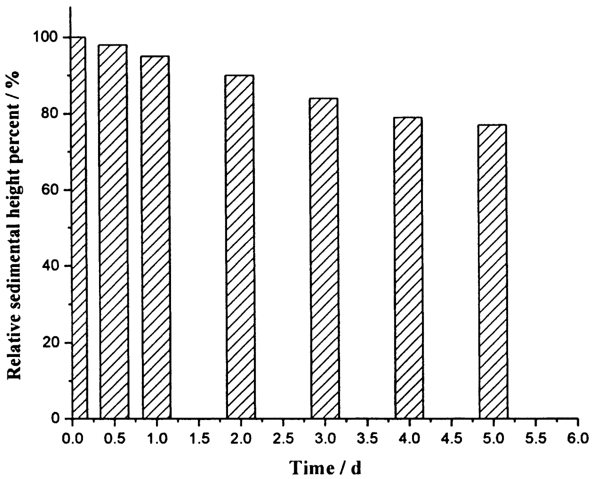

Fig. 5. Stability of PAAM-coated SiC powder.

slow. After 5 days, the relative sediment height percent is still about 80%.

3.3. The solids content of ceramics suspensions

As shown in Fig. 6, pH value has an effect on the solids content. For the uncoated SiC powder, the solids content increases as pH value increases to 8, the highest solids content of suspensions is 35 vol.% but the suspensions has poor rheological property. Under the acid condition, the solids content of suspensions is low. For the PAAM-coated SiC powder, the highest solids content of suspensions is 53 vol.% at pH = 7. This is more than 50% compared to that of the uncoated SiC powder, and the suspensions have proper rheological property. When pH < 7, the suspensions keep relative high solids content except for the change of the rheological capability; the 55 vol.% suspensions with proper rheological property can be prepared at pH = 5 and its

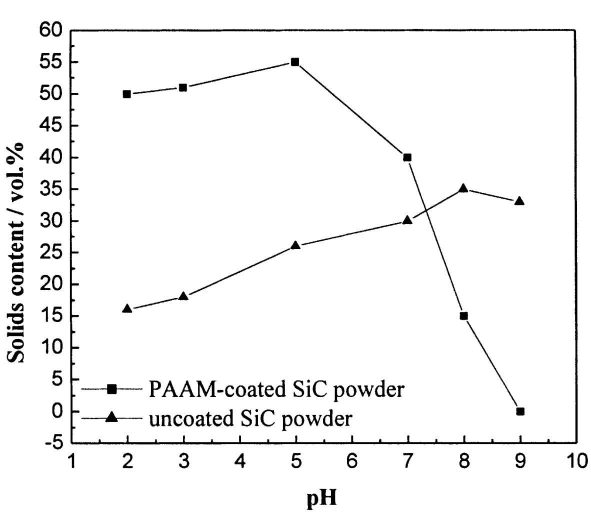

Fig. 6. The influence of pH value on the highest solids content of PAAM-coated SiC suspensions.

viscosity is approximately to that under neutral condition suspensions with solids content of 52–53 vol.%. Compared with the case when pH = 5, when pH = 2,3, suspension can only flow with less solids content and the rheological property decreases. When pH > 7, the solids content of suspensions decreases sharply and loses rheological property and produced flocculation partly, as well.

3.4. Rheological properties of uncoated and PAAM-coated SiC powder

The viscosity of suspensions prepared by uncoated and PAAM-coated SiC powders changes as the shear rate varies, as shown in Figs. 7 and 8.

Under the condition of low solids content (<20 vol.%), the viscosity of suspensions is <1 Pa·s and always keep relative low value. The suspensions are Newton model [19] because the viscosity does not change as the shear rate varies and the flow curve is linear. The suspensions of Newton model fluid can flow at lower stress [20]. The viscosity of suspensions decreases as shear rate increases when solids content increases. The rheological properties of suspensions begin to change and the suspensions shear thinning, that is pseudo-plasticity fluid [21,22]. Generally speaking, it

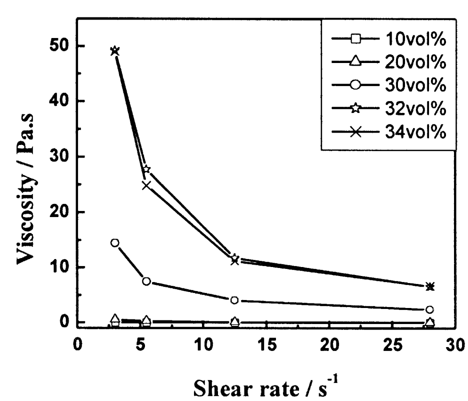

Fig. 7. The rheological property of uncoated SiC powder.

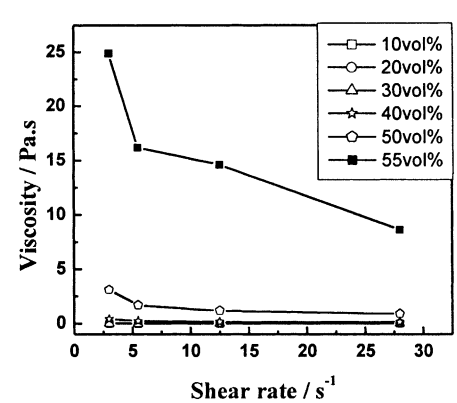

Fig. 8. The rheological property of PAAM-coated SiC powder.

is the structures of particles electrical property in the system that causes the shear thinning behavior. The particles in suspensions produce some frame structures caused by electrolyte repulsive force and Van der Waals attractive force between particles. The production and destruction of the frame structure need time and external force, so the fluid depends on time and external force. The frame structure linked together is broken into little frame units when it is shear cut. As shear rate increases to some value, the little frame units can flow and then the proper rheological properties of suspensions forms.

For the uncoated SiC powder, its rheological property is not discussed in detail because the solids content was not high. For the PAAM-coated SiC powder, when the solids content is >40 vol.%, the rheological property of suspensions decreases and the viscosity increases sharply as the solids content increases because the effective volume increases and the relative movement between particles becomes difficult. It is because the volume of phase linked together has been reduced, the distance between particles decreased sharply and the organic compound is coated on the surface of powders [23]. For concentrated suspensions, the relationship between viscosity and solids content might be charactized by Quemada model [24]:

$$\eta_r = (1\text{-}\phi/\phi_m)^{-2} \qquad (1)$$

Φ_m, the highest solids content, is about 0.5–0.75, concerning the shape of particles. The reality solids content has been increased because, on one hand the colloid probability between particles increased, the other was the irregular shape of particles caused Φ_m is relatively little, so η_r is led to increase sharply. At the same shear rate, the viscosity increases as exponent increases when the solids content rises from 40 to 55 vol.%.

3.5. The properties of suspensions prepared by two particles size

In theory, the suspensions which contain more than 70 vol.% solids content of proper rheological property can be prepared because of the broadened particles size and the increased particle packing density. It is important for ceramics or refractory materials to prepare highly concentrated suspensions. When the solids content is high enough in the suspensions, on one hand, the sediment of coarse particles in suspensions can be avoided or slowed down; on the other hand, it is of advantage to improve the density of green body and the products. As shown in Figs. 9 and 10, when added the coarse particles, the solids content of system increases with the decrease of the viscosity. When the grading of particle is of 52 wt.% coarse powder and 48 wt.% PAAM-coated SiC powder, the solids content is 65–70 vol.% at pH = 5, and the suspensions have proper rheological property. Compared with the suspensions prepared only by PAAM-coated SiC powder, the chart shows that for the same solids content the viscosity of suspensions made by mixture of two grades of particles is considerably lower than that of single grade particle suspensions. Conversely, for comparable viscosities, a mixture of particles size yields a higher solids content than that obtained by using a single particle size grade.

3.6. The rheological property of highly concentrated suspensions containing coarse particles

The different rheological phenomena between 60 and 65 vol.% suspensions prepared by 52 wt.% coarse powder and 48 wt.% PAAM-coated SiC powder and the suspensions prepared only by PAAM-coated SiC powders are observed. As shown in Figs. 11 and 12, the viscosity of suspensions decreases as shear rate increases at low shear rate, whereas the viscosity of suspensions increases as shear rate increases at high shear rate.

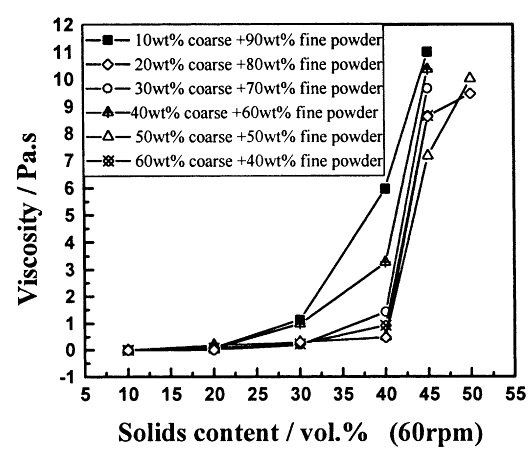

Fig. 9. The relationship of viscosity vs. the solids content of uncoated SiC with different size.

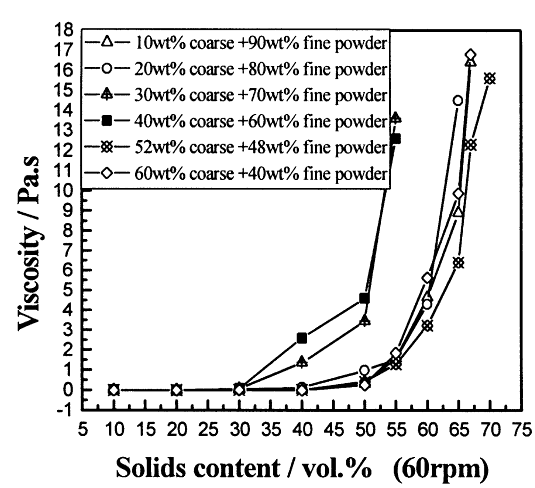

Fig. 10. The relationship of viscosity vs. the solids content of PAAM-coated SiC with different size.

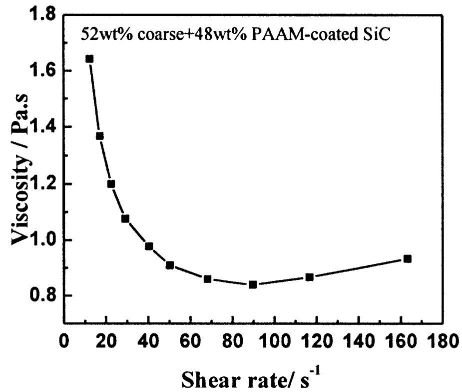

Fig. 11. The rheological property of SiC suspensions with 60 vol.%.

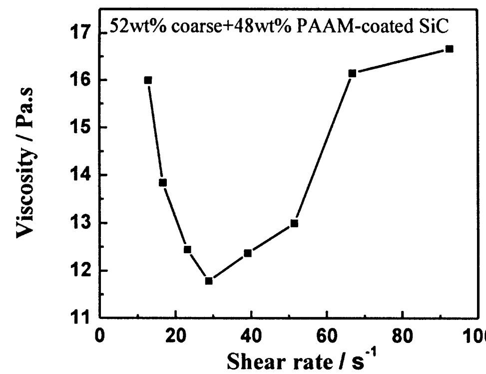

Fig. 12. The rheological property of SiC suspensions with 65 vol.%.

Generally, ceramics suspensions are shear thinning but for highly concentrated ceramics suspensions containing coarse particles sometimes it shears thickening.

Generally, shear thickening occurrence is mainly caused by the conversion between order and disorder of suspensions [25,26]. When shear rate decreases, stress decreases and the electrostatic repulsive force between particles dominates over the attractive Van der Waals force. When shear rate increases, the balance point will deviate, which makes the particles disordered and the viscosity of suspension increases. Considering the mechanism, it is presumed that the phenomenon of shear thickening easily happens when solids content is high, particles size is big and the surface Zeta-potential of particles is low. All this is identical to the experimental results. However, it is difficult to explain the converse process of shear thickening by the conversion between order and disorder of the suspensions that is, when suspensions have formed shear thickening, the shear rate slows down, the viscosity decreases and restores to its former state. Another new opinion is that shear thickening is the interaction results of the repulsive potential barrier between particles. When shear rate increases, stress increases and thus makes the particles closer but because of the interaction of repulsive potential barrier between particles, highly repulsive force comes forth and the viscosity of suspensions increases in macroscopic view. It is believed in this opinion, the higher the Zeta-potential of particles surface is, the bigger the dimension of the repulsive potential barrier is, and this will cause shear thickening to occur more easily.

4. Conclusion

After researching the solids content and rheological property of the result, it is found that the highly concentrated SiC suspensions of stability and homogeneity and proper rheological property is prepared more easily by using PAAM-coated SiC powder than by using the uncoated SiC powder. The highly is prepared easily by using PAAM-coated SiC powder compared with the uncoated SiC powder. It indicates that coating the SiC powder with PAAM is one of the ways to prepare the highly concentrated ceramics suspensions. At the same time, when keeping the proper rheological property, the solids content of the suspensions with PAAM-coated SiC powder added to coarse particles powder is improved obviously, which shows broadening particles size distribution is of advantage to increase the solids content.

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