

Dispersion stability and its effect on tape casting of solvent-based SiC slurries

Jong-Hyun Lee^a, Parlindungan Yonathan^a, Dang-Hyok Yoon^{a,*}, Weon-Ju Kim^b and Ji-Yeon Park^b

^aSchool of Materials Science and Engineering, Yeungnam University, Gyeongsan 712-749, Korea

^bNuclear Materials Research Division, Korea Atomic Energy Research Institute, Daejeon 305-353, Korea

Slurries containing well-dispersed ceramic particles are essential for further processing, such as tape casting and infiltration to a woven fabric, to produce high quality products. In this study, various types of suspensions were prepared with 4 different types of commercial dispersants to examine the dispersion mechanism and determine the optimum conditions for the micro-sized α - and 50 nm-sized β -SiC systems in a toluene/ethanol mixed solvent. According to the sedimentation and rheological results, 3 and 20 wt.% of a polyester/polyamine co-polymeric dispersant were found to be the most effective dispersant for α - and β -SiC suspensions, respectively. An electrostatic mechanism did not play a major role in the mixed solvent system when a dispersant was added. The optimum amount of dispersant for the slurry was less than that for the suspension due to the dispersing effect of the polyvinyl butyral (PVB) binder. Due to the high specific surface area of the nano-sized β -SiC powder, 40 wt.% binder resin was needed to achieve a tape with desirable properties, while 15 wt.% of binder was adequate for the slurry with α -SiC with a lower surface area. Overall, the tape properties, such as green morphology and density, were strongly related to the dispersion state of the slurry.

Key words: SiC, Dispersion, Zeta potential, Tape casting.

Introduction

Due to its excellent thermal and mechanical properties, silicon carbide (SiC) or SiC fiber-reinforced composites (SiC_f/SiC composites) is one of the most attractive materials for applications under severe conditions. SiC or SiC_f/SiC composites can be used as high temperature heating elements, as various parts for semiconductor processing, as nozzles, as mechanical seals, in gas turbines, for space shuttles and even for nuclear fusion reactors [1-4]. For many of these applications, slurry processing is widely used because the ceramic powder itself is inherently difficult to handle and shape into the desired components. For example, the recently introduced nano-infiltrated transient eutectoid process (NITE), which is a method for synthesizing SiC_f/SiC composites for various applications, utilizes slurry infiltration and hot pressing to enhance the density and mechanical properties [5, 6]. Moreover, the alternatively layered structure of SiC fiber fabric and SiC tape prepared by slurry processing was also introduced to enhance the density of the SiC_f/SiC composite [7]. For the NITE process, slurries containing nano-sized SiC powder are preferred for a high infiltration rate to the vacant sites of a SiC fiber-woven fabric provided the dispersion stability of nano-particles is ensured.

The long-term dispersion stability of slurries depends on the sign and magnitude of the total energy of the interaction between particles [8]. Stabilization can be achieved via

electrostatic and steric mechanisms, which both prevent particles from approaching each other using the electrostatic repulsive force and hindrance by the adsorption of polymeric molecules on the particle surfaces, respectively [9, 10]. It is generally believed that the dispersion of nano-sized particles is quite difficult because of their strong tendency to form aggregates. Since the complete dispersion of SiC particles in a liquid vehicle or binder solution during slurry processing is essential for preserving the final quality of the products, several studies have examined the surface chemistry of SiC powders and their dispersion behavior [11-13]. However, these authors only considered the dispersion of micrometer-sized SiC in water at a low solid loading.

The most prominent process using well-dispersed slurries is tape casting, which produces large-area, thin and flat ceramic parts. Depending on the liquid vehicle used to dissolve the binder, a slurry system can be divided into water- or solvent-based systems. It was reported that a solvent-based slurry system generally shows a faster drying rate, lower crack sensitivity, higher green strength and density, and smoother green morphology. In addition, it shows easier dispersion than water-based systems [14, 15]. However, to the best of the authors' knowledge, there are no reports on systematic dispersion studies with nano-sized SiC, and the corresponding tape casting results in solvent-based systems in spite of the importance of dispersion and tape casting using a nano-sized powder.

This study examined the dispersion behavior of nano-sized SiC particles through a comparison with micro-sized particles by measuring the suspension viscosity, sedimentation and zeta potential. In addition, the optimization of parameters for

*Corresponding author:
Tel : +82-53 810 2561
Fax: +82-53 810 4628
E-mail: dhyoon@ynu.ac.kr

tape casting and the resulting green tape properties are also reported to be associated with their dispersion behavior.

Experimental Procedure

Two types of SiC powers were used in this experiment: micro-sized α -SiC (FCP-13C, Saint-Gobain, France) and nano-sized β -SiC (4620KE, NanoAmor Inc., USA). The average particle size was 1,080 and 52 nm, and the specific surface area was 13 and 80 m²/g, respectively. Scanning electron microscopy (SEM; Hitachi S-4100) and high-resolution transmission electron microscopy (HRTEM: H-7600, Hitachi) were used to observe the morphology of SiC particles.

The zeta potential behavior for 5 wt.% SiC suspensions was characterized using an electroacoustic-type zeta potential analyzer (ZetaProbe using both aqueous and non-aqueous options, Colloidal Dynamics, USA) in ethanol as well as in a mixed solvent of toluene/ethanol at a ratio of 6/4 (in wt., hereinafter mixed solvent). The pH of the suspension was adjusted using NH₄OH and CH₃COOH. However, the ionic strength was not considered based on a preliminary test. This study also examined the behavior of the zeta potential after adding commercial dispersants for β -SiC suspension.

Four types of dispersant were chosen to compare the dispersion efficiency of the commercial dispersants, as shown in Table 1. The rheological behavior of the suspensions containing 20 wt.% of α - or β -SiC With different amounts of dispersant were characterized using a computer-controlled viscometer (LVDV-II+ Pro, Brookfield, USA) with a small sample adapter and a SC4-18 spindle at 20 °C. A fixed shear rate of 132 s⁻¹ was chosen for the comparison among the viscosity values. For the sedimentation tests, suspensions containing 5 wt.% of β -SiC in a mixed solvent and 20 wt.% of dispersant with respect to β -SiC were stored in

a graduated cylinder for 20 days, and the final sedimentation height was recorded.

Six types of α - and β -SiC slurries for tape casting, as shown in Table 2, were prepared using the multi-step process described below. Polyvinyl butyral (PVB) resin with an average molecular weight of 55,000 g/mole (Butvar B-98, Solutia, USA) was used as the binder phase, and 6 wt.% of sintering additives (Al₂O₃ : Y₂O₃ : MgO = 6.4 : 2.6 : 1.0 in weight) were added. After dissolving 10 wt.% of the binder solution in a toluene/ethanol mixture, dioctyl phthalate (DOP) was added as a plasticizer. The dispersants described in Table 2 and 50 g of SiC powder were added to these binder solutions. After high energy milling (MiniCer, Netzsch, Germany) of these slurries using 0.8 mm ZrO₂ beads at 3,000 rpm for 1 hour, the viscosity was measured using the same method described above. Tape casting was performed for the six slurries on a moving polyester film using a table top tape caster with a casting rate of 60 cm/minute. The cast tapes were dried at an air flow temperature of 80 °C. The resulting green tape thickness was 40-60 mm. The green microstructure of the tapes was observed using SEM after sputter-coating the samples with platinum. The green density of the tapes was measured using geometrical methods after preparing eight K-squares for each condition. Each K-square was a small square-shaped specimen (1.0 × 1.0 cm²) that was produced by stacking the green tapes into a 1 mm thickness, pressing them under 300 kPa at 90 °C, and cutting them into size. The thickness and length were measured using a micrometer accurate to 0.001 mm and the weight was measured using a scale accurate to 0.1 mg.

Results and Discussion

As shown in Fig. 1, α -SiC has an irregular particle

Table 1. Details of the four dispersants used in this study

Dispersant	Abbreviation	Supplier	Suppliers' description on the functional group of dispersant
Rhodafac RE-610	RE 610	Rhodia	Nonylphenol ethoxylate based phosphate esters
Disperbyk-103	BYK 103	BYK	Copolymer with pigment affinic groups
EFKA 5044	EFKA 5044	Ciba	Unsaturated polyamide and acid ester salts
Hypermer KD1	Hypermer KD1	ICI	A polyester/polyamine co-polymer

Table 2. Slurry formulations used in this study.

No	Powder	Binder ¹ (wt.%)	Dispersant	Dispersant ² (wt. %)	Plasticizer ³ (wt. %)	Solid content ⁴ (wt. %)	SiC content ⁵ (wt. %)
1	α -SiC	15	Hypermer KD1	1	40	42.3	36.5
2	β -SiC	40	Hypermer KD1	3	60	26.2	18.8
3	β -SiC	40	BYK 103	3	60	26.3	18.9
4	β -SiC	40	Hypermer KD1	20	60	26.6	17.0
5	β -SiC	40	BYK 103	20	60	27.3	17.5
6	β -SiC	40	None	0	60	26.1	19.2

1. Amount of binder with respect to the ceramic powder, 2. Amount of dispersant with respect to the ceramic powder, 3. Amount of dispersant with respect to the binder resin, 4. Solid content including SiC and polymers in the slurry, 5. SiC content in the slurry

morphology with a coarse size, while β -SiC is very fine with an almost spherical shape. The fine β -SiC is highly crystallized even though the particle size is very small, and its surface is covered with a < 2 nm thick SiO_2 layer, as shown in the HRTEM image in Fig. 1 (c). Therefore, the surface groups of SiC particles would be similar to that of SiO_2 . The dispersion of nano-sized β -SiC is expected to be more difficult than that of micro-sized α -SiC due to its high van der Waals attraction, even though fine particles are desirable for infiltrating the voids of α -SiC fabric for NITE process applications.

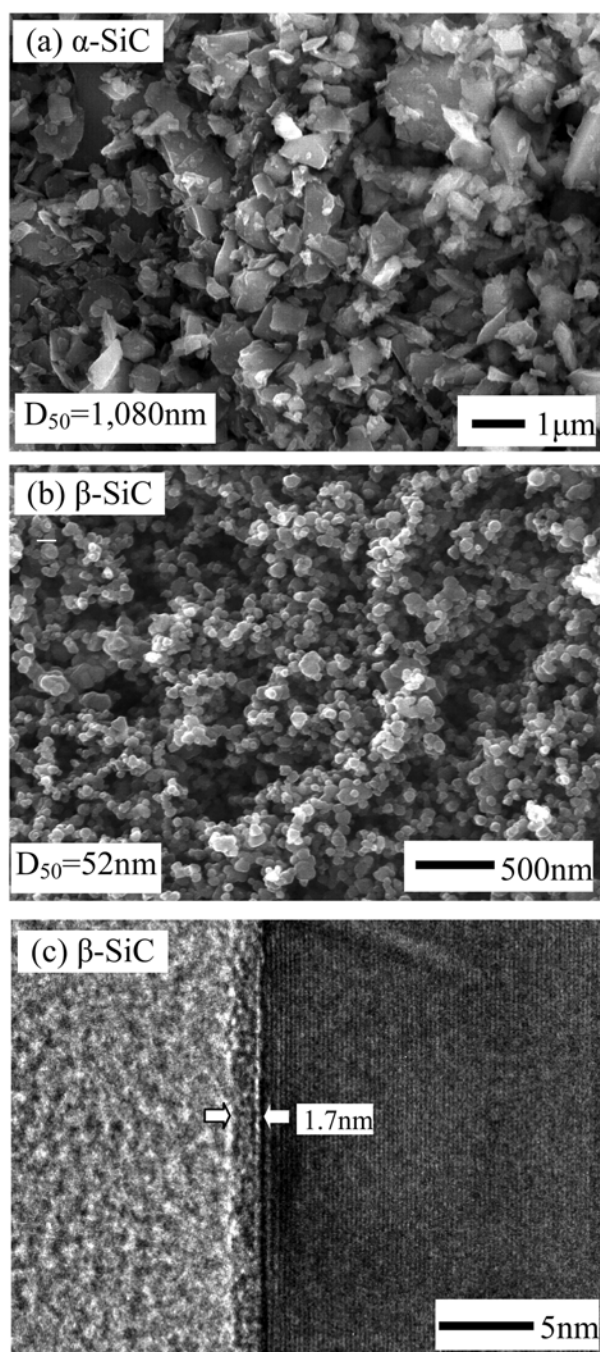


Fig. 1. SEM images of the (a) α -SiC and (b) β -SiC, and (c) HRTEM image of the β -SiC powder.

Fig. 2(a) shows the zeta potentials of 5 wt.% α - and β -SiC suspensions in ethanol measured using an electroacoustic method. This method measures the amplitude of sound waves generated by the charged particles when a very high frequency (MHz level) electric field is applied to the suspension. The zeta potential of a highly concentrated suspension up to 60 vol.% can be determined reliably within a very short time using this method [16, 17]. On the other hand, the widely used electrophoretic method can only be used effectively on an extremely dilute suspension by tracing each particle's motion under an electric field. The dilution process itself can alter the zeta potential because the electrical double layer of each particle can superimpose at high solid concentration [18]. The isoelectric points (IEPs) in ethanol for α - and β -SiC were 7.54 and 7.27, respectively, while the absolute zeta potential value for β -SiC was higher than that of α -SiC under acidic and basic conditions. The IEP of α -SiC in water was 3.5, which is similar to the reported values for SiC and SiO_2 [19, 20]. Fig. 2(b) shows the zeta potential behavior of β -SiC in a mixed solvent as a function of the dispersant content for the four commercial dispersants used. The overall behavior of the zeta potential in ethanol was quite similar

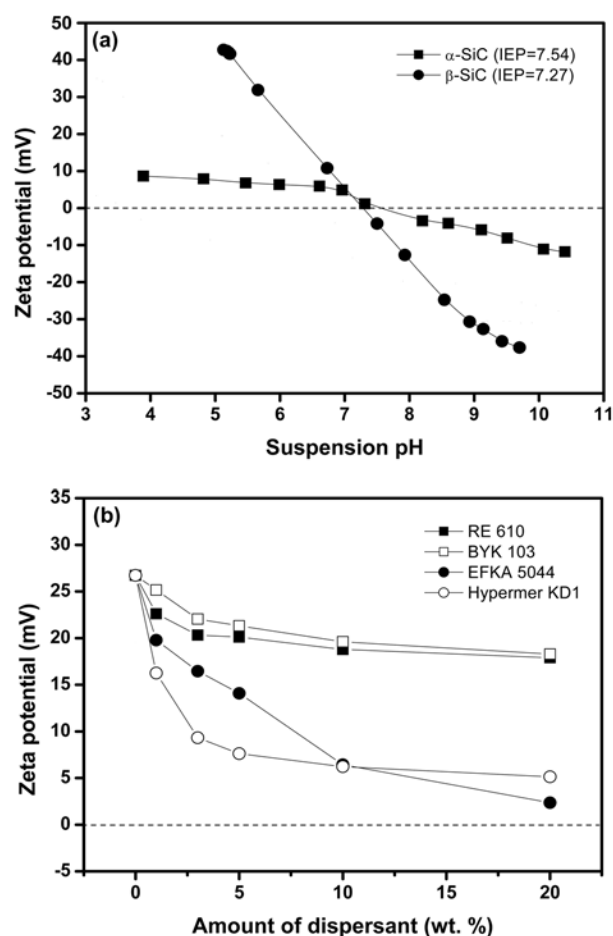


Fig. 2. Zeta potential of (a) α - and β -SiC suspensions in ethanol, and of (b) β -SiC suspension in a mixed solvent as a function of the dispersant content.

to that in the mixed solvent while the latter was smaller than the former due to the smaller dielectric constant of toluene ($\epsilon_r = 2.4$) than ethanol ($\epsilon_r = 24$). The zeta potential decreased with an increase in the amount of dispersant in all cases. Considering a SiC slurry with a pH of 7.5–8.5 after adding the PVB binder, which is close to the particle IEPs, the effective electrostatic repulsion of SiC particles in the slurry cannot be expected due to the low zeta potential value in this region. An absolute zeta potential $> 30\text{mV}$ is desirable for effective electrostatic dispersion [8, 10]. For this reason, a steric mechanism using polymeric species would be more efficient in dispersing the SiC particles in ethanol and a toluene/ethanol mixed solvent. It is known that a tape casting slurry consisting of a toluene/ethanol mixture has greater solubility for PVB, which is the reason for using the mixed solvent in this study [21].

Figs. 3(a) and (b) show the viscosity of suspensions containing 20 wt.% of α - and β -SiC, respectively, in a mixed solvent as a function of the dispersant content at a fixed shear rate of 132 s^{-1} . The dispersant forms a polymeric barrier layer on the particle surface when it

is added, and increases the stability of the suspension via a steric mechanism. Therefore, a well-dispersed suspension has a lower viscosity due to the particle mobility offered by the fluid interparticulate layer [10]. Suspensions containing insufficient and excessive amounts of dispersant show a relatively higher viscosity than those with an adequate amount due to the insufficient surface coverage and bridging flocculation between polymeric species, respectively [22]. Hypermer KD1, a polyester/polyamine co-polymer, showed the lowest viscosity in both cases, indicating it is the best dispersant of the 4 commercial ones examined. The optimal amount of dispersant is generally 20 wt.% for β -SiC suspensions due to its high surface area ($80\text{ m}^2/\text{g}$), while that for α -SiC ($13\text{ m}^2/\text{g}$) suspensions is 3 wt.%. It was also found that the overall viscosity of α -SiC suspensions was much lower than that of β -SiC with the same solid content. This can be also explained by the effect of the difference in surface area.

Fig. 4(a) shows the sedimentation height of β -SiC suspensions containing 20 wt.% of different dispersants in a mixed solvent after 20 days, and (b) the resulting sedimentation density. The sedimentation technique is a well accepted method to establish the degree of particle dispersion and packing, which gives a visual representation

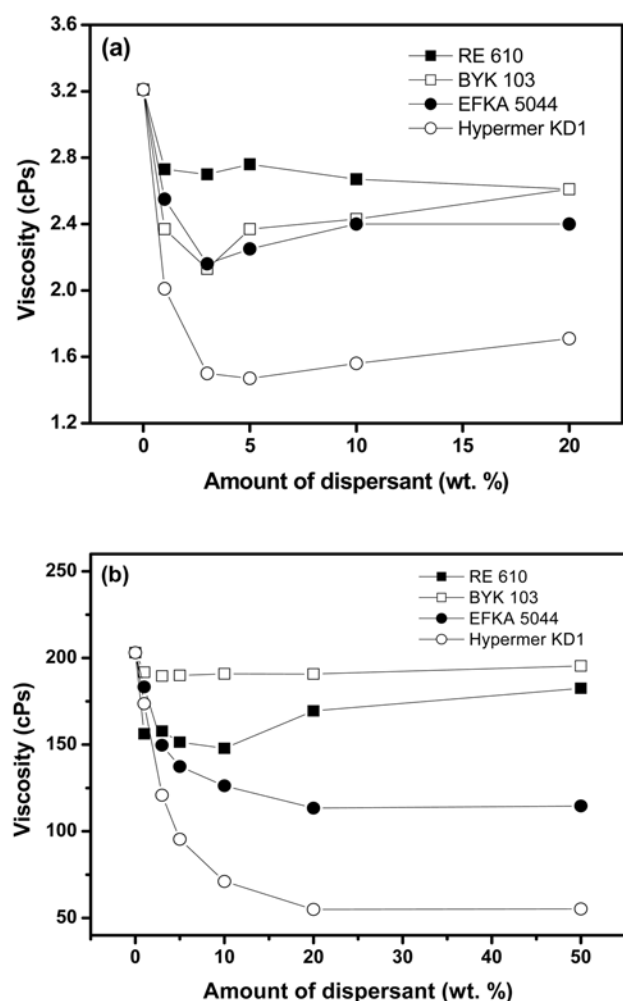


Fig. 3. Viscosity behavior of the (a) α -SiC and (b) β -SiC suspensions at a fixed shear rate of 132 s^{-1} as a function of the dispersant content.

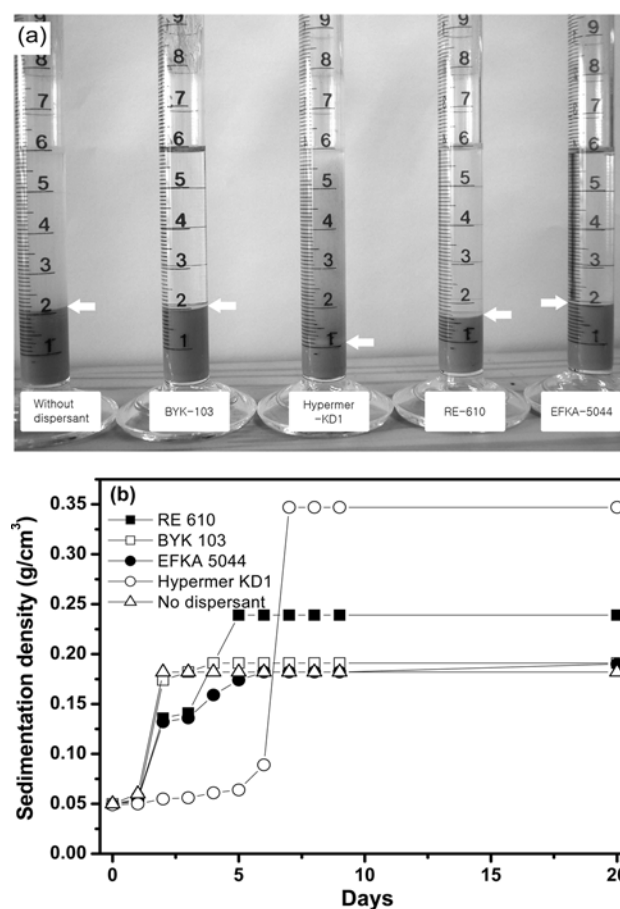


Fig. 4. (a) Sedimentation height of β -SiC suspensions containing 20 wt.% of different dispersant in a mixed solvent, and (b) the resultant sedimentation density behavior.

of dispersion. When particles are stirred vigorously in a liquid so that a homogeneous suspension is formed and then stirring is stopped, the particles start to settle due to the gravitational force, which is related to the size of particle by Stokes' law. Stokes' law is expressed by:

$$D = \left[\frac{18\eta \cdot v}{(\rho - \rho_0)g} \right]^{1/2} \quad (1)$$

where D is the diameter of the spherical particle, v is the equilibrium sedimentation velocity, ρ is the particle density, η is the viscosity of the liquid medium, ρ_0 is the liquid density, and g is the acceleration due to gravity. By applying the above theory to our SiC suspensions, it can be estimated that the less dispersed SiC sediments rapidly due to a larger effective diameter, while the better dispersed one falls slowly. In general, the particles will settle at a lower rate with a blurred particle/liquid boundary and achieve a higher packing density, if the particles are better dispersed. Therefore, these sedimentation results can be used for the evaluation of various dispersants as long as other conditions are fixed at the same condition. The arrows in Fig. 4(a) indicate the boundary between the particle and mixed solvent, while the boundary of the suspension containing Hypermer KD1 is unclear. The suspension with Hypermer KD1 showed the slowest sedimentation rate along with the highest sedimentation density, as shown in Fig. 4 (b), which is consistent with the rheological results.

Fig. 5 shows the viscosity behavior of the 6 types of α - and β -SiC slurries according to Table 2. Based on a preliminary test, the optimum slurry formulation for a micro-sized α -SiC system was 15 wt.% of PVB resin with respect to the ceramic powder and 40 wt.% of plasticizer with respect to the weight of the binder resin. On the other hand, nano-sized β -SiC required 40 wt.% binder resin and 60 wt.% plasticizer for the optimum tape properties. Because of these differences in optimum formulation, the solid and SiC contents differ considerably between slurries containing α - and β -SiC, as shown in Table 2. The detailed optimization process for the general ceramic slurry system

using a design of experimental technique can be found in our previous reports [14, 23]. Since polymeric species cover the surface of the ceramic powder, β -SiC powder with a higher specific surface area requires a larger amount of binder resin, plasticizer and dispersant than α -SiC. All slurries showed pseudo-plastic behavior with a gradual decrease in viscosity with increasing shear rate. The slurry with coarse α -SiC showed the highest viscosity at a low shear rate, which can be explained by the increased resistance to the spindle rotation due to the irregular particle morphology. All slurries showed a viscosity ranging from 230 to 350 cPs at a fixed shear rate of 25 s^{-1} , which is suitable for tape casting. However, a difference in rheological behavior between the suspension and slurry can be found for the β -SiC system. The amount of dispersant for the lowest suspension viscosity is 20 wt.% for both of Hypermer KD1 and BYK 103, as shown in Fig. 3, while slurries containing 20 wt.% of dispersant showed a higher value than that containing 3 wt.%, as shown in Fig. 5. Moreover, slurries containing 20 wt.% of both dispersants show a higher viscosity than those that without a dispersant. This is due to the effect of the PVB resin, which acts as a binder and dispersant at the same time. PVB with a low molecular weight of approximately 50,000 g/mole has been reported to be an efficient dispersant, even though PVB with a molecular weight of 50,000-150,000 is widely used as a binder [24]. Due to this dispersing role of PVB, 20 wt.% of Hypermer KD1 or BYK 103 dispersant is too much for the system, showing a higher slurry viscosity than those containing 3 wt.% due to the bridging flocculation between polymeric species.

Fig. 6 shows the characteristic green surface microstructures of the cast tapes according to Table 2. The tape made from α -SiC shows a rough and porous surface morphology, as shown in Fig. 6(a), while the tapes with β -SiC and 3 wt.% of Hypermer KD 1 and BYK 103 dispersant showed a smooth and well-packed surface, as shown in Fig. 6(b) and (c), respectively. However, the β -SiC tapes change to a quite agglomerated and loosely packed surface morphology as a result of an increase in the amount of dispersant to 20 wt.%, as shown in Fig. 6(d) and (e) for both dispersants. On the other hand, the β -SiC tape without the dispersant in Fig. 6(f) shows a relatively dense surface morphology. These results are consistent with the slurry viscosity behavior shown in Fig. 5.

Fig. 7 shows a box plot of the green density behavior of K-squares for the 6 samples. A line was drawn across the box at the median, and the dot inside the box indicates the mean of 8 K-squares for each condition. By default, the bottom of the box is at the first quartile and the top is at the third quartile. The lines that extend from the top and bottom of the box indicate the highest and lowest density of the samples, respectively. The green density values of 48 K-squares ranged from 1.64 to 1.95 g/cm³, which are 51.3-61.0% of the theoretical SiC density (3.2 g/cm³). Sample No. 2 with β -SiC and 3 wt.% of Hypermer KD 1 showed the highest green density of 1.93 g/cm³ (61.0% of

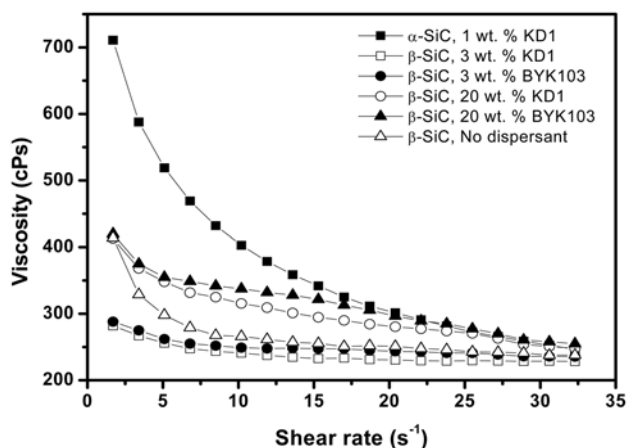


Fig. 5. Viscosity of the slurries with α - and β -SiC for tape casting containing different types and amounts of dispersant.

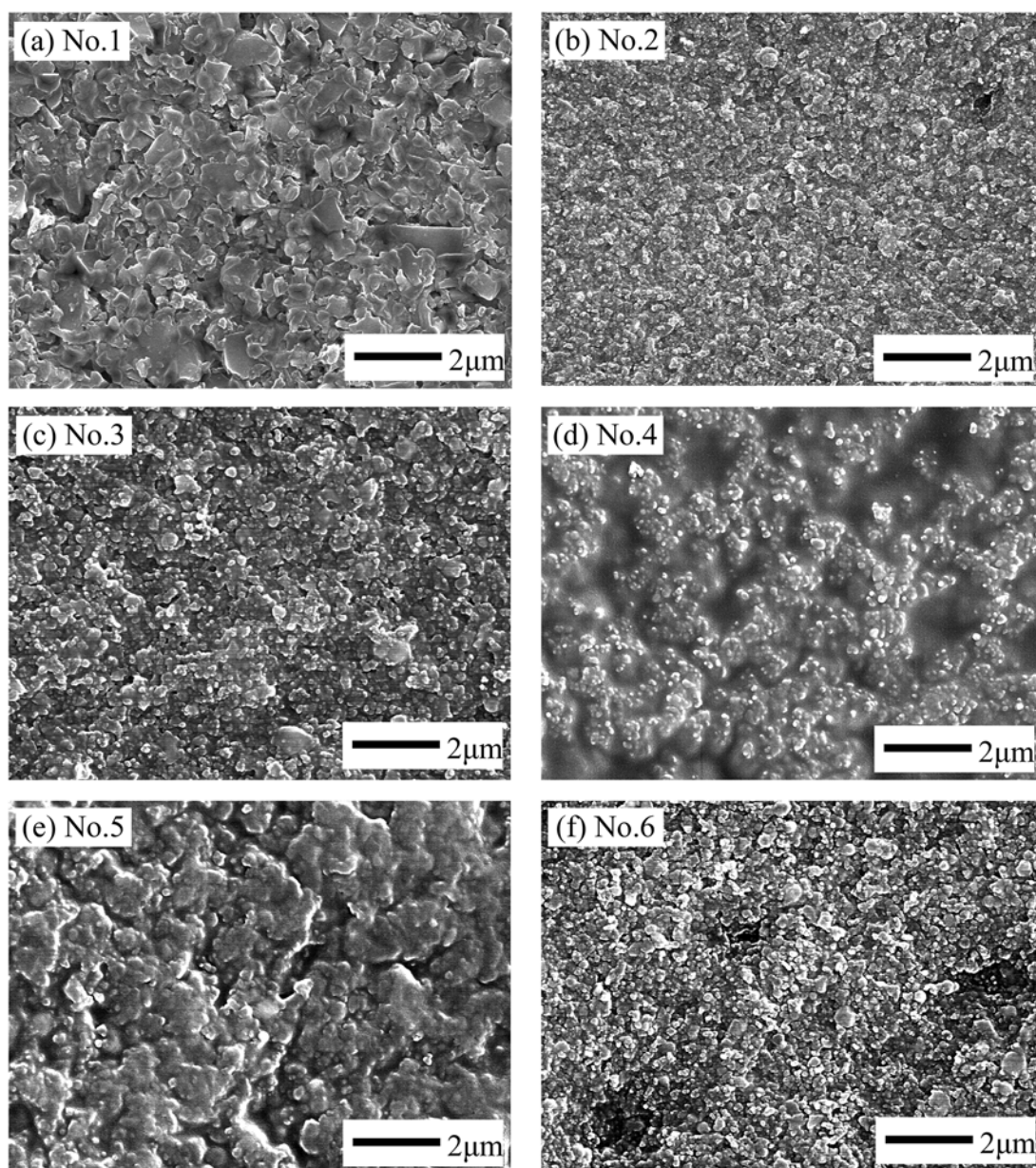


Fig. 6. SEM microstructures of the top surface of green tapes made from α - and β -SiC with different types and amounts of dispersant (The details of slurry formulation for the above samples are given in Table 2).

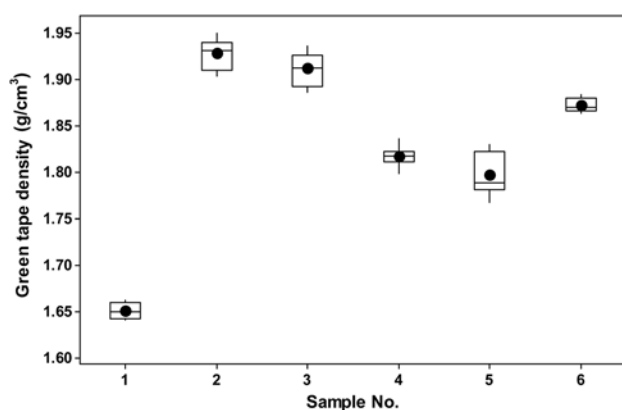


Fig. 7. Green density distributions of the K-squares for the six different slurry formulations, given in Table 2.

theoretical density), while α -SiC showed the lowest density of 1.65 g/cm^3 (51.6%). The samples containing β -SiC and 20 wt.% of dispersant showed a lower green density than those containing 3 wt.%, which is consistent with the slurry viscosity behavior and green surface morphology.

Conclusions

A systematic study of the SiC suspension and slurry system in terms of the dispersion and green tape properties was carried out using two different sizes of SiC particles and four types of commercial dispersants. It was found that steric hindrance is more efficient than an electrostatic mechanism for the dispersion of β -SiC in a toluene/ethanol mixed system, particularly in the presence of a dispersant.

For the optimum suspension dispersion, 20 wt.% dispersant was essential for nano-sized β -SiC due to its large surface area, while 3 wt.% was sufficient for micro-sized α -SiC. However, this optimum amount of 20 wt.% dispersant had decreased to 3 wt.% for the β -SiC slurry due to the inherent dispersing characteristics of the PVB binder resin with a low molecular weight of 50,000 g/mole. A significantly higher amount of binder and plasticizer was required to achieve the optimum tape properties for β -SiC than for α -SiC system. It was also found that the green tape properties, including the density and surface morphology, were significantly dependent on the dispersion state, indicating the importance of optimum formulation. Consequently, a green tape density > 60% with respect to the theoretical SiC density could be achieved with a β -SiC slurry containing 40 wt.% binder with 3 wt.% of a polyester/polyamine co-polymeric dispersant.

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