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Dispersion and tape casting of silicon carbide through aqueous route

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Dispersion behaviour of SiC in aqueous media was studied using four different dispersants and as a function of pH. The slurry was characterized in each case by sedimentation, viscosity and rheological studies. The best dispersant was selected and its optimum amount was determined. For this system, the pH was varied over a range of 2–11. The slurry displayed the minimum viscosity as well as near-Newtonian behavior at pH range 8–11. SiC tapes were obtained by Double doctor blade tape-casting process, with polyvinyl alcohol as binder and PEG and BBP as plastisizers. The stability of the tape casting slurry was determined by rheological characteristics. As-cast tapes were dried in air at room temperature. The results show that it is possible to obtain homogenous defect-free green tapes of 57.7% solid loading and 53% green density with smooth surface using the optimized tape casting slurry.

1. Introduction

Tape casting is one of the major processing techniques used to produce thin ceramic sheets for multilayered electronic devices [1, 2]. Organic-solvent based tape-casting systems are widely used mainly because one can obtain improved quality of tape and because of easy and fast evaporation of solvents during drying stage. Wider range of binders and plasticizers are available for organic-solvent systems [3, 4]. However, stringent environmental regulations and health concerns force processing industries to look for alternatives. On the other hand, aqueous-based tape casting offers the advantages of non-toxicity, incombustibility and low-cost.

Aqueous tape casting is an involved process and one has to overcome a series of technological challenges before achieving good quality green tapes. The major challenges are, slower drying rate, controlling cracks, difficulty in achieving high solid loading, bubbles in the slurry which produce pinholes in the dried tapes and high sensitivity even to the slightest process variations [5]. In spite of these challenges, in recent years, much effort has been made to replace the highly toxic organic systems by aqueous medium [6–9]. Also the large amount of experience and effort that has gone into other similar colloidal processing techniques like slip casting and gel-casting comes handy in understanding dispersion of ceramic powders in aqueous medium [10–12].

Dispersion of ceramic powder in a medium is usually achieved by the addition of optimum amount of dispersant. Dispersion is achieved through electrostatic mechanism, steric mechanism or a combination of both. The addition of polyelectrolyte as dispersing agent achieves stabilization by a combination of electrostatic and/or steric mechanism [13]. An advantage of aqueous processing is that apart from dispersant, pH of the medium also plays a crucial role in dispersion. In water, good dispersion can be achieved either by pH adjustment alone or by pH adjustment in combination with the addition of polyelectrolytes [14].

Silicon carbide is of technological importance because of its use in the field of high temperature structural applications and as heat exchangers. It has high strength, hardness, creep resistance and oxidation resistance. SiC green tapes are required for Si/SiC and other composite/functionally graded materials/applications [19–21]. Non-aqueous tape casting of SiC has been described in literature [19, 20]. Literature exists on aqueous processing of SiC also [22, 23]. However, a systematic study of the dispersion and aqueous processing of SiC is needed for this technologically important material.

In the present study, dispersion of SiC in deionised water is compared by using four different dispersants. The best of them is selected, its weight percentage is varied and the optimum amount is selected. With this optimum amount of dispersant, pH of the slurry is varied from acidic to basic range and the best range is selected. In all the above cases, optimum condition is selected by characterizing the suspension using sedimentation and rheological studies. Measurement of sedimentation rate and final sediment height is a well-accepted method to establish the degree of particle dispersion and packing density [10–13]. As far as the rheological characterization is concerned, the system which gives the minimum viscosity and near-Newtonian flow behavior is selected as the best dispersed condition [13, 14]. The yield stress τ_0 is an important parameter that defines whether a system is well dispersed or not. This parameter is defined as the minimum tension necessary

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to cause flow, which in a ceramic suspension indicates the tension to break 3-D structures of weakly attracted particles. The yield stress can be obtained by fitting the viscosity data into Cassons model [13, 14]. This value helps us to quantitatively compare the flow behaviour of different samples.

Finally, tape-casting slurry is prepared at the optimum dispersion condition by adding, plasticizers, binders etc. The slurry was found to exhibit shear-thinning behavior. The results show that it is possible to obtain homogeneous defect-free green tapes of 57.7% solid loading and of 53% green density with smooth surface from the optimized slurry.

2. Experimental procedure

2.1. Starting material

The source of SiC powder used in the present study is from Carborundum Universal, India; with an average particle size of 1 μm. XRD analysis (AXS Bruker D5005 diffractometer, Germany) reveals that it is a mixture of 6H as major phase and 4H as minor phase and contained traces of SiO_2. The average surface area of the powder measured was 4.76 m^2/g using BET surface area analyzer (Quanta chrome Instruments, USA).

The different dispersants used in the present study are Darvan C (R. T. Vanderbilt Co., USA) which is ammonium salt of polymethyl acrylic acid, Disp.Graid1000 (Shubham colloids, India), which is a complex amino hydroxy salt of carboxylic acid, Tetra sodium pyro phosphate (Ottochemi, India), and Sodium hexa meta phosphate (Nice, India). pH adjustments were carried out with HCl and NH_4OH. For the preparation of tape casting slurry, Polyethylene glycol 600 (Merck, India) and Benzyl butyl phthalate (Sigma Aldrich, India) were used as plasticizers. 10 wt% polyvinyl alcohol (S. D. fine, India, MW 1,25,000) was used as binder. Oleic acid was used as an anti-bubbling agent.

2.2. Slurry preparation

Dispersion studies were carried out with 33 wt% of solid content. With the desired wt% of dispersant, the slurry was ultrasonicated for 10 min, then ball milled for 24 h with Zirconia balls as milling media for effective deagglomoration and dispersion. Sedimentation and rheological studies were then carried out. For the optimum amount of the dispersant, the pH of the slurry was varied between 2 and 11. In each case, sedimentation and rheological studies were carried out after the pH has been stabilized at the desired value. Zeta potential analysis were carried out using Zetasizer 3000HS (Malvern Instruments Ltd., Malvern, U.K.)

2.3. Sedimentation studies

For sedimentation study, 10 ml of the slurry was transferred to a graduated measuring cylinder. The sediment height was recorded as a function of time. The slurry was allowed to settle undisturbed for weeks and the final packed-bed height is noted.

2.4. Sedimentation studies

Rheological characterization was carried out using a shear-controlled Rheometer (Brookefield Programmable DV III+ Rheometer) using UL adapter for dispersion studies and small sample adaptor (Spindle SC4-18) for tape casting slurry. The general flow behaviour was studied by plotting the variation of viscosity with shear rates in the range 12.23 to 122.3/s. These viscosity data were analysed by fitting with different mathematical models using the Rheocalc Software (Brookefield Engineering, USA). Casson's equation [13, 14] gave the best fit.

Casson equation is,

$$(\tau)^{1/2} = (\tau_0)^{1/2} + (\eta \mathrm{D})^{1/2}$$

where, τ: shear stress, τ_0: yield stress, η: Viscosity and D: shear rate.

From this, the value of yield stress can be readily calculated. This value helps us to quantitatively compare the flow behaviour of different samples. Lower viscosities and lower yield stress values indicate a stable system.

For the optimized dispersion system as well as for the tape casting slurry, time dependent properties were studied by applying on-off stepwise sequences at two constant shear rates (39.6 and 79.2/s, each for 3 min, with a 3 min no-shear interval in-between). Such an on-off procedure can provide useful information on the thixotropic response of a sample, as it can reveal whether the structural recovery under rest condition is appreciable or not [14].

For the tape casting slurry, hysteresis behaviour was studied by applying ascending and descending shear rate ramps. A good superposition of up and down curves (psuedoplasticity) indicates desired characteristics of tape casting slurry [13, 14].

2.5. Tape casting

Tape casting slurry was prepared with the optimum concentration of the selected dispersant at the selected pH. Polyethylene glycol 600 and Benzyl butyl phthalate were selected as plasticizers. The binder used was 10 wt% polyvinyl alcohol. Double-step slurry preparation was carried out. At the first stage, powder, solvent and dispersant alone was ball milled with Zirconia balls as milling media for 24 h. This treatment was effective in breaking down the soft agglomerates and to ensure equilibrium adsorption of the polyelectrolytes on the powder surface. After pH adjustment, other additives were added and rolled for 24 h.

Tape casting was carried out using Double doctor blade technique on a clean glass bed using a laboratory batch type tape caster (E. P. H. Engineering, U.S.A.). The blade gap was kept at 250 μm. Tapes were made at 3 different speeds. After natural drying for 4 h, tapes were released and inspected for potential defects. Thickness and green densities were measured.

3. Results and discussion

3.1. Effect of dispersant

Minimum in the final sedimentation height indicate good dispersion as individual particles settle to give maximum packing density. Higher sediment heights, often in a loose lump form indicate agglomeration. The rate at which the dispersed powder settles under gravity is also a clear indication of the state of dispersion and stability.

The settling rate and viscosity measurements for SiC with 1 wt% of different dispersants are shown in Figs 1 and 2. From Fig. 1 it is clear that even though the initial rate of sedimentation is the same for different dispersants, the final sediment height differs. Tetra sodium pyrophosphate and Sod.hexa metaphosphate show identical final H/H_0 whereas Darvan C, which is ammonium salt of polymethyl acrylic acid and Disp.Graid1000, which is a complex amino hydroxy salt of carboxylic acid, behave identically.

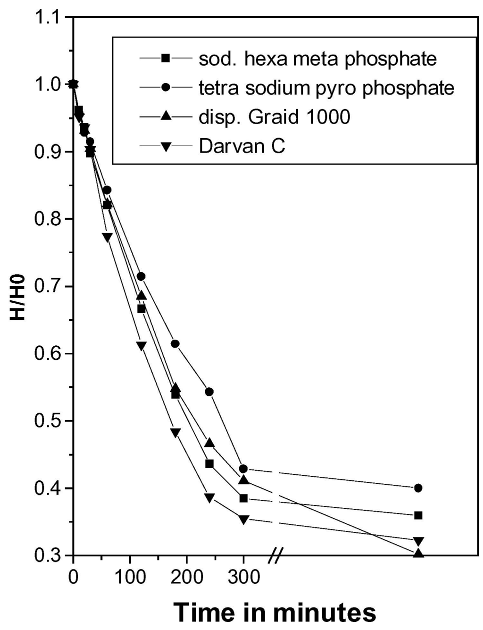

Figure 1 Relative sedimentation height (H/H_0) plotted as a function of time for different dispersants.

Fig. 2 shows the rheological characteristics of these slurries. Here again it is observed that tetrasodium pyrophosphate and sod.hexa metaphosphate behave identical, exhibiting shear-thinning behaviour. Darvan C and Disp.Graid1000 behave similarly with the later giving the minimum viscosity and near-Newtonian behaviour. The yield stress values of the slurry with sodium hexa metaphosphate and tetrasodium pyrophosphate are 0.13 and 0.1 D/cm^2 respectively. As expected, minimum Yield stress of 0.03 and 0.02 D/cm^2 is obtained for Darvan C and Disp.Graid1000, respectively.

Since Disp.Graid1000 showed minimum in viscosity, further studies were carried out using this as dispersant. To analyse the optimum concentration of Disp.Graid1000, wt% of the dispersant was varied from 0 to 2 and in each case, the slurry was characterized by sedimentation studies and rheological studies (Fig. 3). Though the initial rate of sedimentation was nearly the same, 0.5 wt% exhibited the minimum sedimentation height. As shown in Fig. 3, 0.5 wt% exhibits minimum in viscosity and near-Newtonian behaviour too. The yield stress is also minimum (0.01 D/cm^2) for 0.5 wt%, supporting the fact that it is the optimum dispersant concentration. When dispersant concentration is increased, increase in viscosity is observed. This may be explained as follows. The optimum amount of dispersant corresponds to the amount giving monolayer coverage on the particles [14]. A further increase of the dispersant concentration corresponds to a condition where saturation adsorption limit is exceeded and the presence of excess polymer leads to particle destabilization by a bridging mechanism [23]. A clear correlation between the yield stress and final H/H_0 was observed.

With the optimum amount of dispersant, time-dependant flow behaviour was also studied using the rheometer by applying on-off stepwise sequences at

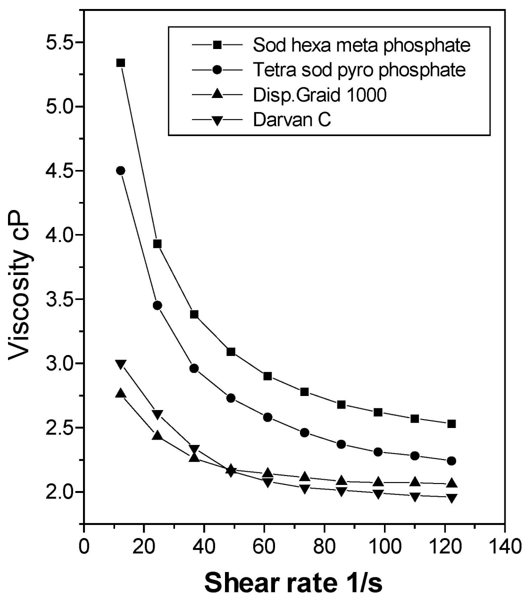

Figure 2 Viscosity versus shear rate for 33 wt% SiC slurries for different dispersants (1 wt%).

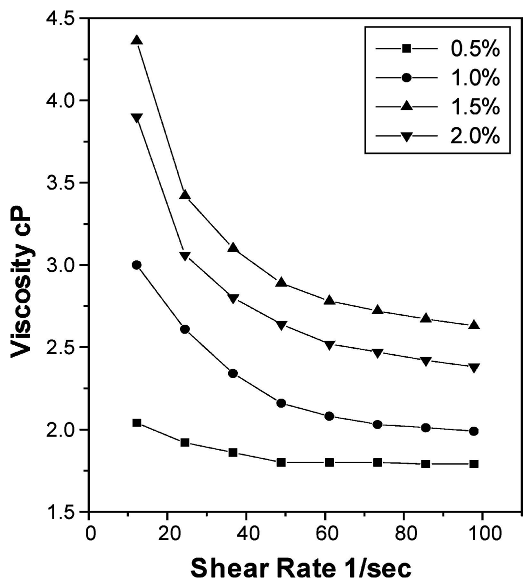

Figure 3 Viscosity versus shear rate for varying concentrations of Disp.Graid 1000.

two constant shear rates (39.6 and 79.2/s), each for 3 min, with 3-min no-shear interval in-between. Viscosity values obtained at constant shear rate do not depend on the shearing time, indicating high degree of stabilization [14].

3.2. pH variation

To analyze the combined effect of dispersant and pH, slurries were prepared using optimum amount of dispersant and pH was varied between 2 and 11. In each case, after pH stabilizes at the desired value, it was characterized by sedimentation and rheological studies (Fig. 4). The Point of zero charge (pzc) of SiC has been reported as 3.7 [22]. But anionic dispersants like Darvan C and Disp.Graid1000, which are basic intrinsically (13), shift the pzc towards more acidic direction, while shifting the pH of the suspension slightly towards the basic direction. In the present study, viscosity at pH 2 is almost two orders higher than the other cases. The yield stress is also the highest, 3.94 D/cm^2 compared to 0.01 D/cm^2 at pH 8 and 11. At pH 2, the viscosity curve shows clear shear-thinning behaviour indicating the presence of weakly agglomerated powder particles which are broken down under the effect of increased shear rate. At this pH, SiC is reported to form flocculated particle clusters [22] as the pH is closer to pzc. These results are also supported by zeta potential measurements as a function of pH (Fig. 5). Zeta potential is minimum at pH 2 and as we go away from this pH it increases appreciably.

As we go away from pzc, we get more homogeneous slurry, indicated by low viscosity (Fig. 4) low yield stress and higher zeta potential. In the pH range 8–11, the slurry exhibits minimum viscosity, lowest final sediment height and higher zeta potential. In this range, it is also observed that the viscosity curves are near Newtonian in nature, proving optimum dispersed condition. So, further tape casting studies were carried out at pH 8 since it is always better to avoid extreme pH conditions.

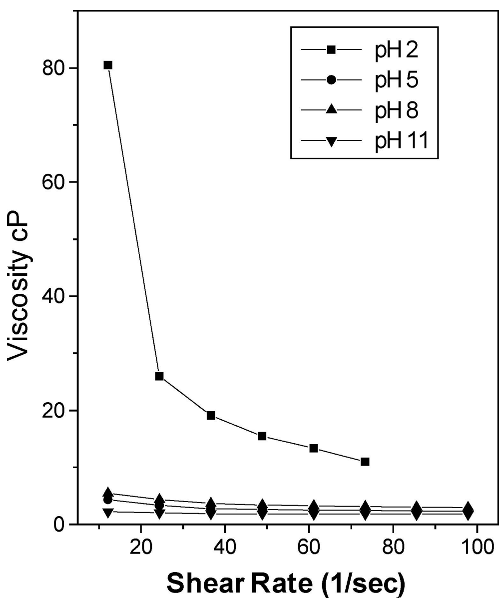

Figure 4 Viscosity of SiC suspensions as a function of pH.

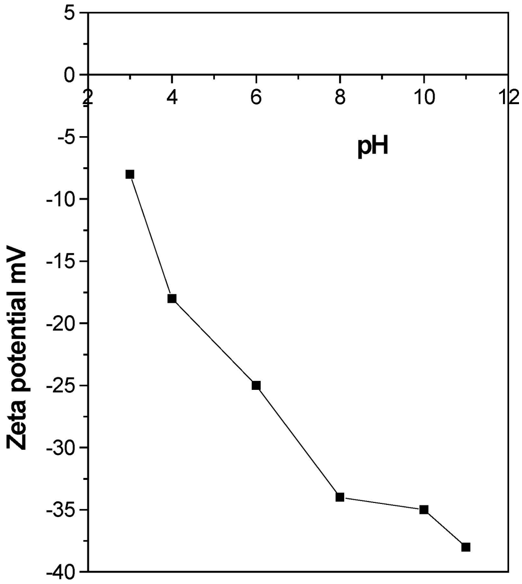

Figure 5 Zeta potential of SiC slurry as a function of pH.

3.3. Influence of polyelectrolytes and pH

Polyelectrolytes have been used extensively for effective dispersion of ceramic powder [13]. Polyelectrolytes being long polymeric chains with ionic groups, can dissociate in polar medium. These dissociated polyelectrolytes adsorb onto the oppositely charged surfaces of particles providing a physical barrier to particle agglomeration as well as electrostatic repulsion originating from the charged group leading to electrosteric mechanism of dispersion.

In the present experiment, it is found that both Darvan C (ammonium salt of polymethyl acrylic acid) and Disp.Graid1000 (a complex amino hydroxy salt of carboxylic acid) are found to be efficient dispersants in the higher pH range of 8 to 11. The structure of these dispersants is as follows

```
R– C –O⁻N⁺H₄    (Darvan C)
   ||
   O

R– C –O⁻ N⁺ –OH    (Disp.Graid1000)
   ||     |
   O      H₃
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The functional group in both dispersants is carboxylic acid which may remain neutral or dissociated depending on the pH. It is well known [11, 16] that these polyelectrolytes are fully dissociated at pH $\geq$ 9 and becomes negatively charged.

SiC exhibits positive zeta potential at pH levels lower than pzc (3.7) and negative at higher pH. The pzc and other surface properties of SiC have always been attributed to the formation of a silica layer on the surface of SiC particles. Experimental evidence exists for the formation of silica on the surface of SiC by oxidation [13]. TEM observations have demonstrated that SiC powder contains 0.3 to 0.7 nm coating of native amorphous SiO_2 layer [16, 22]. In view of the presence of

SiO_2 layer on SiC the number of positively charged $SiOH_2^+$ sites becomes greater than negatively charged SiO^- sites at pH lower than IEP. The opposite is true for pH greater than pzc.

Even though both polyelectrolytes and SiC are negatively charged at higher pH, the surface can still provide some positive sites for adsorption. It has been proved [22] recently that the minority positive surface $SiOH_2^+$ sites help to anchor the negatively charged polyelectrolyte on the surface of SiC, leading to electrostatic repulsion between the particles. In a similar case, negatively charged sodium polyacrylate was found to be effective in dispersion of Alumina at higher pH where the particles are also negatively charged [11, 13, 15]. Since carboxylic acid group in polyelectrolytes dissociate, poly acrylic acids form negatively charged macromolecules. The conformation of these types of polymers in solution is influenced mainly by ionization [17, 18]. While they form compact coils under acidic conditions (low degree of ionization) they undergo transformation to a stretched conformation at basic pH, because of electrostatic repulsion between neighboring ionized carboxyl groups. Molecules in stretched conformation are highly effective in providing high repulsive barrier for better dispersion [13, 17]. Hence in the present case, the negatively charged polyelectrolytes in stretched confirmation at higher pH are adsorbed on to the minority $SiOH_2^+$ sites of SiC leading to electrosteric mechanism of dispersion between the particles.

4. Tape casting

Tape casting slurry was prepared by retaining 0.5 wt% dispersant and pH of 8. The flow chart for tape casting process is shown in Fig. 6. The optimized slurry composition is given in Table I. The slurry was characterized by rheological studies (Fig. 7). Fig. 7A shows the rheological characteristics of the slurry after the plasticizer addition and Fig. 7B shows the rheological characteristics of the binder solution alone and that of the final tape casting slurry. The optimized final tape casting slurry exhibits shear-thinning behavior. When moderate, this

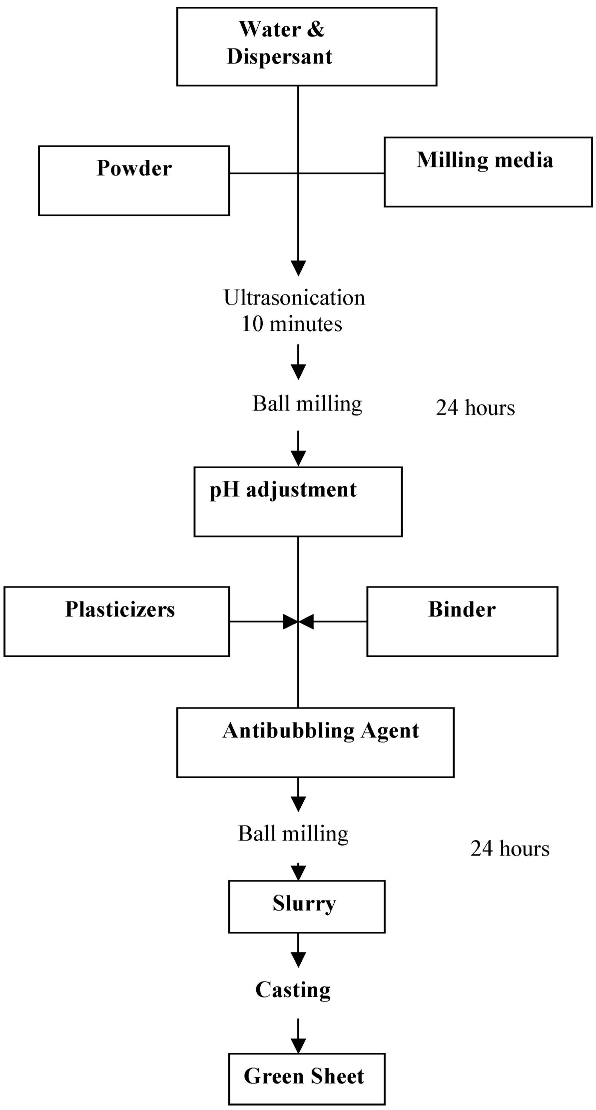

Figure 6 Flow chart for tape casting process.

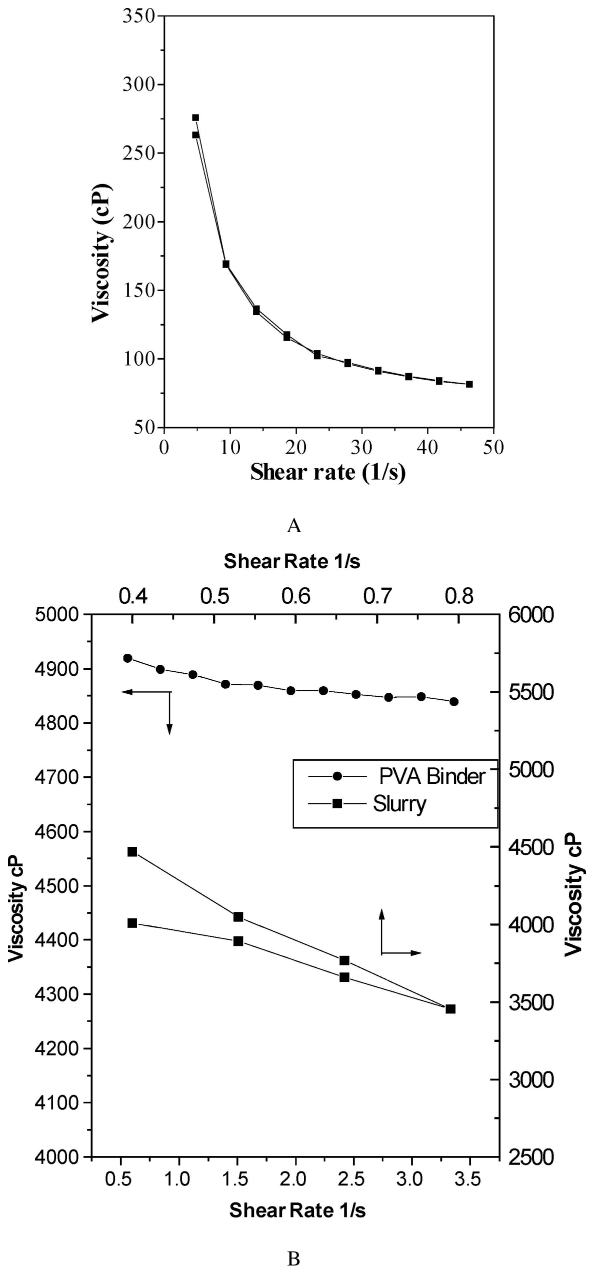

Figure 7 Rheological characteristics of SiC slurry. (A) After the addition of plasticizers and (B) Final tape casting slurry. The rheological characteristic of binder solution alone is also shown.

TABLE I Tape casting slurry composition

Constituent	Wt%
SiC powder	57.71
Water	22.43
Disp. Graid 1000	0.50
BBP	1.70
PEG	1.72
PVA	15.24
Oleic acid	0.70

property is desirable in tape casting under the action of moving blade/carrier. Tape casting was done at three different speeds, 5, 10 and 20 mm/s, keeping the blade gap at 250 μm in all the cases. With increasing casting speed, the thickness of the tape gradually decreased from 100 to 80 μm.

5. Conclusions

Based on this study, the following conclusions are drawn.

(1) The sedimentation studies and viscosity measurements showed that, out of the four dispersants tried, Disp.Graid1000 (which is a complex amino hydroxy salt of carboxylic acid) is the best for preparing concentrated SiC suspensions in aqueous medium. The amount of dispersant required to achieve a minimum in viscosity for 33 wt % suspension is 0.5 wt%.

(2) In the presence of 0.5 wt% dispersant, 33 wt% SiC slips exhibited Near Newtonian behavior. The rheological measurements showed that time dependent effects were negligible. Yield stress showed low values indicating that the SiC slips were homogeneous and well stabilized.

(3) Dispersion studies in the presence of 0.5 wt% dispersant and pH adjustments between 2 and 11 showed that pH had significant influence on the rheological properties of SiC slips. Around pH = 2 which is close to the pzc of SiC, the slurry exhibited high viscosity, high yield stress and lowest zeta potential. When the pH is away from pzc, viscosity and yield stress decreased, and the best results were obtained in the range 8–11.

(4) Finally, when tape-casting slurry was prepared at the selected optimum amount of dispersant and pH range, it exhibits shear thinning behavior, characteristic of tape casting slurries. With the optimized slurry composition, defect free green tapes of 57.7% solid loading and 53% green density with smooth surfaces could be obtained.

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