Stabilization of highly-loaded boron carbide aqueous suspensions

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ABSTRACT

Injection molding of boron carbide (B_4C) slurries affords the production of complex-shaped personal armor. To injection mold, however, requires preparation of a well dispersed, flowable suspension with > 45 vol% B_4C loadings to reduce porosity that must be removed during sintering. In the present study, the preparation of highly-loaded B_4C suspensions is investigated using zeta potential and rheological measurements, varying dispersant type, molecular weight, and amount. Of those dispersants investigated, polyethylenimine (PEI) with a molecular weight of 25,000 g/mol was found to produce suspensions with up to 56 vol% B_4C and the requisite rheological properties suitable for injection molding. A PEI concentration of 1.83 mg/m^2 was established as the appropriate to produce highly-loaded B_4C suspensions. The effect of a prior B_4C powder treatment (ethanol washed or attrition milled) on rheological properties of the suspensions was also investigated. The PEI was completely burned out in argon, nitrogen, and air at 450 °C.

1. Introduction

Boron carbide (B_4C) is the third hardest material after diamond and cubic boron nitride. Depending on how it is processed, hardness values approaching 35 MPa can be achieved [1,2]. B_4C is frequently used in high wear applications, e.g. sand blasting nozzles; it is also desirable as an abrasive and for cutting tools. Its neutron absorption capacity makes B_4C a common material for shields and control rods in nuclear reactors [3]. Due to its low density of 2.52 g/cm^3, B_4C is also widely used for personal armor. In many cases, it is required to form the B_4C into complex shapes. Forming methodologies such as slip-casting, [4] tape-casting, [5,6] or even additive manufacturing and non-traditional injection molding [7–10] have been used to form ceramics into useful shapes. To minimize the amount of porosity that must be removed during sintering, additive content is kept low while ceramic powder loading is maximized. In each of these methods, the fundamental obstacles for preparing a highly loaded ceramic suspension are tailoring rheology and maximizing ceramic content, both of which are dictated by particle dispersion.

Aqueous suspensions are produced by mixing ceramic, water, and dispersant in appropriate proportions. Suspensions can demonstrate yield pseudo-plastic flow behavior that are modeled by the Herschel-Buckley model as shown in Eq. (1):

$$\sigma = \sigma_0 + K\dot{\gamma}^n \tag{1}$$

where σ_0 is the yield stress, K is the consistency index, $\dot{\gamma}$ is the applied shear rate, and n is the flow index. The consistency index is defined as a proportional constant that determines the apparent viscosity of the system for a fixed shear rate. These suspensions often demonstrate shear-thinning behavior; as a higher shear rate is applied, the viscosity of the system decreases i.e., the flow index, n, is less than 1. The yield stress must be overcome prior to flow of the suspension and is a consequence of the weakly flocculated particles in the suspension [11]. The partially aggregated condition creates large 3D structures that help keep particles from settling. The application of shear, and eventual flow, breaks down the gelled structure. Viscosity changes are due to a dynamic balance between shear conditions and the gelation of the suspension [11].

For ceramic processing approaches such as injection molding, it is desired to maximize ceramic powder content while keeping the viscosity of the suspension relatively low. To achieve a highly-loaded flowable suspension, effective colloidal dispersants are needed. Unfortunately, dispersants for highly loaded ceramic systems cannot be readily predicted from suspensions with dilute concentrations like those used for zeta potential measurements [12,13]. The present study investigates multiple dispersants for preparation of boron carbide suspensions with the goal to maximize powder loading while maintaining a flowable suspension. The fundamental phenomena and colloidal behavior that allows for the stabilization of highly-loaded boron carbide suspensions is discussed. The focus of this study is how the stability of the system is affected by dispersant molecular weight and concentration, as well as the effect of B_4C particle surface chemistry.

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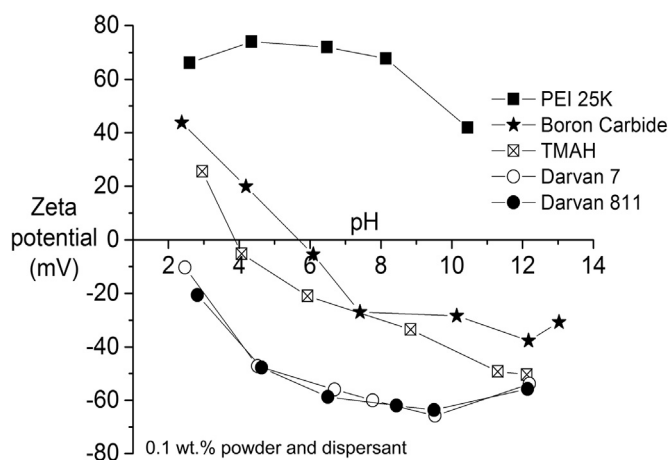*E-mail address:* adiazcan@purdue.edu (A. Diaz-Cano).

Fig. 1. Zeta potential values for as-received B_4C powders as function of pH for dispersants that demonstrated a zeta potential with an absolute value greater than 40 mV. Hydrochloric acid (HCl) and sodium hydroxide (NaOH) were used to change the pH of the suspension. The isoelectric point of boron carbide corresponded to a pH between 5 and 6. The electrostatic dispersion effects of polyethylenimine (PEI) 25k (positive), Darvan 7, and Darvan 811 (both negative) have comparable net charges with different signs.

2. Experimental procedure

2.1. Materials and methods

Boron carbide (H.C Stark grade HS) with a vendor reported mean particle size of 1.2 μm and specific surface area of 15–20 m^2/g was used in this study. Three different approaches were used to alter the surface and/or size of the B_4C powders. In the first approach, the powders were attrition milled in ethanol for 2 h at 50 RPM. Spherical tungsten carbide (WC) with a diameter of 3 mm was used as milling media. The milling container and turn bar were lined with polyethylene. The powder to milling media mass ratio was 10:1 and each batch contained 100 g of B_4C. The milling media was massed before and after milling to determine the amount of WC contamination. In a second approach, the same equipment and parameters described above were used; however, no milling media was used. These powders are referred to as "washed". After both approaches, ethanol was evaporated at 150 °C for 24 h. As a consequence of ethanol evaporation, large agglomerates were created. Agglomerated powders were dry ball milled for 24 h. In a third approach, B_4C powder was neither attrition milled nor washed, but used directly from the container. Powder in this condition is referred to as "as-received."

Specific surface area was determined of the attrition milled, washed, and as-received powders via the Brunauer, Emmett and Teller (B.E.T) theory. Degassing was performed in a N_2 atmosphere at 300 °C. Powder chemical analysis was performed via inductively coupled plasma mass spectroscopy (NSL Analytical, Cleveland, OH).

The effect of different dispersants on B_4C suspension stability was initially analyzed via zeta potential (Malvern zetasizer nano series *nano-Z*). Many common dispersants suggested by the literature were investigated including the following: Darvan® CN, Darvan® 821A,[1] Duramax™ D-3005,[2] APM95,[3] Dolapix CE64,[4] Dolapix A88[4], Darvan 811[1], Darvan 7[1], Tetramethylammonium hydroxide (TMAH),[5] Tris(2-aminoethyl)amine[5], and different molecular weights of PEI[5]: 1300(1.3k), 25,000(25k), 750,000(750 K), and 2,000,000(2000k) g/mol [14,15]. In preparation for each zeta potential measurement, B_4C

powder was suspended in deionized (DI) water and sonicated (Branson digital sonifier) for 3 min, applying 1 s on-off pulses with an amplitude of 50%. DI water was used to reduce screening effects or changes in ionic strength. The dispersant and powder content were kept constant at 0.1 wt% for all measurements. The pH was adjusted using hydrochloric acid (for pH values below 7) and sodium hydroxide (for pH values above 7). pH was measured with a pH meter (*Oakton pH 5 acorn series*).

2.2. Rheology measurements and thermogravimetric analysis

Dispersants with measured zeta potential values greater than 40 mV, either negative or positive, were used to prepare higher concentration suspensions (i.e. ~40 vol% B_4C) to study their rheological performance. To prepare these suspensions, the dispersant was first dissolved in DI water.

The pH was balanced to ~7 using equal concentrations of hydrochloric acid and dispersant (based on volume). Powder was added in three equal batches. After the addition of each batch, the suspension was mixed for 2 min using a planetary rotary mixer (*Flacktek SpeedMixer DAC 400.1 FVZ)* at 800 RPM and 1200 RPM, for 1 min respectively. After the addition of the third batch, four 12.7 mm diameter WC satellites were added as milling media. The suspensions were then mixed again at 800 RPM for 15 s. Finally, the suspensions were ball milled for 24 h. 50 ml of suspension were produced for each dispersant type.

Suspension flow curves were obtained using a *Bohlin Gemini HR nano rheometer* with a 25 mm cup & bob feature; 13 ml of the suspensions were sampled. Tests were performed at room temperature with a gap of 150 μm. Controlled shear rates, 0.01 s^{-1} to 35 s^{-1}, were applied while shear stresses were measured. A wet sponge was placed on top of the fixture in order to avoid premature drying of the suspension.

Thermogravimetric analysis of the boron carbide and dispersant was performed using a *TA instruments Q50* equipment with a heating rate of 30 °C/min. The experiments were performed under flowing atmospheres of argon, nitrogen, or air. Sample mass changes were recorded as temperature changed from room temperature to 1000 °C.

3. Results and discussion

3.1. Zeta potential measurements for As-received powders

Fig. 1 shows the zeta potential for B_4C powder as a function of pH. The isoelectric point of as-received B_4C was located in a pH range of 5–6. Differences in the B_4C isoelectric point compared to other studies [15] may be due to variations in surface chemistry. Treatments such as acid or solvent washing, alter B_4C surface chemistry by removing boria (B_2O_3) [16]. Hence, surface chemistry could have an impact on charge distributions and Stern layer thickness [17]. Fig. 1 also shows zeta potential behavior as a function of pH of those dispersants considered to be candidates to form a stable suspension. Thus, dispersants with zeta potential values between −40 mV and 40 mV over a pH range of 2–13 (Darvan CN, Darvan 821 A, Duramax D-3005, APM95, Dolapix CE64, Dolapix A88) are not shown because of their relative ineffectiveness in preventing flocculation of powders [11,12].

Tetramethylammonium hydroxide (TMAH) has been previously suggested as an effective dispersant for B_4C [15]. However, its stabilization mechanism relies mainly on pH adjustment. As boron carbide is added to water, the pH of the suspension is reduced [18]. As reported by Li et al. [15], when added to the suspension, TMAH (as a base) increases pH. This pH increment increases electrostatic stability of the suspension (shift towards higher zeta potential). Due to its low molecular weight TMAH lacks a steric component, making its stabilization highly dependent on charge.

Darvan 811 and Darvan 7 showed their most effective zeta potential
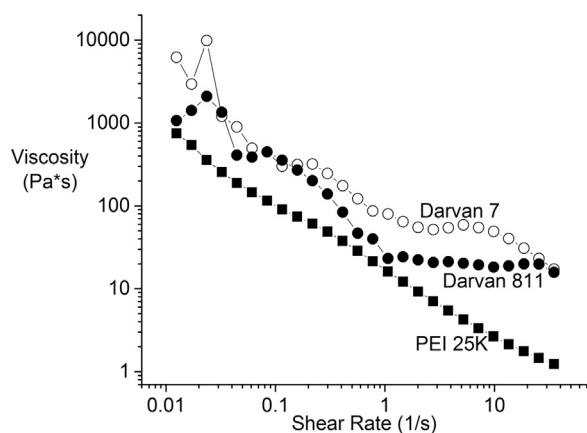

Fig. 2. Rheological behavior of 40 vol% as-received boron carbide suspensions with 5 vol% dispersant. Viscosities change as a function of applied shear rates. PEI 25k showed the lowest viscosity and uniform shear-thinning behavior.

at pH of 9.5 (i.e., −63.8 mV and −63.6 mV, respectively). Polyethylenimine (PEI), with a molecular weight of 25,000 g/mol (25k), had a maximum zeta potential of 74 mV at a pH of 4.3.

3.2. Rheological measurements for As-received powders

Based on the absolute value of zeta potential being greater than 40 mV, Darvan 811, Darvan 7, and PEI 25k were used to form aqueous suspensions with powder concentration of 40 vol% B_4C. In these initial studies the dispersant amount was kept constant at 5 vol%. Fig. 2 shows the change in viscosity versus shear rate behavior (0.01 s^{-1} to 35 s^{-1}) for the three suspensions formed. Based on previous studies [7–10], shear rates of 1–10 s^{-1} are of interest for processes such as injection molding and additive manufacturing approaches.

Although Darvan 811, Darvan 7, and PEI 25k, had similar electrostatic effects as determined by the zeta potential measurements, their flow behaviors were dissimilar. Darvan 811 demonstrated a reduction in viscosity up to 1 s^{-1}. For shear rates greater than 1 s^{-1} the viscosity was constant at 10 Pa*s. Darvan 811 shows a complex transition behavior from shear-thinning to Newtonian, with possible shear-thinning behavior for shear rates close to 30 s^{-1}. Darvan 7 showed viscosity versus shear rate behavior similar to Darvan 811 and displayed the maximum viscosity in the shear rates of interest, 1–10 s^{-1}. The flow behavior for suspensions made with 45 vol% B_4C and dispersed with either Darvan 811 and Darvan 7 (not shown) were not flowable due to lumps and aggregates. Ultimately suspensions dispersed with Darvan 811 and Darvan 7 were not further studied because of their complex and non-uniform flow behavior and corresponding higher viscosities.

Boron carbide suspensions dispersed with PEI 25k displayed significantly lower viscosity than suspensions made with Darvan 811 and Darvan 7. The continual decrease in viscosity as shear rate increased is consistent with a yield pseudo-plastic behavior for this suspension. A 45 vol% B_4C suspension dispersed with PEI 25k (Fig. 4) displayed similar yield pseudo-plastic behavior, suggesting further investigations of this dispersant were warranted.

3.3. Stability behavior various boron carbide-PEI systems

3.3.1. Effect of PEI molecular weight on the electrostatic stability of boron carbide

Although PEI has been previously suggested for B_4C and other ceramics systems (e.g. SiC [19–23]), the effect of its molecular weight and concentration on the stability of B_4C aqueous suspensions has not been reported. Therefore, different PEI molecular weights were investigated. The tested PEI molecular weights include: Tris(2-ami-
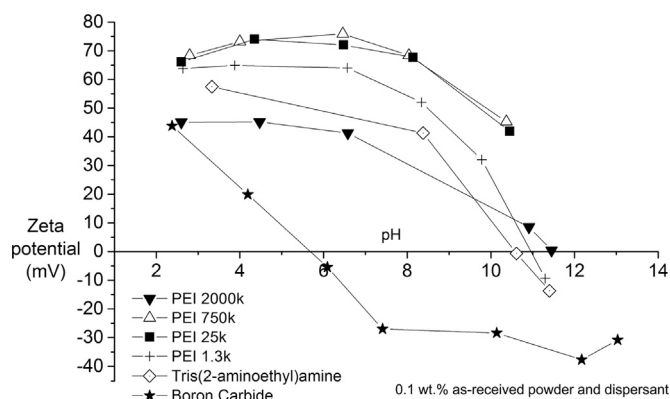

Fig. 3. Zeta potential of as-received B_4C as function of pH and molecular weight of the PEI dispersant. The intermediate PEI molecular weights, e.g. PEI 25k and PEI750k, showed the highest zeta potentials.

noethyl)amine, with a molecular weight of 146.23 g/mol, PEI 1.3k, 750k, PEI 25k, and 2000k. Tris(2-aminoethyl)amine was used since is the same repeating unit of PEI. Fig. 3 shows the effect of PEI molecular weight on the B_4C zeta potential.

The lowest and highest PEI molecular weights (i.e., Tris(2-aminoethyl)amine and 2000k) had the lowest electrostatic effects on the B_4C powders. The Tris(2-aminoethyl)amine had a maximum zeta potential of 57.5 mV at a pH of 3.3 while the PEI 200k had a zeta potential of 45.2 mV at a pH of 4.5. PEI 1.3k had an intermediate zeta potential among the PEI dispersants tested. Its maximum zeta potential was 64.9 mV within a pH range of 2.6–6.7. Intermediate PEI molecular weights of 25k and 750k showed the maximum zeta potential (i.e., 74 mV at a pH of 4.3, and 75.9 mV at pH of 6.5, respectively). Hence, PEI 25k and 750k are expected to efficiently produce B_4C suspensions via electrostatic mechanisms. In the case of PEI 2000k, even though a large size polymer chains may affect electrophoretic mobility (and, therefore, the calculated zeta potential), differences in flow behavior were conclusive (see Fig. 4).

3.3.2. Effect of PEI molecular weight on the electrostatic stability of boron carbide

As differences in polymer chain size may affect steric stabilization, the rheological performance of suspensions with 45 vol% B_4C and 5 vol% dispersant were investigated. Tris(2-aminoethyl)amine showed unstable flow behavior for applied shear rates of up to ~0.8 s^{-1}. At shear rates approached 1 s^{-1} there was a clear decrease in viscosity suggesting shear thinning behavior. For shear rates higher than 1 s^{-1} the viscosity slightly decreased, then increased again. The curve concavity
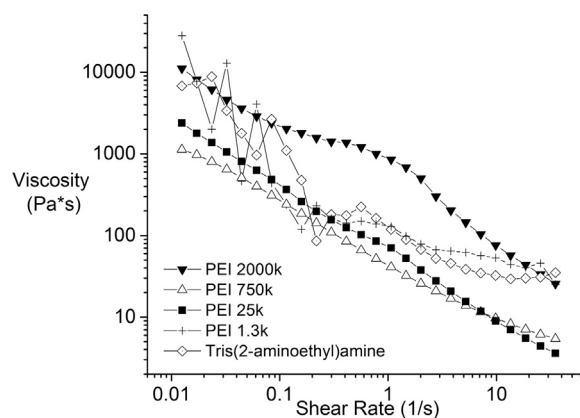

Fig. 4. Rheological behavior of 45 vol% as-received boron carbide suspensions of varying molecular weight PEI. All suspension contained 5 vol% dispersant. PEI molecular weights of 25k and 750k showed the lowest viscosities for shear rates from 1 to 10 s^{-1}.

suggests a gradual change from shear thinning to shear thickening behaviors [11]. Viscosity increments could be a consequence of a dominant particle-particle interaction. Suspensions made with PEI 1.3k followed the flow behavior of suspensions made with Tris(2-aminoethyl)amine.

Although tris(2-aminoethyl)amine, and PEI 1.3 k showed zeta potential values close to 40 mV [17], their rheological performance suggests poor stability. Due to their low molecular weight, short polymer chains may allow particle-particle interaction easily (i.e., a low steric component). Ultimately, the flow behavior of suspensions made with Tris(2-aminoethyl)amine and PEI 1.3k were erratic and inconsistent, and would not be desirable for ceramic forming processes such as injection molding.

Despite its almost uniform shear thinning response, suspensions dispersed with PEI 2000k had the highest viscosity. The lower electrostatic dispersion (45.2 mV at a pH of 4.5) may favor floc formations due to van der Waals attractions. Additionally, polymer chain entanglement and/or particle bridging may favor viscosity increments observed in these suspensions. On the other hand, polymer that has not been adsorbed on B_4C particles may increase the viscosity of the suspension or even impact the bulk charge distribution [11,12].

As observed in Fig. 4 boron carbide suspensions dispersed with PEI 25k or 750k showed uniform shear thinning behaviors without abrupt changes in viscosity. For shear rates below $7 \, s^{-1}$, suspensions made with PEI 750k showed lower viscosities than PEI 25k. This may be due to longer adsorbed polymer chains maintaining greater mean distance between particles. Additionally, polymer unabsorbed on the B_4C surface may move relatively freely. As the shear rate is increased above $7 \, s^{-1}$, the gelled structured is broken down and the mean particle distances are reduced, increasing the resistance to flow due to more frequent particle-particle interactions. Hence, for shear rates above $\sim 7 \, s^{-1}$, the interaction among particles, in addition to excessive polymer length chains, make PEI 750k suspensions more viscous than PEI 25k suspensions [11].

For most ceramic forming processes, maximizing solids loading while still retaining the necessary flow behavior of the suspension is desired. With this in mind, suspensions dispersed with PEI 25k and 750k were made and tested at higher B_4C loadings. The viscosity versus shear rate behavior of boron carbide suspensions with 50 vol% powder and 5 vol% dispersant are shown in Fig. 5. Both suspensions demonstrated uniform flow behavior without abrupt changes in viscosity as shear rate was increased. However, suspensions made with PEI 25k demonstrated lower viscosities for the whole range of tested shear
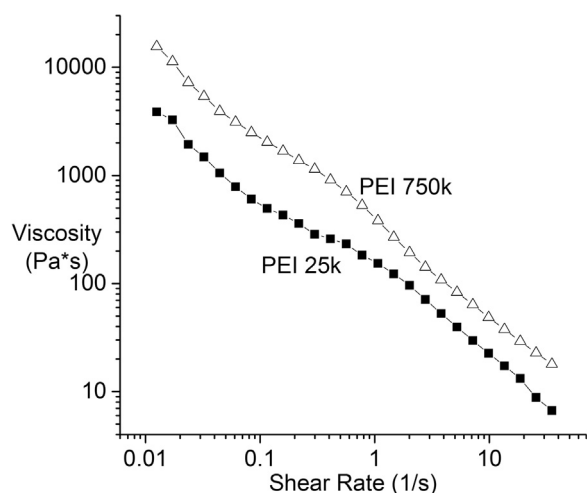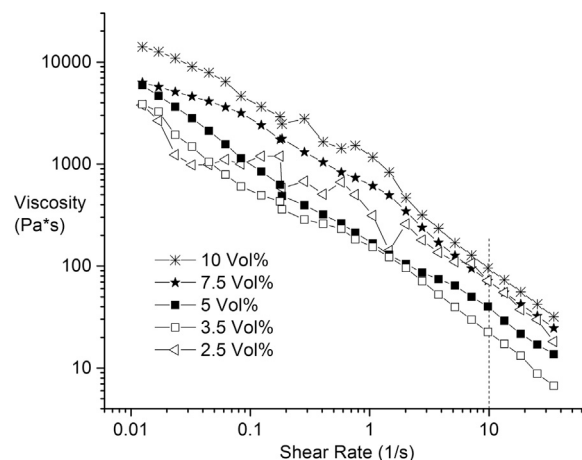

Fig. 6. The effect of PEI 25k concentration on viscosity of suspensions with 50 vol% as-received boron carbide. Vertical dash line viscosity corresponds to a shear rate of $10 \, s^{-1}$. Suspensions made with 3.5 vol% PEI 25k produced the lowest viscosity.

rates. At low concentrations of B_4C (e.g. 40–45 vol%) and low shear rates (less than $7 \, s^{-1}$), the mean distance between particles provides enough space for polymer chain deformation and relatively free movement of non-adsorbed chains. Therefore, the difference between shorter PEI chains (e.g. 25k) and longer PEI chains (750k) may not be apparent. However, once the concentration is increased to 50 vol%, the mean distance between particles is reduced increasing particle-particle interactions. Additionally, longer chains may get closer and entangled having as a final effect an increase of viscosity. Ultimately, suspensions dispersed with PEI 25k are suggested as the most efficient molecular weight to produce boron carbide aqueous suspensions at high concentrations.

In order to optimize dispersant content such that there is enough dispersant to effectively stabilize the suspension but prevent excess dispersant from contributing to viscosity, the viscosity versus shear rate behavior of suspensions with 2.5, 3.5, 5, 7.5, and 10 vol% PEI 25k were studied. The results are shown in Fig. 6. The B_4C concentration was held constant at 50 vol% for all samples and the viscosities were compared at a shear rate of $10 \, s^{-1}$ (dotted vertical line in Fig. 6). For a PEI 25k concentration of 2.5 vol%, there was an unstable flow response for shear rates below $2 \, s^{-1}$. The small volume of dispersant may give rise to particle jamming and promote aggregation at low shear rates [11]. However, the system showed clear shear-thinning behavior for higher rates. The viscosity was proportional to shear rate for PEI 25k contents of 3.5 vol% and greater. The suspension made with 10 vol% PEI 25k demonstrated the highest viscosity values. A PEI 25k concentration of 3.5 vol% showed the lowest viscosity, 22.58 Pa*s, at a shear rate of $10 \, s^{-1}$, suggesting this to be the optimum amount of dispersant required.

Based on this observation, the optimum concentration of PEI with respect to the surface area of the powders can be calculated. From the B.E.T. results, the specific surface area of the as-received boron carbide was $15.59 \pm 0.20 \, m^2/g$. Hence, based on a concentration of 50 vol% B_4C and 3.5 vol% PEI25k (for a 50 ml suspension), $1.83 \, mg/m^2$ (or $3.58 \times 10^{-3} \, cm^3/m^2$) was determined as the optimum PEI 25k content to stabilize highly loaded boron carbide aqueous suspensions. Using this concentration of PEI, suspensions with B_4C contents of 54 (using 3.8 vol% PEI) and 56 vol% (using 3.9 vol% PEI) were made with rheology sufficient for forming. Fig. 7 shows the rheological behavior of these suspensions with the solid line indicating fit of a Herschel-Buckley model to the experimental data. Table 1 presents the fitting coefficients of the flow curves from Fig. 7 (solid lines). All samples showed flow indices (*n*) values lower than 1 (see Table 1), and were thus highly shear thinning. Suspensions with 50, 54, and 56 vol% B_4C displayed uniform and stable shear-thinning behaviors with viscosities

Fig. 5. Viscosity versus shear rate data of PEI 25k and 750k suspensions. All suspensions had a (as-received) B_4C concentration of 50 vol% with 5 vol% dispersant. Suspensions made with PEI 25k had the lowest viscosity for the whole range of tested shear rates.
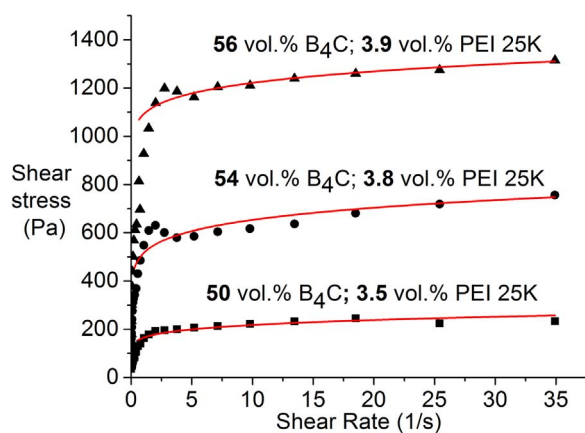
Fig. 7. Shear stress as a function of applied shear rate for suspensions with 50, 54, and 56 vol% as-received B_4C powder loadings with the determined optimum concentration (1.83 mg/m^2) of PEI 25k. Shear-yield stresses are proportional to B_4C content. Solid lines show the behavior predicted by Herschel-Buckley model with the fitting parameters presented in Table 1.

Table 1
Coefficients of Herschel-Buckley model for suspensions with 50, 54, and 56 vol% B_4C with shear-yield stresses σ_0, consistency index K, and flow index n. The shear-yield stresses increased as the B_4C solid loading increased. All samples showed shear thinning behavior, n values lower than 1.

B_4C vol%	σ_o (Pa)	K (Pa*s)	n
50	67	97.5	0.19
54	100	413.3	0.13
56	691	398.1	0.12

of 22.6, 62.9, and 123.6 Pa*s (at shear rates of 10 s^{-1}) respectively. Suspensions showed yield shear stresses of 67, 100, and 691 Pa, respectively. Yield shear stresses can be tailored having the proposed ratio of 1.83 mg/m^2 as an initial value. Although, it was possible to achieve 58 vol% B_4C, it was not possible to properly place the sample inside the equipment due to the high viscosity of the suspension.

The optimum PEI 25k content of 1.83 mg/m^2 (or 3.58×10^{-3} cm^3/m^2) was further verified by preparing 56 vol% B_4C loaded suspensions with concentrations slightly less (1.17 mg/m^2) and more (2.34 mg/m^2) PEI 25k. These concentrations corresponded to PEI vol% of 2.5 and 5 vol%. Viscosity was higher for PEI 25k contents of 2.5 vol%, with a viscosity of 581.2 Pa*s, at a shear rate of 10 s^{-1}. This is substantially higher than the measured viscosity of 123.6 Pa*s at 10 s^{-1} for the suspension with the optimum concentration of PEI 25k. The 2.5 vol% PEI suspension displayed erratic viscosity versus shear rate behavior as well. These results resembled those shown by ineffective dispersants (e.g. Darvan 7, Darvan 811, and low PEI molecular weights) at low shear rates (see prior Fig. 4). Using a PEI content of 5 vol%, higher than the optimum concentration, resulted in increased viscosity. It was not possible to properly place the sample inside the rheometer due to its high viscosity. These results confirmed 1.83 mg/m^2 as the optimal content of PEI 25k in order to stabilize B_4C in highly loaded aqueous suspensions.

Given its high covalent character [24,25] and low sintering ability, densification of B_4C is challenging. As an attempt to improve relative density and hardness, different milling techniques and powder treatments have been proposed [26–37]. Therefore, the effects of powder treatment (i.e. attrition milling and ethanol washing) on suspension stability and rheology was investigated.

3.4. Effect of powder surface preparation on zeta potential and rheology

Higher B_4C relative densities haven been reported when boria

(B_2O_3) is removed from the surface [15,38,39]. Boria hinders densification unless it is removed prior heating to > 2000 ºC. However, boria removal may also have an impact on the rheological performance of B_4C suspensions. Boria can be removed by washing B_4C powders in an acid or solvent, such as ethanol [40]. Hydrochloric acid (HCl) (present in the suspension) has been reported to remove boria as well [41,42]. This suggests a potential synergistic effect when using both ethanol and HCl for removal of B_2O_3 as is the case in the present study. Attrition milling, where powders are fractured, creates new surfaces where boria is not present and, thus, may alter densification and rheology. Furthermore, ~13 wt% WC was incorporated into the powders as a consequence of attrition milling. The presence of WC may modify packing factors and flow behaviors of suspensions.

The specific surface area of the as-received B_4C was 15.59 ± 0.20. Specific surface areas for washed and milled powders yielded higher values, 16.23 ± 0.11 (4.2% higher), and 16.63 ± 0.20 m^2/g (6.7% higher), respectively. Although, powder treatment generated a reduction on B_4C particle size, there was no statistical difference between treatment results. Only minor particle size reduction was expected due to high B_4C hardness. SEM imagines reveal no morphological difference between powders, showing angular particles for all samples (as-received, washed, and milled). Zeta potential measurements for milled and washed B_4C powders mixed with PEI 25k were shifted ~10 mV below the zeta potential of as-received boron carbide powders mixed with PEI 25k (see previous Fig. 3) for all pHs tested. Although the zeta potential values were reduced, their electrostatic repulsion remained within an acceptable range to maintain suspension stability (> 40 mV).

Based on ICP chemical analysis, boria content of as-received, washed, and milled powders was: 0.39%, 0.39%, and 0.36% respectively. Although this technique did not measure any change in the boria content of washed powders, the treatment had an impact on the rheological performance of suspensions made with these powders. Similar studies conducted with ZrB_2 suggest improvements in suspensions stability after milling [43,44]. Authors propose similar effects may take place when washing and attrition milling B_4C Further research is advice in order to fully understand the surface chemical modification produce by such powder treatments in boron carbide.

Fig. 8 shows the changes in flow curves for suspensions using as-received, washed, and milled B_4C at a 50 vol% loading and 3.5 vol% PEI (1.83 g/cm^2). The suspension made up of as-received powders possessed the highest yield stress, and demonstrated higher shear stresses for all shear rates. The suspension made up of attrition milled powders had the lowest yield stress, with the lowest shear stresses for each of the shear rates investigated. The suspension comprised of washed B_4C powders demonstrated lower viscosity at 10 s^{-1} (~8.74 Pa*s) than the suspension using the as-received powder (~22.58 Pa*s).
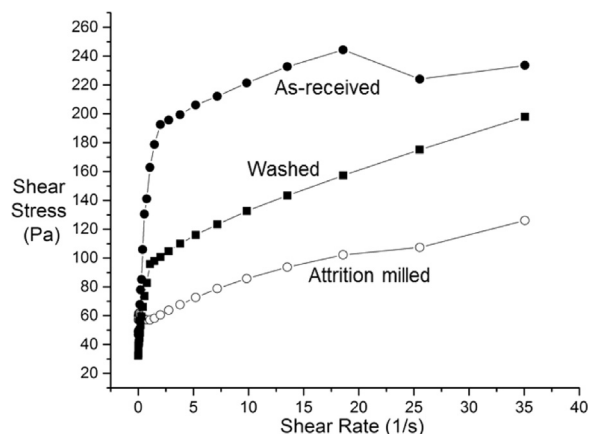

Fig. 8. Flow curves of suspension made with as-received, ethanol-washed, and attrition-milled B_4C powders at a 50 vol% loading and 3.5 vol% PEI 25 K.
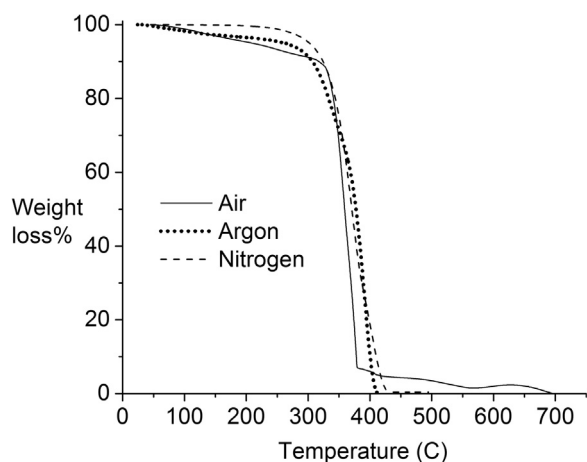
Fig. 9. Thermogravimetric analysis of PEI 25k in three different atmospheres. PEI 25k can be completely removed at 450 ℃ in an argon or nitrogen atmosphere.

The effect of powder treatment on flow behavior could be caused by several synergistic affects: removal of B_2O_3, minor changes in particle size and presence of WC (for milled powder). When boria comes in contact with water, hydrogen ions are released. These ions may protonate PEI amine groups and change charges and conformation of the polymer chains. Physical conformation of PEI chains may alter particle/particle and particle/polymer interactions, changing the gelled structure and rheological behaviors of the suspensions. Similarly, HCl added initially to balance the pH of the suspension (and improve electrostatic stabilization) affects the physical conformation of PEI chains as well.

3.5. Effect of gas composition on PEI burnout

Although some studies suggest the use dispersants and binder as a source of carbon as sintering aid [45,46], present study aims to produce green bodies where sintering aids can be analyzed as an isolated factor. Thus, to be useful as a dispersant, PEI needs to be cleanly removed during burn out leaving no residues. Thermogravimetric analysis of PEI 25k (Fig. 9) showed that it can be completely removed under argon and nitrogen atmospheres at 450 °C. For air atmosphere, higher temperatures, ~700 °C, are needed. Given that the oxidation of B_4C begins at ~600 °C, argon and nitrogen gases are recommended for PEI burn-out.

4. Conclusions

PEI has the highest zeta potential (74 mV) and the lowest viscosity when compared to other dispersants suggested by previous research. Production of B_4C high concentrations suspensions was achieved with a PEI molecular weight of 25k g/mol. Suspensions with 50 vol% B_4C and 3.5 vol% PEI 25k showed the lowest viscosity: 22.58 Pa*s (at shear rate of 10 s^{-1}). A PEI 25k content of 1.83 mg/m^2 is shown as the optimum amount to produce highly loaded boron carbide suspensions at concentrations up to 56 vol%. PEI can be completely removed, leaving no residue in nitrogen, argon, and air atmospheres. Ethanol washing and attrition milling reduced suspension viscosity and yield points. Additionally, surface chemistry may be modified by the removal of boria with water, ethanol, and/or hydrochloric acid. However, future studies are needed in order to completely understand the effect of powders treatment on rheological performance of highly loaded B_4C suspensions.

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