Dispersion and stability of colloidal boron carbide suspensions

Yazid Lakhdar[1], Christopher Tuck[1], Anna Terry[2], Ruth Goodridge[1]*

[1] *Centre for Additive Manufacturing, University of Nottingham, Nottingham, NG7 2GX, UK*

[2] *AWE, Aldermaston, Reading RG7 4PR, United Kingdom*

* Corresponding author, *ruth.goodridge@nottingham.ac.uk*

Summary of Novelty

The influence of diverse types of dispersing agents on the stability of aqueous boron carbide suspensions has been investigated. The best dispersants for aqueous B_4C suspensions could not be accurately determined from zeta potential and settling experiments. Rheological measurements on concentrated slurries enabled identification of the optimal concentration of each dispersant and showed that PEI cationic polyelectrolytes were most effective.

Abstract

The effects of several anionic, cationic and non-ionic polyelectrolyte dispersants on the stability and rheology of aqueous boron carbide (B_4C) suspensions were investigated using zeta potential measurements, settling experiments, and rheological studies. Zeta potential measurements and settling experiments were useful to narrow down the best pH range for each dispersant while using minimal amounts of material. However, these techniques did not effectively predict which dispersants would ultimately be the most effective. Slurry milling for 2 to 4 hours was essential to obtain stable homogeneous slurries (30-45 vol%), while more viscous pastes (50 vol%) would require longer milling times. The best concentration of each dispersant could be identified using rheological measurements. The viscosity of highly-loaded slurries containing the optimum concentration of each dispersant was compared, showing that cationic PEI 25k was the most effective dispersing agent. The importance of average particle size and particle size dispersion was also demonstrated.

***Keywords**:* Boron carbide; aqueous suspensions, dispersants; electrosteric stabilisation; rheology

1. Introduction

Boron carbide (B_4C) is an advanced non-oxide ceramic material characterised by its extreme hardness, high elastic modulus, low density (2.52 g/cm^3), high melting point (~2500°C), and excellent neutron absorption, making it the material of choice for a number of high-value industrial applications such as abrasive tools, blasting nozzles, radiation shielding panels, and lightweight ballistic armours [1]. Most technical applications of boron carbide require dense sintered monolithic bodies [2] but due to its low plasticity, low self-diffusion coefficient and strong B-C covalent bonding, the densification of B_4C monoliths is challenging [3]. Thus, the manufacture of dense B_4C components for commercial industrial applications is typically performed by uniaxial hot pressing [4]. However, in order to enable the fabrication of more complex shapes, fabrication techniques based on colloidal processing – e.g. tape casting, slip casting and additive manufacturing – followed by pressureless sintering are increasingly gaining in importance [5][6][7]. Pressureless sintering of B_4C requires the application of small amounts of sintering aids; without those, apparent densities of the resulting materials are not satisfactory. A wide range of sintering activators have been used in the literature, such as Al [8], ZrO_2 [9], Al_2O_3 [10], and carbon black [11]. No sintering aid was used in this study, as the focus was purely on the effect of dispersing agents on the stability of B_4C powders in aqueous dispersions, but the authors note that small additions of ceramic or carbon nanopowders could be effectively dispersed in water alongside B_4C powders and would help densification during pressureless sintering.

The formulation of a homogeneous and stable aqueous ceramic suspension with the desired rheological behaviour is essential to obtain a colloidal slurry that will result in high particle packing during fabrication and satisfactory green part properties. Indeed, any undesirable behaviour such as flocculation, lumping and fast settling, can introduce inhomogeneities in the slurry which induce processing flaws and eventually result in lower green density and poor sintering. The behaviour of any given colloidal ceramic system depends on a range of specific parameters, namely the type of ceramic, powder shape, size and purity, the presence of additives, suspension pH, and powder loading. It is well known that the dispersion of inorganic powders in water is mostly controlled by the electrical charge at the surface of the particles. Therefore, the stability of colloidal ceramic suspensions can be improved by pH modification and dispersants addition inducing electrostatic repulsion and/or steric hindrance between ceramic particles. Electrostatic repulsion between ceramic particles can be increased by adding small amounts of ionic dispersing agents and adjusting suspension pH within the pH region where the zeta potential is maximised, while steric hindrance is induced by adsorption of long-chain polyelectrolytes. Well dispersed and stable colloidal systems are often based on a combination of the two mechanisms, providing electrosteric stabilisation.

In this study, the influence of diverse types of dispersants on the stability of aqueous boron carbide suspensions has been investigated. Anionic, cationic, and non-ionic dispersing agents were studied and their effects were contrasted and compared. Zeta potential measurements, sedimentation experiments and rheological characterisation were performed to evaluate the stabilising power of each dispersion mechanism in aqueous boron carbide suspensions, and to compare the relative usefulness of each experiment in predicting the effects of dispersants and pH. Other important considerations such as milling time and particle size dispersion were also discussed.

2. Experimental

2.1. Materials

The boron carbide powders used in this study were B_4C powder grades HD07 and HD15 (H.C.Starck, Germany) with a specific surface area of 6-9 m^2/g and 15-21 m^2/g, respectively (manufacturer’s specifications). **Figure 1**~~**Figure 1**~~**.a** shows the particle size distribution of as-received B_4C powders measured by laser diffraction on a Mastersizer 3000 (Malvern, UK). It can be observed that powder HD07 had a wide size distribution with a mean particle size of 2.48 µm, while HD15 had a bimodal distribution, with the main particle population between 0.2 µm and 10 µm (peak at ~0.675 µm) and a much smaller population of particles sub 200 nm with a mode at ~130 nm. The measured characteristic sizes of this distribution compare well with manufacturer’s data. It is worth mentioning that studies have shown that a bimodal particle size distribution is usually considered beneficial as it can help achieve higher sintering densities and more uniform sintered microstructures [12][13].

Scanning electron microscopy was then performed (SEM TM3030, Hitachi, Japan) to obtain an image of the powder and correlate its size distribution and morphology (**Figure 1**~~**Figure 1**~~**.b**). Images were acquired at 15kV accelerating voltage in secondary electrons mode at a 10mm working distance. Samples were sputter coated with a thin layer of gold to avoid sample charging and improve resolution.

Several dispersants were investigated in order to compare their respective effectiveness in stabilising aqueous B_4C suspension: Darvan® 7N (R.T. Vanderbilt Holding Company, USA), Dispex® AA4040 (BASF, Germany), two branched polyethyleneimine, PEI 2k and PEI 25k, with a molecular weight MW of 2,500 and 25,000, respectively (Sigma-Aldrich, UK), Zephrym™ PD 4913, Zephrym™ PD 7000 and Zephrym™ 3300B (Croda, UK). **Table 1**~~**Table 1**~~ provides a summary of the main characteristics of all the dispersants used in this study. Aqueous colloidal slurries were prepared using deionised water as the solvent and the pH was adjusted using 0.1M hydrochloric acid (HCl) and sodium hydroxide (NaOH) solutions, both obtained from Sigma Aldrich.

2.2. Zeta potential measurement

The zeta (ζ) potential is a measure of the electric potential at the plane of shear or slipping plane, which is the outer layer of the interfacial double-layer surrounding dispersed colloidal particles in suspension [14]. The zeta potential is considered to be a good indicator of the degree of repulsion between adjacent colloidal particles of same electric charge in suspension: a high absolute zeta potential should indicate a good colloidal stability while colloids with a potential closer to $\zeta=0$ tend to flocculate and settle faster. The ζ potential can be determined by measuring the velocity of suspended particles in an electrical field. It was acquired on a Zetasizer Nano ZS (Malvern, UK) on 0.01 vol% suspensions of B_4C powder in DI water at various values of pH while the concentration of dispersant was kept at 2.5 ±0.5 wt% relative to the weight of the dry powder. To prepare suspensions, 15 g of B_4C powder was added to 400 ml of DI water pre-mixed with the required amount of dispersant, then sonicated in an ultrasonic bath for 5 min, and mechanically stirred overnight. The suspension was then divided into several vials and the pH was adjusted in the range 2-12 with 0.1 M HCl and 0.1 M NaOH, while the background electrolyte used to regulate the ionic strength was kept constant at 10^{-3} M KNO_3.

2.3. Settling experiment

Suspension stability can be assessed with a batch settling test, i.e. by recording the evolution over time of the sedimentation volume in a suspension of known concentration left to settle. The faster the suspension settles, the less stable it is. Sedimentation volume also provides useful information about suspension stability: a stable dispersed suspension where repulsion forces dominate results in a dense close packed sediment, while attractive inter-particle forces in an aggregated suspension lead to the formation of a loose sediment of larger volume [14].

To investigate the influence of pH and dispersing agents on the settling behaviour of aqueous boron carbide dispersions, 5 vol% B_4C powder suspensions with a dispersant's active ingredient concentration of 0.5 wt% relative to B_4C were prepared. Each suspension was then divided into five different vials for pH adjustment and mechanically stirred overnight. The suspensions were sonicated for 5 min and vigorously hand-shaken for 30 sec to ensure an optimum state of dispersion at the start of the experiment. They were then poured into 10mm glass test tubes, placed on a rack and left to settle at room temperature for 2 weeks with readings taken after 1, 2, 5, 6, and 8 days (**Figure 2**~~Figure 2~~). The results and observations drawn from this settling experiment were then compared and contrasted with the expected behaviour based on zeta potential measurements.

2.4. Rheological measurements

Rheological measurements were carried out on a rotational rheometer (Kinexus Pro, Malvern, UK) with a cone-and-plate geometry using a 40mm cone with a 4° angle. Viscosity was measured at 25°C by performing a table of shear rates from 0.01 to 1000 s^{-1}. Several 30 vol% (52 wt%) slurries using different dispersing agents were prepared and their rheological properties were investigated. First, the dispersant was added to DI water whose pH had already been adjusted towards the target pH of the final suspension. B_4C powder was then slowly added under mechanical stirring. All suspensions were then milled in a planetary ball mill (Fritsch Pulverisette 5 model IV, Fritsch, Germany) using 250ml zirconia milling bowls and 20 mm zirconia milling balls with a 3:1 ball-to-powder weight ratio in order to ensure a homogeneous state of dispersion by breaking down soft and hard powder agglomerates. A milling speed of 140 rpm was selected, corresponding to approximately 75% of the critical speed of milling as per the following equation:

$$S_C = \frac{42.3}{\sqrt{(D-d)}}$$

where S_C is the critical milling speed, D is the diameter of the milling bowl, and d is the diameter of the milling balls. Milling was performed in steps of 3 min with 6 min pause to allow for the any pressure build-up inside the milling bowl to fully dissipate after each step. Therefore, an effective milling of 1 hour was actually completed in 3 hours, and a 4-hour milling actually took 12 hours to complete.

In the literature, a milling time of 24 h is often reported without further information [15][16][17][18]. However, it can be important to minimise milling time so as to obtain the desired fluid properties and particle size while maximising throughput and minimising wear of the milling media, especially when working with materials as hard as boron carbide. Milling time was initially varied between 3min and 4 h in order to investigate its effect on dispersion homogenisation, particle reduction, and slurry viscosity.

3. Results and Discussion

3.1. Zeta potential

The ζ potential was measured as a function of pH, in the absence of dispersant and also in presence of each one of the dispersants listed in Table 1~~Table 1~~. The ζ potential of plain B_4C powder in water (Figure 3~~Figure 3~~) ranged between -31.4 ±2.2 mV at pH 2.34 and -54.0 ±2.6 mV at pH 11.49, and compared very well with most previous studies [19][20][21][22]. An absolute value of ζ potential of 30 mV is usually taken as a minimum |ζ| above which a colloidal suspension is considered stable. Therefore, these ζ potential values alone would suggest that pristine B_4C powder was already stable in water in the whole pH range. However, the use of a carefully selected dispersing agent is essential when formulating concentrated ceramic slurries or pastes for colloidal processing and manufacturing. Indeed, beyond the fact that dispersants may increase the $|\zeta|$ potential to yield a much stronger electrical double layer repulsion, they can also induce a liquefying effect to reduce the viscosity of ceramic slurries, decrease the surface tension of the solvent and, in the case of polyelectrolytes, provide short-range steric stabilisation [23][24][25]. Without these added benefits, highly concentrated ceramic slurries that are well dispersed and stable cannot be formulated.

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Dispersants had different effects on the ζ potential depending on their type and mode of action. First, both Zephrym PD7000 and Zephrym PD4913 had a very limited effect on the ζ potential, even leading mostly to a slight decrease towards less negative values (**Figure 3**~~**Figure 3**~~). Both dispersants are polymeric in nature, with Zephrym PD7000 being just slightly cationic according to its manufacturer, while Zephrym PD4913 is a non-ionic acrylic copolymer with OH^- functional groups. Due to their non-ionic nature, these two dispersants have negligible to no effect on the ionic strength of the solution, and thus have a negligible influence on the surface charge of B_4C particles. They therefore act primarily by steric hindrance, as long-chain polymers with polarised functional groups are adsorbed onto the particles surface. Zeta potential measurement may therefore not be the best technique to assess the true effect these type of dispersants have on suspension stability: sedimentation and/or viscosity measurements would provide further insight on the true effect of non-ionic dispersants.

The addition of anionic polyelectrolytes Darvan 7N, Zephrym 3300B, and Dispex AA4040 mostly resulted in a substantial increase of the $|\zeta|$ potential over a wide range of pH, particularly at pH 5 and above (**Figure 4**~~**Figure 4**~~). Darvan 7N is an alkali metal salt that releases Na^+ and $R\text{-}COO^-$ ions when dissolved in water, increasing the ionic strength of the solution. As the ionic concentration increases, anions $R\text{-}COO^-$ are adsorbed at the surface of B_4C particles, increasing the surface charge and thus the ζ potential. Dispex AA 4040 is an ammonium polyacrylate polymer of low molecular weight with efficient dispersing properties and liquefying effect. It behaves similarly to Darvan 7-N when dissolved in water by releasing NH_4^+ and $R\text{-}COO^-$ ions. Furthermore, particle dispersion by anionic polyelectrolytes is induced not only by electrostatic repulsion, but also by steric hindrance thanks to the adsorption of long-chain polymers onto the surface of inorganic particles.

As expected, the effect of cationic PEI dispersants on the ζ potential was the opposite of that of anionic dispersants, leading to a complete shift of the ζ potential curves towards positive values (**Figure 4**~~**Figure 4**~~). PEI 25k addition resulted in a higher ζ potential than PEI 2k due to its higher molecular weight. Besides, PEI 2k shifted the IEP of B_4C particles to the alkaline pH of 10.4 from an initially very acidic pH < 2 for plain B_4C. The influence of PEI 25k was even greater with an IEP at pH > 11.2 (out of experiment boundaries). However, none of these two cationic dispersants imparted a ζ potential strictly greater than 50 mV at any pH value. This ζ

potential measurement would thus suggest a somewhat lesser impact of these cationic dispersants on inter-particle repulsion than anionic dispersants.

Table 2~~Table 2~~ provides an overview of the influence of each dispersant on the ζ potential of dilute B_4C suspensions. The effect of dispersants on foaming behaviour was also recorded as it was considered relevant since it could affect subsequent slurry processing. It was for instance observed that Zephrym 3300B addition resulted in the formation of substantial and persistent foaming upon shaking. This formulation would therefore require the addition of a defoaming agent for milling and processing of slurries, and it was therefore discarded at this stage. Zephrym PD 4913 and Zephrym PD 7000 also resulted in microbubble formation upon shaking which would eventually disappear given enough time. On the other hand, neither Darvan and Dispex nor the cationic PEI dispersants resulted in any foaming, even upon vigorous shaking.

3.2. Batch settling

Batch settling experiments were conducted in order to obtain further insight into the different effects of dispersing agents on suspension stability.

Zephrym 3300B was not investigated as it induced a very significant amount of bubbling which was deemed detrimental to slurry processing, although this could be resolved by adding a defoaming agent. The effect of Zephrym PD 4913 on viscosity was not studied for the same reason. A recent study has shown that PEI 25k provides better slurry stabilisation performance and lower viscosity than PEI of lower or higher molecular weight [26], so PEI 25k was preferred over PEI 2k for viscosity measurements.

The effect of dispersants on settling behaviour was strongly dependent upon suspension pH, as evidenced in **Figure 5**~~Figure 7~~, and as expected after results from zeta potential measurements. All dispersants seemed to provide a stabilising effect at a given pH. Non-ionic dispersants (Zephrym PD 4913 and Zephrym PD 7000) provided a good stabilising effect over a wide range of pH, while anionic dispersants (Darvan 7N and Dispex AA4040) provided similar levels of suspension stabilisation performance at pH 7 and above. On the other hand, cationic PEI dispersants were more effective at pH ranging from 2 to 6, but highly ineffective at higher pH.

Figure 6~~Figure 8~~ shows the evolution of the sedimentation volume of 5 vol% B_4C suspensions over 8 days for each of the dispersants at their respective best pH. Anionic and non-ionic dispersants induced almost exactly the same settling behaviour, while cationic dispersants were slightly less effective.

Overall, results from settling experiment were mostly consistent with zeta potential measurements, although settling experiments showed a tendency to instability and higher settling at high pHthat was not observed with zeta potential measurements. Furthermore, it should be noted that non-ionic dispersants were effective at stabilising B_4C suspensions, despite the fact that they did not provide any electrostatic repulsion between ceramic particles and acted only by steric hindrance. This demonstrated the superiority of settling experiments over zeta potential measurements to obtain a more accurate picture of the effects of dispersants and pH on suspension stability, although it was expected that viscosity measurements would provide even further insight, especially when considering highly concentrated slurries and pastes.

3.3. Rheology

First, in order to determine the best milling time for the formulation of homogeneous slurries without affecting the powder size, 30 vol% boron carbide slurries were milled for between 3 min and 4 hours and the viscosity was measured after each milling step (**Figure 7**~~**Figure 9**~~). Non-milled slurries were extremely inhomogeneous and contained very large lumps of agglomerated powder; their viscosity was therefore not measured. Slurries exhibited the expected pseudoplastic (shear thinning) behaviour widely reported in the literature for aqueous ceramic slurries with similar solid loadings [27][19]. First, slurries without dispersants (**Figure 7**~~**Figure 9**~~**.a**) had a significantly higher viscosity than slurries containing 1.25 wt% Dispex AA4040 at all shear rates (**Figure 7**~~**Figure 9**~~**.b**), highlighting the well-known importance of adding a dispersant to formulations in order to lower the viscosity of ceramic slurries. Secondly, variations in viscosity as a function of milling time were not significant and no direct correlation between milling time and viscosity could be observed. However, particle size distribution measurements displayed in **Figure 8**~~**Figure 10**~~ revealed that slurries milled for only 3 min and 1 h contained a significant amount of particles > 10 µm, showing that these short milling times were not sufficient to break up soft particle agglomerates, while longer milling times affected the size distribution. Indeed, a 4 h milling provided removing complete removal of particles > 4 µm, while the 2 h milling provided nearly the same results as 4 h milling, although a small amount of particles with a diameter between 4 µm and 12 µm still remained. 2 h milling time could therefore be considered sufficient in case of time constraints or if issues with excessive wear of the milling media were critical, although the 4 h milling should be preferred since the additional removal of particles > 4 µm should be highly beneficial to the sinterability of boron carbide powders. The mass of the zirconia balls was recorded before and after milling to quantify the amount of ZrO_2 added into B_4C slurries. Because of wear of the milling media, it was found that B_4C slurries milled for 4 h only contained between 0.2 and 0.4 wt% ZrO_2. This slight ZrO_2 doping may actually be beneficial to the densification of B_4C during pressureless sintering [9].

Moreover, a thixotropy measurement carried out on slurries milled for 3 min, 2 h, and 4 h, respectively, displayed in **Figure 9**~~**Figure 11**~~, showed another beneficial effect of milling slurries for 4 h compared to milling for shorter times. Indeed, although none of the slurries displayed a thixotropic behaviour regardless of milling time, the initial viscosity measured at low shear rates was highly unstable with slurries milled for only 3 min and 2 h while it was much smoother and constant with the 4 h-milled slurry, likely because weak particle agglomerates still remained in the 3 min- and 2 h-milled slurries. Furthermore, the viscosity of the latter slurry fully recovered to its initial value while it did not for the other two slurries, showing that the 4 h milling time provided a much more stable colloidal system.

To identify the ideal concentration for each dispersant, 30 vol% slurries containing various amounts of dispersant were formulated and ball milled for 4 h. The effect of the amount of dispersant on slurry viscosity was evaluated and, as the amount of each dispersant in slurry is increased, the concentration at which the lowest viscosity is obtained is considered to be the ideal dispersant concentration. The increase in slurry viscosity with further dispersant addition from the ideal dispersant concentration is a well-known phenomenon, usually attributed (i) to the increasing ionic strength caused by excess dispersant in solution resulting in compression of the electrical double layer and a decrease in electrostatic repulsion between particles, and (ii) to the bridging effect from excess polymer chains causing particle flocculation [20][28][29]. The viscosity of 30 vol% slurries at various dispersant concentrations is displayed in **Figure 10**~~**Figure 12**~~, showing the concentration at which the viscosity is minimal with Dispex AA 4040 and Darvan 7N anionic dispersants, Zephrym PD 7000 non-ionic dispersant, and PEI 25k cationic dispersant.

The lowest viscosity obtained with Zephrym PD 7000 and PEI 25k were lower than that obtained with anionic dispersants, showing that the non-ionic and cationic dispersants should both be more effective at dispersing B_4C powder in water than their anionic counterparts. For each dispersant, respectively, the lowest viscosity was measured at:

- 649 mPa s with 0.8 wt% Dispex AA4040
- 347 mPa s with 1.2 wt% Darvan 7-N
- 130 mPa s with 1.0 wt% PEI 25k
- 88 mPa s with 5.7 wt% Zephrym PD 7000

Zephrym PD 7000 enabled to reach a lower viscosity than other dispersants but a significantly larger concentration of the additive was required to reduce the viscosity of slurries. Indeed, while the other dispersants were most effective under 1.5 wt%, Zephrym PD 7000 still did not affect the viscosity even at 2.5 wt% and a dramatic decrease in viscosity was observed after adding 4 wt% and more. Zephrym PD 7000 is therefore highly effective in dispersing B_4C in water but a concentration approximately 4 times higher than other dispersants was required. This can be attributed to the fact that Zephrym PD 7000 was a non-ionic dispersant and as such acted only by steric hindrance, whereas the other three dispersing agents were anionic (Dispex and Darvan) or cationic (PEI) polyelectrolytes that acted by electro-steric stabilisation. A higher concentration of the non-ionic dispersant was likely necessary to compensate for its lack of electrical double layer repulsion. The higher concentration of long polymeric chains at the surface of B_4C particles enabled to overcome short-range interparticle attraction forces through more steric interactions, without creating the adverse effects seen with high ionic polyelectrolyte concentrations that lead to excessive ionic strength and compression of the electrical double layer.

Figure 11~~Figure 13~~ shows the difference in appearance and homogeneity of three different slurries with a B_4C concentration of 50 vol% (~72 wt%) before and after they were ball milled for 4 h. 50 vol% suspensions made with the finer powder (grade HD15) yielded extremely viscous and inhomogeneous pastes before ball milling, making their formulation tedious. Highly viscous pastes could be produced after ball milling, although the paste containing Darvan 7N as dispersant remained highly inhomogeneous even after ball milling. Thus, while a ball milling time of 4 h was sufficient to yield highly dispersed and homogeneous 30 vol% slurry, longer milling time would likely be required for slurries with a higher solids loading. Since there was no such issue with slurries having a solids loading of 45 vol% and below, the 50 vol% pastes were diluted and ball milling was completed. Nevertheless, it was observed that PEI 25k was more effective than Darvan 7N in dispersing and stabilising these highly loaded 50 vol% pastes. The viscosity of a 50 vol% slurry made with the coarser B_4C powder (grade HD07) was significantly lower than with grade HD15, making the preparation and handling of this mix much easier. This shows the importance of characterising the morphology and size distribution of starting powders in order to know what to expect in terms of viscosity and processability when preparing concentrated slurries and pastes.

The viscosity of a number of concentrated slurries of various solids loadings – between 30 and 50 vol% – made with either HD15 or HD07 B_4C powder grade, and using various dispersing agents at their pre-determined best working pH and dispersant concentration, was measured and the corresponding graphs are provided in **Figure 12**~~Figure 14~~.

As expected after the information gained from **Figure 10**~~Figure 12~~, at a given ceramic powder concentration, a higher viscosity was obtained with Dispex AA4040 than with other dispersants, especially at high solids loading. In fact, Dispex effectively promoted the formation of a gel, which on the one hand tended to be more viscous than the colloidal sols produced using other dispersants, but on the other hand yielded slurries that would not dehydrate and that stayed stable for months. Slurries made using Darvan 7N and PEI 25k had relatively similar viscosities at all solids loading, although the latter yielded slightly more fluid slurries overall. This is further evidenced in **Figure 13**~~Figure 15~~, which shows that the viscosity of slurries increased exponentially with powder fraction as highlighted by the fitting exponential curves on the logarithmic chart. A possible explanation for the lower viscosities observed with PEI 25k is that polyelectrolytes that caused a polarity reversal compared to the charge sign of pristine ceramic powder are more effective dispersing agents. Indeed, based on zeta potential measurements, the main difference between PEI and pristine B_4C powder or anionic dispersants was in the sign of the ζ potential. Although, the absolute ζ potential values were very similar, this polarity reversal may have provided a stronger electrostatic repulsion than a same-sign increase of the ζ potential. However, colloidal stabilisation is the result of a number of complex chemical and physical phenomena that may be either competing or acting in parallel, such as the adsorption of ions from the solution, the dissociation of surface groups, the compression of the electrical double layer due to counterions, surface tension, and steric interactions due to adsorbed polymer chains [30]. However, the ζ potential technique is limited to measuring only long-range electrostatic repulsion and it does not take into account the contribution of short-range steric interactions, which are very significant in concentrated ceramic slurries where interparticle distances are much shorter. Therefore, the better performance of PEI 25k may also have been the result of the formation of a more effective steric barrier compared to other polyelectrolytes due to its relatively long polymeric chains and higher molecular weight (MW of 25,000 compared to MW < 15,000 for all the other polyelectrolytes).

As pointed out earlier, slurries made using grade HD07 were substantially less viscous than slurries made with powder HD15. This can be explained by the fact that the coarser powder (HD07) had a lower specific surface area than the finer powder (HD15), thus resulting on the one hand in less physical interaction between particles' surface, dispersant, and water, and on the other hand in less influence from van der Waals interparticle interactions. Furthermore, the larger distance between coarser particles suspended in water compared to the smaller interparticle distance for finer powders in suspensions of the same solid loading also lead to fewer interactions between particles, and thus to a lower viscosity. Thus, the viscosity of a 50 vol% HD07 slurry was approximately equivalent to the viscosity of a 35 vol% HD15 slurry (**Figure 13**~~Figure 15~~). Therefore, significantly higher solids loading should be attainable using powder HD07, which may have important repercussions during ceramic processing when trying to maximise ceramic content and minimise the volume fraction of solvent while keeping viscosity of slurries and pastes as low as possible.

4. Conclusions

The influence of several non-ionic, anionic, and cationic dispersing agents on the stability of aqueous colloidal boron carbide suspensions and slurries was investigated. The study combined zeta potential measurements, sedimentation experiments and rheological measurements to evaluate the effects of a range of polyelectrolyte dispersants on colloidal properties.

It was found that zeta potential measurements carried out on highly diluted suspensions can be used reliably to identify the best working range of pH for each dispersant, although it was not entirely successful in predicting the effects that dispersants would have on the stability of more concentrated slurries. Furthermore, zeta potential measurements did not provide any insight on the stabilising effect of non-ionic dispersants since this type of dispersants did not affect the ionic strength of the solution and, more importantly, did not induce any changes in the surface charge of the particles. Further insight was acquired through settling experiments with suspensions of low concentration to confirm the ideal working pH for each dispersant, respectively. This measurement suggested that a higher stabilising effect would be obtained with anionic and non-ionic dispersants than with cationic PEI polyelectrolytes. Viscosity measurements on concentrated slurries were then performed to either confirm or invalidate the conclusions drawn from ζ potential and batch settling experiments.

Ball milling of concentrated slurries was essential to reach target particle size distribution and produce well homogenised slurries. It was demonstrated, however, that milling slurries for 24 h – as is commonly reported in the literature – is not always necessary, depending on the starting viscosity and inhomogeneity of the slurry to be milled; thus, milling time was optimised in order to increase processing throughput and minimise wear of the milling equipment. Viscosity measurements enabled to identify the respective ideal dispersant concentration required to provide the best state of dispersion possible for each dispersant, which was 1.2 wt%, 0.8 wt%, 5.7 wt%, and 1.0 wt% for Darvan® 7-N, Dispex® AA4040, Zephrym™ PD 7000, and PEI (MW 25,000), respectively. The viscosity of highly-loaded slurries made using two different boron carbide powder grades was measured using the optimum dispersants concentration, showing that PEI 25k resulted in lower viscosities and therefore was more effective at dispersing B_4C powders in water at high solids loading. Finally, the importance of average particle size was also demonstrated, as stable well-dispersed highly concentrated slurries were much more easily prepared when the average particle size was 2.48 μm than when it was 691 nm.

Declarations of interest: none.

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Figures and Tables

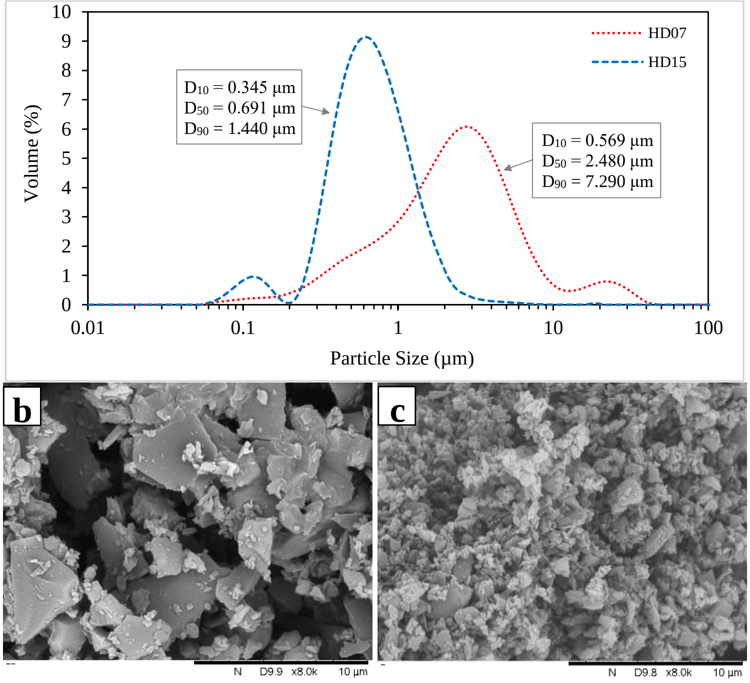

Figure 1: *Particle size distribution of as-received B_4C powders (a) and SEM images of B_4C powder grades HD07 (b) and HD15 (c).*

Table 1: *Dispersants used in this research project.*

Dispersant name	Active ingredient	% active ingredient	Type	Manufacturer
PEI 25k	Branched polyethyleneimine, M_w=25,000	100 %	Cationic	Sigma Aldrich
PEI 2k	Branched polyethyleneimine, M_w=2,000	50 %	Cationic	Sigma Aldrich
Zephrym™ PD 7000	Polyoxyalkyleneamine derivative	100 %	Non-ionic	Croda
Zephrym™ PD 4913	Acrylic copolymer	33 %	Non-ionic	Croda
Zephrym™ 3300B	Benzene sulfonic acid, secondary alkyl derivative with 2-propanamine	100 %	Anionic	Croda
Dispex® AA4040	Polyacrylic acid, ammonium salt (PAA-NH_4)	40 %	Anionic	BASF
Darvan® 7-N	Poly(methacrylic acid, sodium salt) (PMAA-Na)	25 %	Anionic	R.T. Vanderbilt

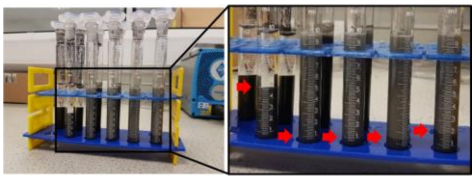

Figure 2: *Setup of the batch settling experiment showing the different levels of sedimentation after 120h (red arrow) depending on dispersant used and suspension pH.*

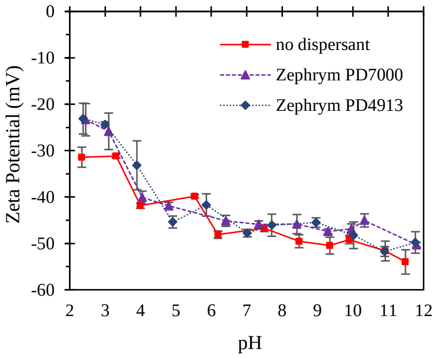

Figure 3: *Effect of non-ionic polyelectrolytes on the ζ potential of B_4C powder grade HD15 as a function of pH.*

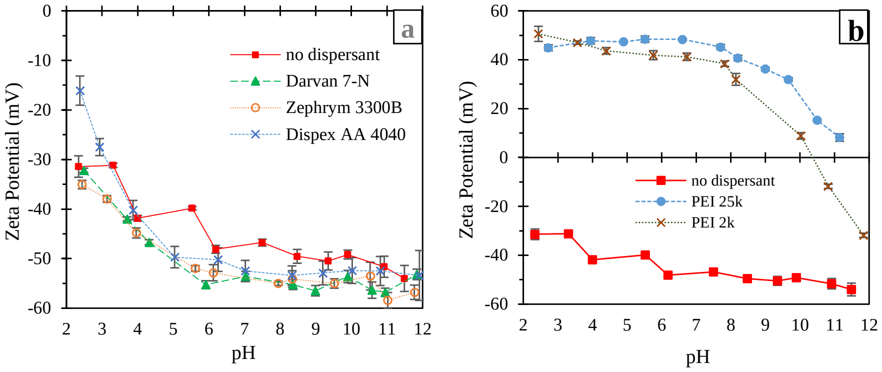

Figure 4: *Effect of anionic polyelectrolytes (a) and cationic PEIs (b) on the ζ potential of B_4C powder grade HD15 as a function of pH.*

Table 2: *Effect of dispersants on the ζ potential, stabilisation range and foaming of dilute B_4C suspensions.*

Dispersant	**Type**	**ζ potential max (mV)**	**pH range for stabilisation***	**Foaming upon shaking**
No dispersant	N/A	-54.0 ±2.6	11 - 12	None
Darvan 7N	Anionic	-56.8 ±0.8	5 - 12	None
PEI 25k	Cationic	+48.3 ±0.5	None	None
PEI 2k	Cationic	+50.6 ±3.1	None	None
Zephrym PD 7000	Slightly cationic	-50.3 ±0.5	None	Medium
Zephrym PD 4913	Non-ionic	-51.7 ±1.1	11	Slight
Zephrym 3300-B	Anionic	-58.4 ±1.6	5 - 12	Substantial
Dispex AA4040	Anionic	-53.4 ±1.9	6 - 12	None

* A ζ potential > ±50 mV was required for a dispersion to be considered stabilised.

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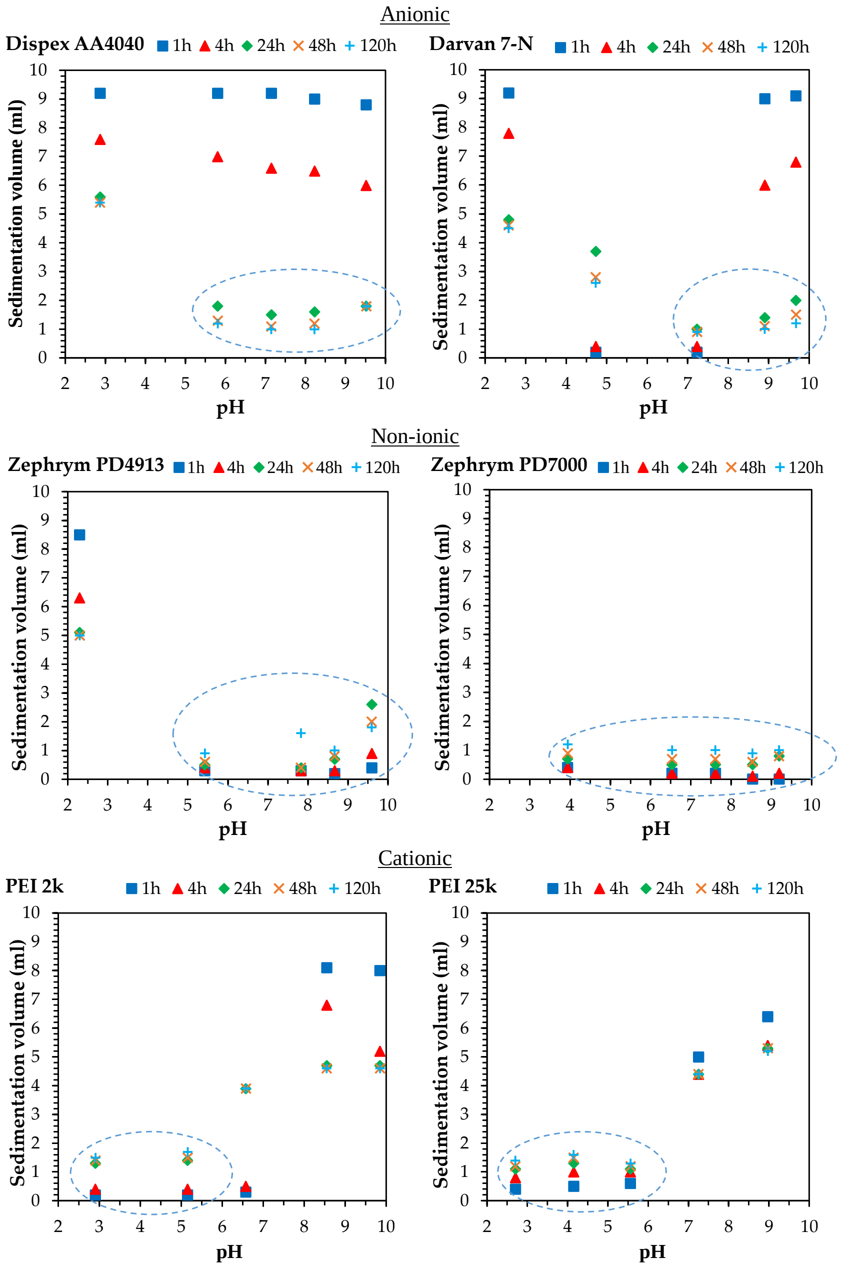

***Figure 5~~7~~:** Evolution of sedimentation volume over 120h as a function of pH for several dispersing agents. The dotted ellipses highlight the pH range were each dispersant was most effective.*

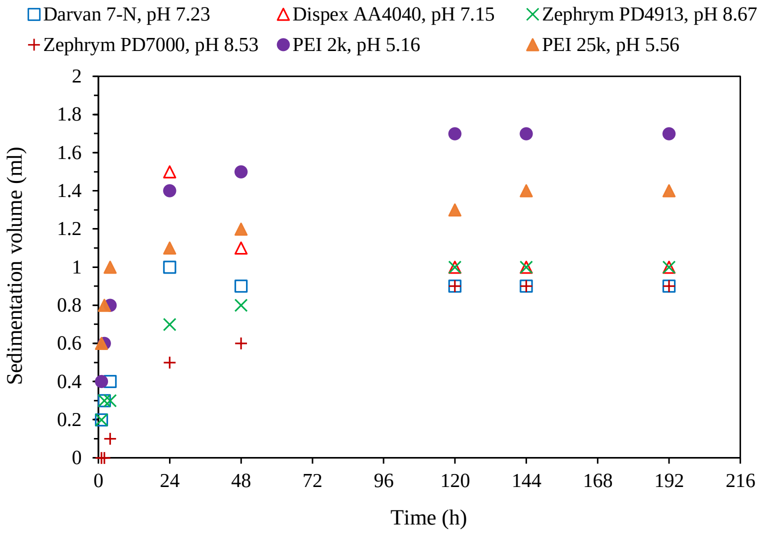

***Figure* *6~~8~~*:** *Evolution of the sedimentation volume of 5 vol% B_4C suspensions over 8 days for each of the dispersants at best pH.*

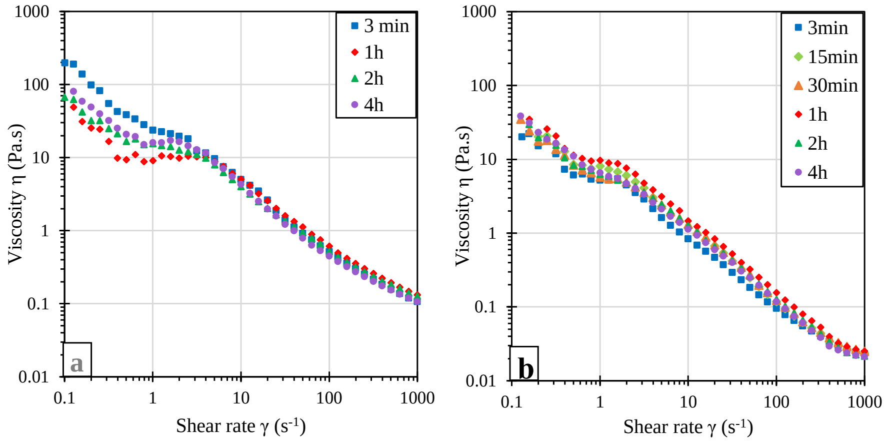

***Figure* *7~~9~~*:** *Effect of milling time on the viscosity of a 30 vol% slurry without dispersant (a) and with 1.25 wt% Dispex AA4040 dispersing agent (b).*

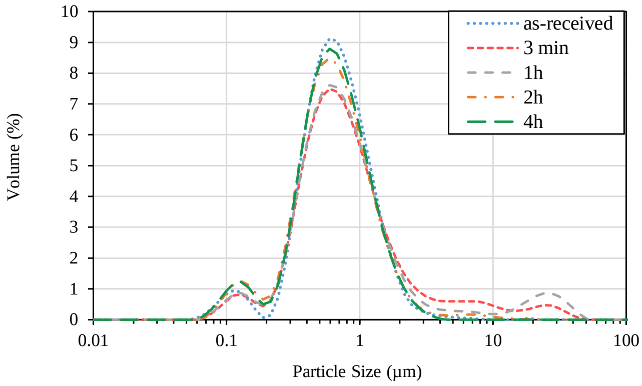

Figure* 8~~10~~*: Particle size distribution of as-received HD15 powder compared with powder collected from slurries milled for different times.

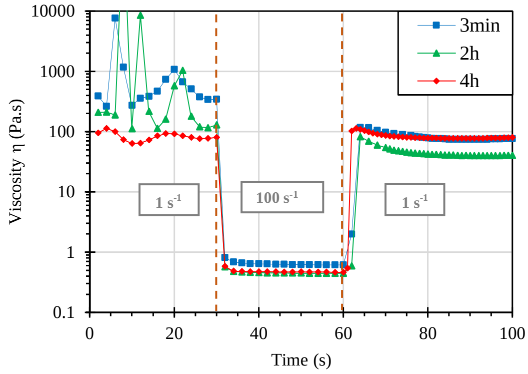

Figure* 9~~11~~*: Results of thixotropy tests (1 s^{-1} – 100 s^{-1} – 1 s^{-1}) of slurries milled for 3 min, 2 h, and 4 h.

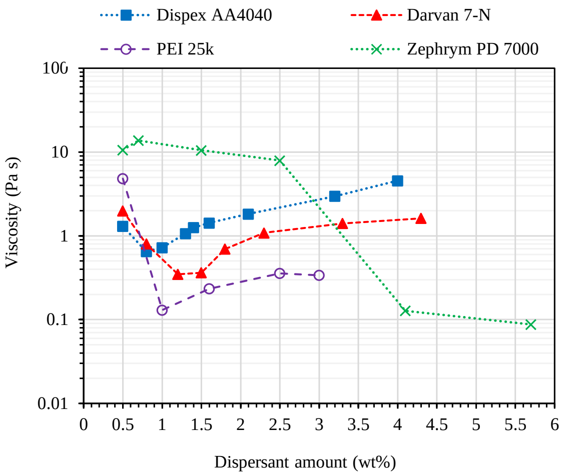

***Figure** 10~~12~~: Viscosity of 30 vol% slurries at 10 s^{-1} shear rate. Determination of the best concentration of each dispersant at their respective ideal working pH*

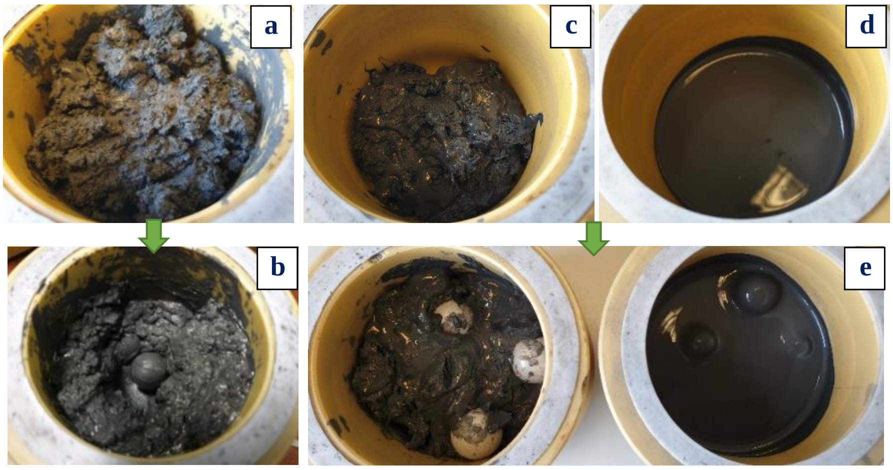

***Figure** 11~~13~~: 50 vol% aqueous B_4C slurry made with grade HD15 powder and Darvan 7N anionic dispersant (a) before and (b) after 4 h ball milling. 50 vol% aqueous B_4C slurries with PEI 25k cationic dispersant and made using powder grade (c) HD15 and (d) HD07 before ball milling and (e) the same slurries after 4 h ball milling.*

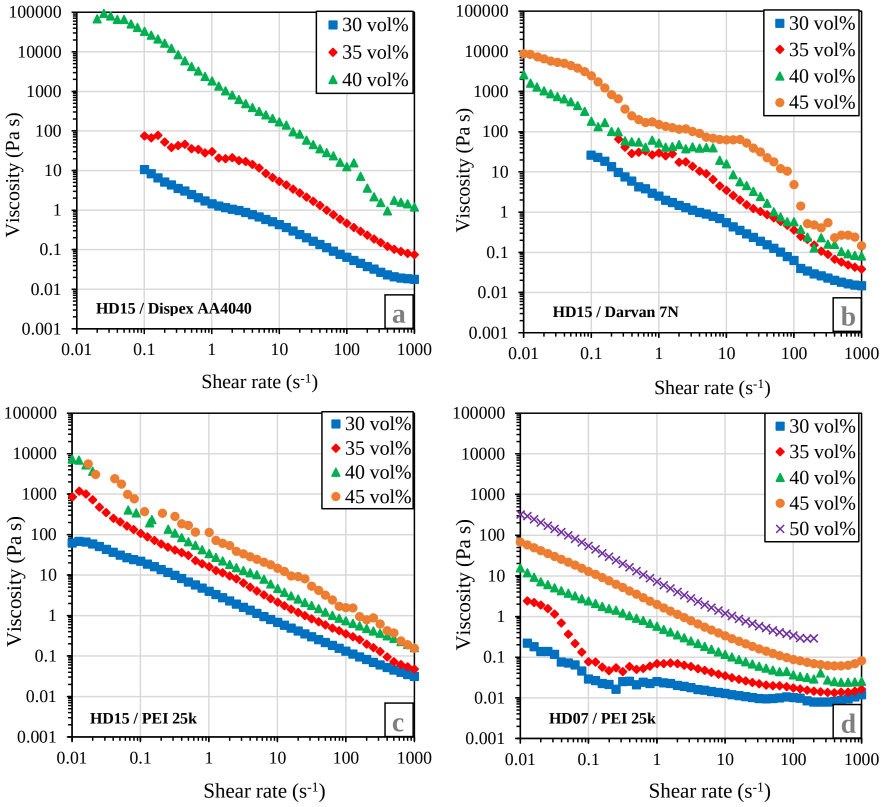

Figure* 12~~14~~*: Viscosity of aqueous B_4C slurries of various solids loading made with (a) grade HD15 and 0.8 wt% Dispex AA4040, (b) grade HD15 and 1.2 wt% of Darvan 7N, and (c) grade HD15 and 1.0 wt% of PEI 25k, (d) grade HD07 and 0.6 wt% of PEI 25k.

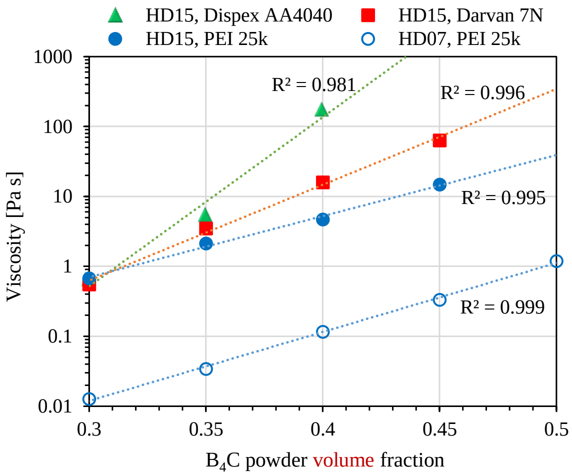

***Figure** 13~~15~~**:** The viscosity of concentrated aqueous colloidal B_4C slurries at 10 s^{-1}increased exponentially with their solids loading.*