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Regular Article

Preparation of highly dispersed and concentrated aqueous suspensions of nanodiamonds using novel diblock dispersants

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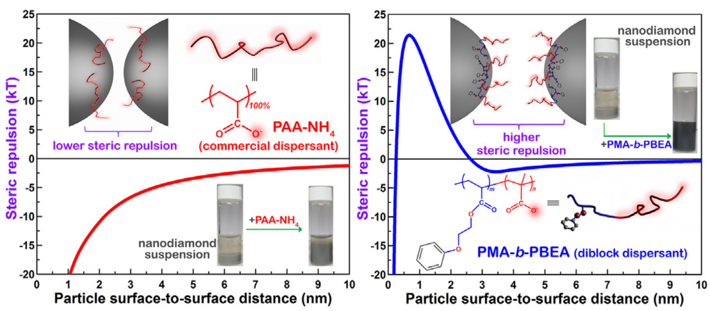
GRAPHICAL ABSTRACT



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ABSTRACT

Hypothesis: Finding an efficient dispersant for obtaining a good dispersion of 5-nm detonation nanodiamond (DND) is always a challenge. Two newly designed diblock copolymers, both poly(ammonium methacrylate)-*block*-poly(2-phenoxyethyl acrylate) (PMA-*b*-PBEA) but with different molar ratios of PMA to PBEA, were proposed to be efficient dispersants in stabilizing the concentrated aqueous suspensions of DND.

Experiments: The dispersion efficiency of dispersants for DND in aqueous suspensions was studied by the measurements of particle size, sedimentation property, and rheological behavior. The interactions between the added dispersants and DND were identified by the zeta potential and adsorption analyses. Calculations based on Derjaguin-Landau-Verwey-Overbeek (DLVO) theory were conducted for clarifying the dominant parameters relating to the dispersion efficiency of dispersants.

Findings: Compared with the commercially popular dispersant ammonium polyacrylate, these two diblock dispersants exhibited superior efficiency in the stabilization of DND suspensions. Using the diblock copolymers as dispersants, good dispersion stability in a DND suspension with an extremely high solid content of 30 wt% was achieved. According to experimental analyses and based on DLVO calculations, a low number of accompanied counter-ions, high adsorption capability, and thick PMA-*b*-PBEA adsorption layer are the main reasons for the extremely high dispersion efficiency of the two new dispersants.

1. Introduction

Since the first production of nanodiamond by the detonation of explosives in the 1960s [1], the detonation nanodiamond (DND)

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has received much attention. A lot of attractive potential uses for DNDs have been proposed [2], these include traditional applications in abrasive suspensions for high-precision polishing [3], nanofluids for thermal conduction [4,5], nanodiamond-polymer composites for functional coatings [6,7], novel applications in drug delivery [8,9], biosensing electrodes [10], and single photon sources [11]. DND powder has extremely small particles with the primary size around 5 nm; however, it tends to form submicron- and micro-sized agglomerates [12,13]. In addition, DND typically has a surface coverage of sp^3- and sp^2-based carbon impurities, including amorphous and graphitic carbon [14]. The carbon-carbon and van der Waals interactions between the graphitic layers also cause the severe problem of powder agglomeration in DND. Therefore, the first task in the application of DND should be powder de-agglomeration.

To obtain good DND dispersion in a liquid medium, the most widely-used methods to date focus on chemical functionalization [6,15–17] and chemical grafting with alkyl chains *via* esterification or silanization [18,19]. These chemical reactions usually take time and the procedures are complicated. In addition to the above chemistry-based methods, a physical method whereby the suspension is mixed with an appropriate dispersant followed by simple ultrasonication has also been proposed [20,21]; this process is much easier and is the recommended one. Nevertheless, the key element for the success of this process is the dispersant, which needs to be very efficient in adsorbing and stabilizing the powder in the suspension. Regarding the liquid medium in the dispersion process, water-based systems have attracted considerable interest due to the concerns about the environment and cost, and a large number of water-based dispersants have been proposed.

Among various types of water-based dispersant, commercially available polyelectrolytes are the most popular due to their good efficiency for a wide range of powder types. For example, polyacrylate salt is a well-known polyelectrolyte-based dispersant, which is commonly used and is highly efficient for a lot of mineral powders [22–24]. In this investigation, two newly designed diblock copolymers are produced and analyzed for their efficiency in the dispersion of DND in aqueous suspension, and the results compared with that of the commercial polyacrylate salt. To determine the relative efficiency of the dispersants, experiments including sedimentation, particle size analysis, and rheology, are performed on various DND suspensions. To clarify the dominant dispersion mechanism of the dispersants, we investigate the electroacoustic zeta potential, the adsorption properties, and the theoretical potential energy for the stabilization of DND based on Derjaquin-Landau-Verwey-Overbeek (DLVO) calculations.

2. Materials and methods

2.1. Raw materials

A commercial DND powder purchased from the Link Korea Corporation (97%, Korea), with an average particle size of 4–5 nm and surface area of 200 $m^2\ g^{-1}$, was used. The powder appeared black to dark-gray in color because of its surface was covered by amorphous and fullerenic carbon [14]. Three dispersants, including the commercially available ammonium polyacrylate ($PAA\text{-}NH_4$) (Darvan-821A, Vanderbilt Minerals, LLC, Norwalk, CT) and two newly synthesized diblock copolymers of ammonium poly(methacrylate)-*block*-poly(2-phenoxyethyl acrylate) (PMA-*b*-PBEA) (ITRI, Taiwan) were used (Fig. S1, Supporting Information) [25,26]. $PAA\text{-}NH_4$ has an average molecular weight of 3500 $g\ mol^{-1}$. The two diblock copolymers have molar ratios of PMA to PBEA of 2:1 and 1:1, denoted as DBDE01 and DBDP04, with average molecular weights of 3000 and 4000 $g\ mol^{-1}$, respectively. Deionized water was used as the dispersion medium.

2.2. Characterizations

The morphology of the as-received DND powder was characterized using a transmission electron microscope (TEM; JEM-2100F, Jeol, Japan) and a field-emission scanning electron microscope (FE-SEM; S-470, Hitachi, Tokyo, Japan). The electroacoustic method (ZetaProbe, Colloidal Dynamics Inc., North Attleborough, MA, USA) was used to characterize the surface chemistry of the DND in water in the absence and presence of different dispersants. For the zeta potential measurements, aqueous suspensions of 0.5 wt% DND with 20 wt% addition of different dispersants were prepared. It is noted that all the contents of the added dispersants were calculated based on the weight of DND in this investigation. The DND suspensions were de-agglomerated with a high-energy ultrasonic horn (Sonifier S-450D, Branson Ultrasonics Co., Ltd, USA). For the particle size analyses and sedimentation experiments, suspensions with 1 wt% solid content and 20 wt% addition of different dispersants were prepared, then de-agglomerated by bead-milling at 1000 rpm using 30 μm-zirconia beads on wet-grinding equipment (JBM-B035, Just Nanotech Co., Ltd, Taiwan) for different time periods. Note that the bead milling is equipped with an inner hydro-cooling system to have a controlled temperature. The particle size was measured using the light scattering method (LB-550, Horiba Ltd., Japan). The viscosity was measured using a concentric cylinder rheometer (AR1000, TA Instruments Ltd., UK) equipped with a cone-plate geometry fixture of 20-mm diameter and with a cone angle of 1°. For the adsorption experiment, 2 wt% suspensions with various concentrations of different dispersants were prepared by two-dimensional (2-D) ball milling (MUBM236, Yeong-Shin, Taiwan) at 150 rpm, using 5-mm zirconia media stabilized with yttrium oxide, for 24 h at room temperature. Then, the powder was separated from the supernatant by centrifugation and the amount of non-adsorbed dispersant in the supernatant determined using a potentiometric titration method [22]. The adsorbed amount of dispersant was then calculated based on mass balance. For the rheological measurements, 30 wt% suspensions with 20 wt % different dispersants added were de-agglomerated using a high-speed 3-D mixer (Power Mixer-CM S200, Chia Mey, Taiwan) at 1000 rpm for 1 h, followed by 2-D ball milling at 150 rpm for an additional 12 h.

3. Results and discussion

3.1. Chemistry of dispersants and agglomeration of DND

To obtain good dispersion stability of DND in aqueous suspension, three dispersants, a commercially available $PAA\text{-}NH_4$ and two synthesized diblock copolymers, DBDE01 and DBDP04, were evaluated, and their dispersion efficiencies were compared. Fig. 1 shows the chemical structures of the three dispersants. As shown in Fig. 1(a), each polymer chain in $PAA\text{-}NH_4$ contains an average of 40 monomer units of ammonium acrylate (AA) that can dissociate in water to carry a negative charge. Each polymer chain in DBDE01, Fig. 1(b), contains an average of 15 and 8 monomer units of ammonium methacrylate (MA) and 2-phenoxyethyl acrylate (BEA), respectively. The monomer unit of MA is like AA unit of $PAA\text{-}NH_4$ and can dissociate in water and carry a negative charge, while BEA is non-dissociable. As shown in Fig. 1(c), the polymer chains of DBDP04 contain equal amounts of 13 monomer units of MA and BEA.

As shown by the SEM image in Fig. 2(a), the as-received DND powder is heavily agglomerated and shows particles of a secondary