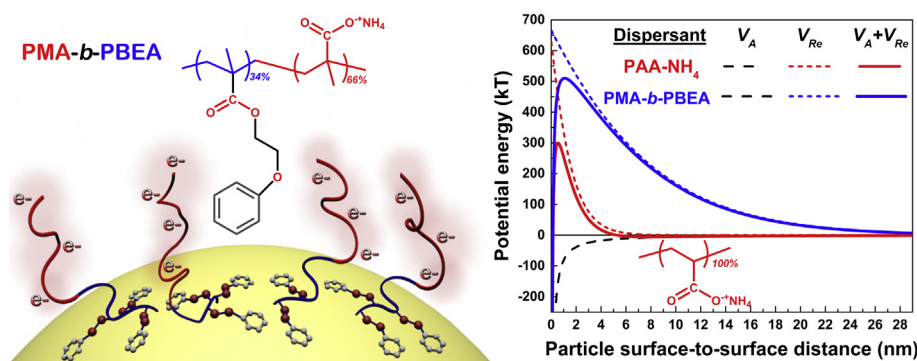


Regular Article

Newly designed diblock dispersant for powder stabilization in water-based suspensions

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GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:

Received 10 June 2017

Revised 10 July 2017

Accepted 15 July 2017

Available online 17 July 2017

Keywords:

Titania
Dispersion
Polyacrylate
Dispersant
Adsorption
DLVO theory

ABSTRACT

A newly designed dispersant for water-based suspensions, ammonium poly(methacrylate)-*block*-poly(2-phenoxyethyl acrylate) (PMA-*b*-PBEA), is proposed in this study. According to the results of rheological analysis, the dispersion efficiency of this new dispersant is superior to that of the commercially available ammonium polyacrylate (PAA-NH₄). The diblock structure of PMA-*b*-PBEA, which simultaneously contains a low-polar anchoring head group and a water-dissociable stabilizing moiety, is the main cause for its extremely high efficiency for powder dispersion. The unique structure not only results in effective adsorption approximately double that of PAA-NH₄, but also produces a low number of counter-ions that compress the electrical double layer and ruin powder stabilization. Based on Derjaguin-Landau-Verwey-Overbeek calculations, the large adsorbance of PMA-*b*-PBEA gives the powder, titania (TiO₂) in this study, a high steric stabilization energy. In addition, PMA-*b*-PBEA provides TiO₂ with a remarkably high electrostatic energy because it generates fewer counter-ions. This energy provides excellent dispersity of powder in the suspensions with a high solid content of 60 wt% without showing any rheological hysteresis.

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1. Introduction

To obtain ceramic products with high mechanical strength and the required physicochemistry, ceramic powders in green bodies

should be densely packed and able to be ultimately densified after sintering. Thus, the powder has to be de-agglomerated and well dispersed during initial slurry preparation, which consists of mixing the ceramic powder in a solvent with a variety of organic and inorganic additives. The solvent is used to achieve homogeneous mixing of all the material components. Depending on the type of solvent used, the as-prepared slurries can be grouped into two cat-

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egories: organic-based/or non-aqueous-based slurries and water-based/or aqueous-based slurries [1–3]. For decades, the aqueous process using water as solvent has been the ideal procedure for slurry preparation due to concerns about environmental consistency and reasonable costs. Nevertheless, the aqueous process has the tendency to cause ceramic powders to form severe agglomerates, while powder agglomeration is less severe in non-aqueous-based slurries. This is because water is a polar protic solvent that exhibits significant hydrogen bonding, capillary forces, and high surface tension, all of which cause water to form strong liquid bridge when agglomerating powders [3–7].

The aqueous process has attracted considerable attention and interest, and many research groups have been involved in studies on dispersants for water-based slurries. Up to now, a large number of water-based dispersants have been proposed [8–26]. Among the various types of dispersant, the polyelectrolyte, which is polymer-based with a water-dissociable electrolyte group, is the most popular because of its high dispersion efficiency. The electrolyte group causes the polymeric dispersant to be charged in aqueous suspension; the dispersant-adsorbed powder is also charged to obtain electrostatic stabilization energy. Regarding the different electrical charges, polyelectrolytes include two major types: polyanions and polycations. The polyanions stay neutral in an acidic environment and begin to dissociate, carrying a negative charge, when the pH is increased. Conversely, polycations stay neutral in alkaline conditions and begin to dissociate, carrying a positive charge, when the pH decreases. For instance, polyethyleneimine is a typical polycation that dissociates to carry positive charge at $\text{pH} < 11$ [23–26]. The most popular polyanion is the polyacrylate salt that dissociates to be negatively charged at $\text{pH} > 2$ [12–22]. Therefore, polyanions are generally used for powders dispersed in alkaline suspensions and polycations are more appropriate for powders in acidic suspensions. However, it is interesting to find that polyacrylate salt is a very powerful dispersant and is frequently found to be suitable for acidic suspensions [12]. It is suggested that interaction between the carboxyl groups of the polyanions and the metal elements of the ceramic powders is the primary reason. A good interaction is helpful for dispersants to achieve effective adsorption onto the powders, which leads to good dispersion stability.

In this investigation, a polyacrylate-derived diblock copolymer poly(methacrylate)-*block*-poly(2-phenoxyethyl acrylate) (PMA-*b*-PBEA), is proposed as an efficient water-based dispersant, even more than commercial polyacrylate salts. This newly-designed dispersant comprises two structures: polyelectrolytic PMA and non-polyelectrolytic PBEA. PBEA is a low-polar undissociable segment, designed to act as an anchoring head for adsorption onto powder surfaces. The polyelectrolytic PMA is dissociable in water and can extend itself into the dispersion medium to act as a stabilizing moiety. As PMA-*b*-PBEA is not a complete polyelectrolyte, only partial chains are charged and it may experience less lateral repulsion from its adsorbing neighbors. This results in higher effective adsorption than with conventional polyacrylate salts. Hence, PMA-*b*-PBEA is expected to be more efficient than polyacrylate salts for powder dispersion. To verify the dispersion efficiency of this new dispersant, the widely-used industrial oxide, titania (TiO_2), was adopted as the study model. TiO_2 is known as a relatively stable powder, which presents no significant dissolution in aqueous suspensions ranging from acid to alkaline. That is, using TiO_2 as the study model has the advantage of preventing unexpected interference from powder dissolution problems. The efficiency of a commercial polyacrylate salt, ammonium polyacrylate (PAA- NH_4), in the dispersion stability of aqueous TiO_2 suspensions was also compared in this study.

2. Experimental section

A commercial rutile- TiO_2 powder (CR-80; Ishihara Sangyo Kaisha, Ltd., Japan) with a median size of 250 nm and surface area of $10 \text{ m}^2/\text{g}$ was used, which the powder information was provided by the manufacturer. Two dispersants, the commercially available PAA- NH_4 (Darvan-821A, Vanderbilt Minerals, LLC, Norwalk, CT) and a newly-designed ammonium salt of poly(methacrylate)-*block*-poly(2-phenoxyethyl acrylate) (PMA-*b*-PBEA) (DBDE01, ITRI, Taiwan) with average molecular weights of 3500 g/mol and 3000 g/mol, respectively, were investigated. The new dispersant, PMA-*b*-PBEA, was synthesized using atom transfer radical polymerization, which brief procedure was shown in [scheme 1](#) (also see [Supporting Information](#)). The obtained PMA-*b*-PBEA is an aqueous solution with a solid content of 47 wt%. Deionized water was used as the dispersion medium.

The chemical structures of the as-synthesized polymers were characterized using NMR spectroscopy (NUITY INOVA-500, Varian, USA) ([Fig. S1, Supporting Information](#)). The microstructure of the powder was characterized using field-emission scanning electron microscopy (FE-SEM; S-470, Hitachi, Tokyo, Japan) ([Fig. S2, Supporting Information](#)), and the surface chemistry was characterized using the electroacoustic method (ZetaProbe, Colloidal Dynamics Inc., North Attleborough, MA, USA). For the zeta potential measurements, aqueous suspensions were prepared with a solid loading of 0.5 wt% by adding various concentrations of dispersant, based on the weight of the powder. The suspensions were deagglomerated using a high-speed three-dimensional mixer (Power Mixer-CM S200, Chia Mey, Taiwan) at 1000 rpm for 1 h. Notably, the equilibrium pH (pH_{eq}) values of the powder suspensions were from 6.6 to 8.1 and 6.6 to 8.3 with the additions of [PAA- NH_4] and [PMA-*b*-PBEA] from 0 to 15 wt%, respectively. In the rheological analysis, shear stress and viscosity were obtained using a concentric cylinder rheometer (AR1000, TA Instruments Ltd., UK). Without the addition of any dispersant, the pH_{eq} values of 10–60 wt% powder suspensions were within 6.6–6.5. With 5 wt% additions of PAA- NH_4 and PMA-*b*-PBEA, respectively, the pH_{eq} values were both 7.6 and 7.7 for 40 and 60 wt% powder suspensions. In the relative viscosity and adsorption measurements, 10 wt% and 40 wt% of aqueous suspensions, respectively, were prepared with the addition of various concentrations of different dispersants. The corresponding pH_{eq} values for both 10 and 40 wt% suspensions are within 6.6–7.7 and 6.6–7.9 when added with 0–15 wt% of PAA- NH_4 and PMA-*b*-PBEA, respectively. The suspensions were mixed and then centrifuged at 5500 rpm to separate the powder from the supernatant. The powder was oven dried and the adsorbed amount (A_s) of dispersant was determined by weight loss obtained from thermogravimetric analysis (Q50, TA instruments Ltd., Crawley, UK). The equilibrium concentration (C_e) of the dispersant, which was also the concentration of the dispersant that was left in the suspension, was obtained by subtracting the initially added amount of the dispersant by the measured A_s . The C_e was calculated based on the volume of the suspension ([Tables S1 and S2, Supporting Information](#)). The chemical interaction between the dispersants and the TiO_2 powder was characterized using Fourier transform infrared (FT-IR) spectroscopy (DA 8.3, Bomen, Canada); FTIR spectra were obtained in the transmission mode on pressed TiO_2 pellets mixed with KBr in a volume ratio of 1:50.

3. Results and discussion

[Fig. 1](#) shows the rheology of the aqueous TiO_2 suspension at various solid loadings. With an increase in solid powder content in the suspension, the viscosity increased and shear-thinning behavior

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