Effects of polyethyleneimine–phosphonate–carboxylic copolymers on the dispersion of boehmite particles

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HIGHLIGHTS

- Novel polyethyleneimine–phosphonate–carboxylic copolymers were synthesised.
- Their dispersant ability was studied on boehmite colloidal particles.
- Their adsorption on boehmite is mainly controlled by electrostatic attraction.
- Electric and van der Waals (or steric) interactions exist between particles.
- Stability of the particles suspension increases at neutral and alkaline pH values.

GRAPHICAL ABSTRACT
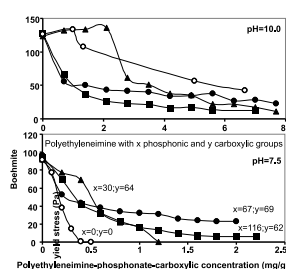
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ABSTRACT

Novel polyethyleneimine–phosphonate–carboxylic copolymers with an increasing number of carboxylate and phosphonate groups have been synthesised. The presence of positively charged amino groups and negatively charged carboxylate and phosphonate groups influenced the adsorption of these copolymers on boehmite colloidal particles and their dispersant ability in solution at pH values below and above the isoelectric point (iep) of boehmite. It was found that the addition of negatively charged carboxylate groups to the polyethyleneimine polymer backbone had a positive effect on polymer adsorption density and affinity for the boehmite surface while the phosphonate groups had a negative effect. The adsorption of these copolymers on the boehmite surface is largely controlled by electrostatic attractions with the positively and negatively charged aluminium sites below and above the iep of boehmite, respectively. The changes in yield stress of the boehmite particle suspension following copolymer adsorption are largely explained by electrical double layer interaction between the boehmite particles, but also by van der Waals or steric interactions between the polymer-coated particles.

1. Introduction

In the titania pigment industry titania colloidal particles are coated with thin layers of solution-deposited silicate and aluminate to improve pigment gloss and degradation resistance. The aluminate coating treatment also provides dispersion compatibility in the application medium [1,2]. Being a colloidal process, the system is very sensitive to solution conditions and any subsequent changes will have major effects on product characteristics and ultimately performance [1]. The conditions encountered during processing when inorganic oxide coatings are applied, involve high temperatures with pH values ranging from 7 and as high as 11. When dispersion is inadequately controlled during the application of the inorganic oxide coatings, pigment

particles aggregate, which is detrimental to gloss, hiding power and colour.

Most of the effective dispersants identified in the literature are low-molecular-weight (e.g., $<5 \times 10^4$ Da), water-soluble polymers [3–5] which contain negative or positively charged groups such as carboxylic acids and amines, generally most effective as dispersants at pH values higher than 5 and lower than 10, respectively (the pK_a of these groups). Farrokhpay and co-workers [6,7] found that polyacrylic acid or carboxylate/hydroxyl-modified polyacrylamide provided similar good titania pigment dispersion behaviour in dry paint films and in alkaline aqueous pigment dispersions. Polyphosphates are commonly used industrially to provide electrosteric stabilisation of the pigment particles [8]; however, they degrade at high temperatures and under alkaline solution conditions [9] which are present during the pigment production process. Phosphonates have been reported to stabilise oxide and offer greater thermal and pH stability than phosphates, due to the presence of the P–C bond [10]. Acrylic acid–phosphonate copolymers have also been reported to provide improved dispersion properties particularly when compared to polyacrylic acid homopolymer [11]. Polyethyleneimine is a cationic polymer which has been found to adsorb strongly on the silica surface, a surface which can be present during titania pigment processing [12,13].

The objective of this study is to combine the benefits of improved adsorption and dispersion performance of the above polymers into one copolymer. In particular, the presence of both cationic and anionic groups in the copolymer should increase polymer adsorption on oxide minerals surface by electrostatic interaction over a wider range of pH values, and also promotes polymer multilayer adsorption. This paper examines the interaction and particle dispersant ability of synthesised, novel polyethyleneimine–phosphonate–carboxylic copolymers as a function of phosphonate and carboxylate group density with boehmite particles. The study investigates the copolymer dispersion properties with boehmite particle suspensions as a function of pH and polymer concentration, proposing mechanisms for boehmite stabilisation provided by the polymer's amine, phosphonate and carboxylate functional groups. High purity boehmite was used in this study, as per the previous study [14], as a model system for titania pigment as several studies have shown that the surface of the titania pigment after inorganic oxide treatment is in a form very similar to boehmite [2,15].

2. Materials and methods

2.1. Materials

High purity boehmite, Apyral AOH 60, used throughout this study was obtained courtesy of Nabaltec, Germany. The BET surface area of the boehmite particles measured by N_2 adsorption was 6.5 m^2/g. The average particle size measured by scanning electron microscopy was 0.75 μm, which is identical to the D_{50} value obtained in solution by laser diffraction. The major surface elements determined by X-ray photoelectron spectroscopy were O, Al, Na, and adventitious C (57, 35, 0.8, and 7 at%, respectively). The boehmite isoelectric point (iep) was 9.4, which is well within the range of iep values reported for boehmite in the literature (see Fig. 5) [16,17].

All reagents were of laboratory grade purity or higher. Polyethyleneimine (Aldrich, MW 25,000), vinyl acetic acid (Aldrich, 97%) and diethyl vinyl phosphonate (Aldrich, 97%) were used for the synthesis of the copolymers. Polyethyleneimine, PEI, was selected as being suitable for grafting phosphonate and carboxylic groups [18,19]. Knowing that PEI has 25 wt% primary, 50 wt% secondary and 25 wt% tertiary amino groups [20–22], and the results

Fig. 1. Reaction scheme of (1st step) grafting of diethyl vinyl phosphonate (DVP) onto polyethyleneimine (PEI), (2nd step) hydrolysis and (3rd step) grafting vinyl acetic acid onto PEI-DVP to produce polyethyleneimine–phosphonate–carboxylic copolymers with $x/y/z/w$ values of 290/51/64/30 for PP25, 290/9/69/67 for PP50 and 257/0/62/116 for PP75, respectively (see text for explanation).

from its elemental analysis (using an Elemental analyser for the carbon, hydrogen and nitrogen, and Inductively Coupled Plasma for the phosphorus) and molecular weight (using Gel permeation chromatography and PSS Polymer Standards Service (Mainz, Germany)), it was calculated that 145 primary, 290 secondary and 145 tertiary amino groups are present in PEI.

The reaction scheme for the synthesis of the polyethyleneimine–phosphonate–carboxylic copolymers is shown in Fig. 1. In the first step, PEI was reacted with diethyl vinyl phosphonate in the presence of methanol at 72 °C for 18 h. After cooling and removing of methanol (under vacuum at 61 °C) and any unreacted PEI (under vacuum at 100 °C), in the second step the product was reacted with hydrochloric acid for 15 h to hydrolyse the phosphonate groups to phosphonic groups [23]. In the third step, the product was reacted with vinyl acetic acid in the presence of methanol at 70 °C for 18 h under nitrogen. After cooling and removing of methanol (under vacuum at 61 °C), the final product was purified by dialysis, yielding a yellowish viscous copolymer (the yield of the reaction was 75 wt%). To produce copolymers with different proportions of phosphonate and carboxylate functional groups, the total amount of diethyl vinyl phosphonate and vinyl acetic acid added was the same but their ratio was different. Copolymers termed in this study as PP25, PP50 and PP75 were formed with addition of 25, 50 and 75 wt% DVP, respectively. The structure of the copolymers was confirmed by using NMR (^{1}H, ^{13}C, ^{31}P and 2D) and FT-IR [24].

The average molecular weight, number average molecular weight, degree of polydispersity and number of functional groups in PEI and the synthesised copolymers are presented in Table 1. The number of phosphonic and carboxylic groups grafted on PEI in these copolymers was calculated from the results of elemental analysis and molecular weight. In the calculations it was assumed that each primary amino group of PEI can react with one diethyl vinyl phosphonate molecule or vinyl acetic acid molecule, and vinyl acetic acid can also attach to a secondary amino group [25]. Results in Table 1 show that the number of phosphonic groups attached to PEI increases from PP25 to PP50 and PP75 but the

Table 1
Average molecular weight (M_w), number average molecular weight (M_n), degree of polydispersity (M_w/M_n) (obtained by gel permeation chromatography) and number of functional groups in PEI, PP25, PP50 and PP75 (see text and Fig. 1 for explanation).

Copolymer	M_w (g/mol)	M_n (g/mol)	M_w/M_n	Number of functional groups	
				Carboxylic (z)	Phosphonic (w)
PEI	25,000	12,000	2.1	0	0
PP25	29,945	18,000	1.66	64	30
PP50	30,220	16,100	1.88	69	67
PP75	38,690	16,000	2.42	62	116