

## Effects of comb copolymer PAA-g-MPEO on rheological and dispersion properties of aqueous CaCO<sub>3</sub> suspensions

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### Summary

The comb copolymer poly(acrylic acid) (PAA) grafted methoxyl poly(ethylene oxide) (MPEO) (PAA-g-MPEO) as dispersant was used in aqueous CaCO<sub>3</sub> suspensions. The PAA-g-MPEO was adsorbed onto CaCO<sub>3</sub> particle surfaces due to the electrostatic attraction. The adsorbed amount increased with increasing PAA-g-MPEO content. The CaCO<sub>3</sub> adsorbed PAA-g-MPEO displayed negative zeta potential. The zeta potential was more negative with increasing PAA-g-MPEO content. Addition of PAA-g-MPEO, the conductivity of aqueous CaCO<sub>3</sub> suspensions decreased firstly, and then increased with increasing PAA-g-MPEO content. Compared to that of aqueous CaCO<sub>3</sub> suspensions, the viscosity of aqueous CaCO<sub>3</sub>/PAA-g-MPEO suspension reduced remarkably, and the liquidity of the suspensions was improved. The dispersion of CaCO<sub>3</sub> particles in aqueous CaCO<sub>3</sub>/PAA-g-MPEO suspensions was significantly improved due to electrostatic repulsions and steric hindrance between CaCO<sub>3</sub> particles adsorbed PAA-g-MPEO.

### Introduction

Polymer species was often added to colloidal suspensions to impart desired stability by adsorbing and forming a steric barrier to aggregation. PAA had carboxylic acid groups which become ionized above their pK<sub>a</sub> of 5 [1], the dispersion of CaCO<sub>3</sub> suspensions with PAA relies on the electrostatically driven adsorption of the negatively charged PAA onto the cationic surface of the mineral [2-4]. Adsorption behavior of PAA on the TiO<sub>2</sub> particle surfaces has been investigated in aqueous suspensions [5]. The steric layers of bis-hydrophilic diblock copolymers formed of poly(methacrylic acid) (PMAA) and poly(ethylene oxide) (PEO) have been investigated through the direct examination of repulsive forces [6]. It is believed that the electrolyte level affects the conformation of the stabilizing PEO chains. Increasing electrolyte levels disrupt the hydrogen bonding between the polymer and solvent needed to create an extended polymer conformation. The comb copolymers with

a backbone and side chains have been designed to optimize the dispersion behavior and shown great promise as colloid stabilizers [7-13]. The effects of PMAA-g-PEO comb copolymer on the electrokinetic and rheological properties of concentrated  $\text{Si}_3\text{N}_4$  suspensions, and the effects of PAA-g-PEO on rheological properties and interparticle forces of aqueous silica suspensions have been discussed [14,15]. The rheological behavior of concentrated cement suspensions in the absence and presence of comb polymers PAA-g-PEO has been reported [16]. The concentrated cement-PAA-g-PEO suspensions exhibited complex rheological behavior ranging from the reversible gel-like response observed at short teeth lengths to a remarkable gel-to-fluid transition observed for systems comprised of longer PEO teeth. The effects of PAA-g-PEO comb copolymers on the stability of aqueous  $\text{BaTiO}_3$  nanoparticle suspensions have been studied [17]. The presence of PEO teeth effectively shielded the underlying PAA backbone from ion interactions, thereby allowing PAA-g-PEO dispersants to impart stability to  $\text{BaTiO}_3$  nanoparticle suspensions.

In this paper, the effects of PAA-g-MPEO comb copolymer on the rheological and dispersion properties of aqueous  $\text{CaCO}_3$  suspensions were investigated. Compared with those of aqueous  $\text{CaCO}_3$  suspensions, the dispersion and stability of aqueous  $\text{CaCO}_3$  suspensions with PAA-g-MPEO were improved.

## Experimental

### *Materials*

Poly(acrylic acid) (PAA) was synthesized in our laboratory. The number average molecular weight of PAA was 3200. Methoxy poly(ethylene oxide) (MPEO,  $M_n=600$ ) was produced by Takemoto Oil & Fat Co., LTD (Japan). Tetrahydrofuran (THF) was manufactured by Shanghai Sihewei Chemical Company (China). Dimethylaminopyridine (DMAP) was produced by Fluka Company (Switzerland). Dicyclohexyl-dimethylcarbodiimide (DCC) was manufactured by Huakang Scientific Company (China). Chloroform was supplied by Shanghai Lingfeng Chemical Reagent Factory (China). Acetic ether was supplied by Nanjing Chemical Reagent Factory (China).  $\text{CaCO}_3$  was obtained from Nanjing Omya Fine Chemical Ind. Co. LTD (China).  $\text{CaCO}_3$  powder with an average particle diameter of  $0.4 \mu\text{m}$ , a specific surface area of  $6.7 \text{ m}^2/\text{g}$  and a density of  $2.7 \text{ g}/\text{cm}^3$  was obtained from Nanjing Omya Fine Chemical Ind. Co. LTD (China).

### *Synthesis of PAA-g-MPEO*

The PAA-g-MPEO comb polymer was synthesized according to PAA: MPEO=4:1 molar ratio. PAA, MPEO and THF were added into a flask and formed homogeneous solution with stirring at first, and then DMAP and DCC were added and reacted at  $50^\circ\text{C}$  for 168 h with stirring. The product was filtrated to remove dicyclohexylurea, and then was put into  $\text{CHCl}_3$  to precipitate PAA-g-MPEO and unreacted MPEO. The deposition was washed with acetic ether to remove unreacted MPEO, and then thoroughly dried in a vacuum oven.

The chemical structure of the PAA-g-MPEO is shown in Scheme 1. The number average molecular weight of PAA-g-MPEO was 9100. The graft degree of MPEO in PAA-g-MPEO was

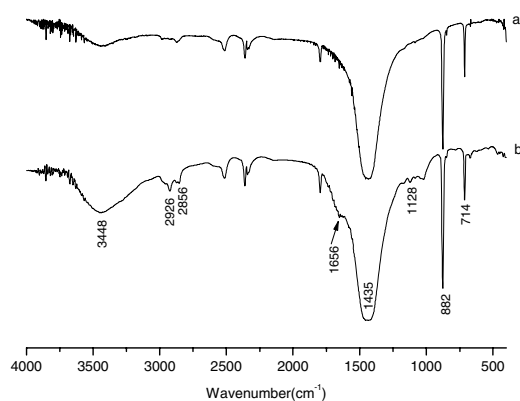


CaCO<sub>3</sub> particle surfaces increased with increasing PAA-g-MPEO content in larger extent within 150 mg/L of PAA-g-MPEO content, and the adsorbed amount increased in smaller extent ranging from 150 mg/L to 250 mg/L of PAA-g-MPEO content. In the range of 370 mg/L ~ 400 mg/L of PAA-g-MPEO content, the adsorbed amount did not increase and became constant with increasing PAA-g-MPEO content. It was shown that the adsorption of PAA-g-MPEO chains onto CaCO<sub>3</sub> particle surfaces was saturated at PAA-g-MPEO content of 370 mg/L, and the amount of saturation adsorption was about 1.1 mg/m<sup>2</sup>.

#### FTIR analysis

The aqueous CaCO<sub>3</sub> suspensions with constant particle weight fractions of 1.0% and PAA-g-MPEO of 0.6% based on the CaCO<sub>3</sub> weight were prepared. The CaCO<sub>3</sub> particles were separated by centrifugation, and the separated CaCO<sub>3</sub> particles were washed with de-ionized water, and then thoroughly dried in a vacuum oven.

FTIR spectra of CaCO<sub>3</sub> before and after adsorption of PAA-g-MPEO are shown Figure 2. The absorption peak at around 3448 cm<sup>-1</sup> was attributed to stretching vibration of O-H. The absorption peak at around 2926 cm<sup>-1</sup> and 2856 cm<sup>-1</sup> was attributed to asymmetric and symmetric stretching vibration of C-H, respectively. The absorption peaks at around 1656 cm<sup>-1</sup> was attributed to vibration of C=O. The absorption peaks at around 1128 cm<sup>-1</sup> was attributed to the stretching vibration of C-O. The FTIR results also showed that PAA-g-MPEO was adsorbed onto CaCO<sub>3</sub> particle surfaces through electrostatic interaction for aqueous CaCO<sub>3</sub>/PAA-g-MPEO suspensions.



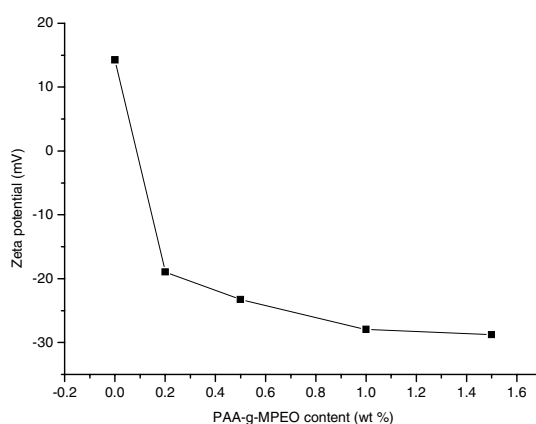
**Figure 2.** FTIR spectra of CaCO<sub>3</sub> before (a) and after (b) adsorption of PAA-g-MPEO.

#### Zeta potential

The aqueous CaCO<sub>3</sub> suspensions with constant particle weight fractions of 1.0% and different PAA-g-MPEO content were prepared.

The zeta potential of CaCO<sub>3</sub> particles at different PAA-g-MPEO content is shown in Figure 3. For CaCO<sub>3</sub> suspensions without PAA-g-MPEO, the non-adsorbed CaCO<sub>3</sub> particles displayed positive zeta potential of 14.25 mV due to the presence of Ca<sup>2+</sup> on

CaCO<sub>3</sub> particle surfaces. For the CaCO<sub>3</sub> suspensions with PAA-g-MPEO, the adsorption of PAA-g-MPEO onto CaCO<sub>3</sub> particle surfaces altered the surface charge of bare CaCO<sub>3</sub> particles to display negative zeta potential. The addition of 0.2% PAA-g-MPEO content based on the CaCO<sub>3</sub> particle weight lead to larger change in zeta potential of the CaCO<sub>3</sub> particle. With increasing PAA-g-MPEO content, the zeta potential became more negative in smaller extent due to the slower increase in the amount of adsorbed PAA-g-MPEO. At PAA-g-MPEO content above 1.0%, the change in the zeta potential became much less. Compared with that of the CaCO<sub>3</sub> particle, the absolute value of zeta potential of CaCO<sub>3</sub> particles adsorbed PAA-g-MPEO increased, thus, the electrostatic repulsive interaction between the CaCO<sub>3</sub> particles adsorbed PAA-g-MPEO increased, and both of the dispersion and stability of the CaCO<sub>3</sub> particles in the suspensions were improved.



**Figure 3.** Zeta potential of CaCO<sub>3</sub> particles at different PAA-g-MPEO content (pH=9.5).

#### *Conductivity of aqueous CaCO<sub>3</sub> suspensions*

The aqueous CaCO<sub>3</sub> suspensions with constant particle weight fractions of 1.0% and different PAA-g-MPEO content were prepared.

The conductivities of CaCO<sub>3</sub> suspensions at different PAA-g-MPEO content are listed in Table 1. Addition of 0.5% PAA-g-MPEO based on CaCO<sub>3</sub> particle weight, the conductivity of CaCO<sub>3</sub> suspensions decreased rapidly. This is due to decrease of the numbers of free ionic in the suspensions induced by the interaction between Ca<sup>2+</sup> and PAA-g-MPEO<sup>-</sup>. When the PAA-g-MPEO content was bigger than that of saturation adsorption, the numbers of free ionic of PAA-g-MPEO<sup>-</sup> in the suspensions increased, and thus the conductivity of the suspensions increased. The conductivity results indicated that PAA-g-MPEO adsorbed onto CaCO<sub>3</sub> particle surfaces through electrostatic interaction.

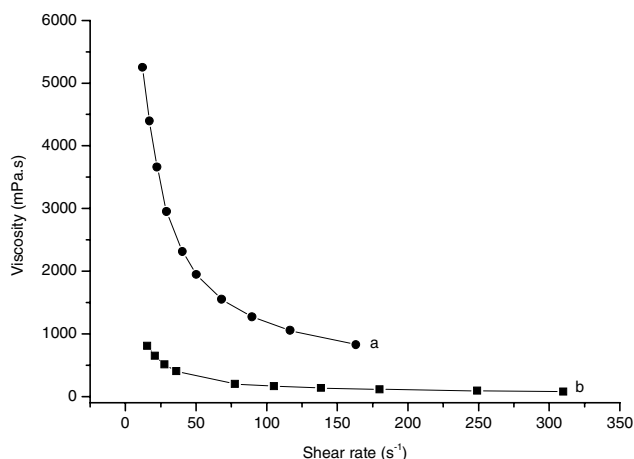
**Table 1.** Conductivity of CaCO<sub>3</sub> suspensions at different PAA-g-MPEO content (pH=9.5).

PAA-g-MPEO (wt%)	0	0.5	1	1.5
Conductivity (ms/cm)	0.30	0.10	0.17	0.25

### Viscosity of aqueous $\text{CaCO}_3$ suspensions

The aqueous  $\text{CaCO}_3$  suspensions with constant particle volume fractions of 38% and PAA-g-MPEO content of 0.1% based on the  $\text{CaCO}_3$  weight were prepared.

The viscosity of  $\text{CaCO}_3$  suspensions and  $\text{CaCO}_3$ /PAA-g-MPEO suspensions at different shear rate are shown in Figure 4. The viscosity of  $\text{CaCO}_3$  suspensions and  $\text{CaCO}_3$ /PAA-g-MPEO suspensions decreased with increasing shear rate, and the suspensions exhibited pseudoplastic flow behavior. At the same shear rate, the viscosity of  $\text{CaCO}_3$ /PAA-g-MPEO suspensions was less than that of  $\text{CaCO}_3$  suspensions, and the liquidity of  $\text{CaCO}_3$ /PAA-g-MPEO suspensions was markedly improved compared with that of  $\text{CaCO}_3$  suspensions. The decrease in viscosity of  $\text{CaCO}_3$ /PAA-g-MPEO suspensions is due to decrease in the  $\text{CaCO}_3$  flocculated size caused by the electrostatic repulsions of PAA backbone and the steric hindrance of MPEO teeth in PAA-g-MPEO adsorbed onto the  $\text{CaCO}_3$  particle surfaces. The decrease in viscosity of the suspensions with PAA-g-MPEO also suggested that the dispersion of  $\text{CaCO}_3$  particles in the suspensions was improved.

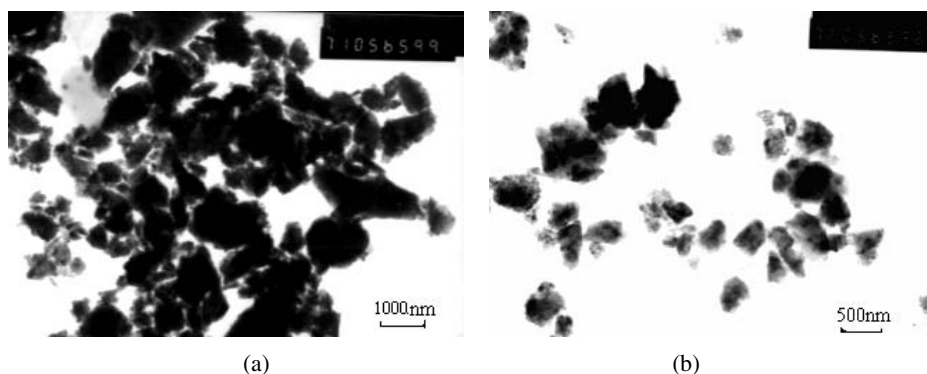


**Figure 4.** Apparent viscosity of  $\text{CaCO}_3$  suspensions (a) and  $\text{CaCO}_3$ /PAA-g-MPEO suspensions (b) at different shear rate (pH=9.5).

### TEM

The aqueous  $\text{CaCO}_3$  suspensions with constant particle weight fractions of 3% in the presence and absence of PAA-g-MPEO were prepared. The aqueous  $\text{CaCO}_3$  suspensions were treated by ultrasonic dispersion for 3 min, and then stirred for 20 min. The above  $\text{CaCO}_3$  suspensions were dripped on the copper netting, thoroughly dried, and then the dispersion of the  $\text{CaCO}_3$  particles were observed through TEM.

As shown in Figure 5, the  $\text{CaCO}_3$  particles in  $\text{CaCO}_3$  suspensions without PAA-g-MPEO were agglomerated and the dispersion of  $\text{CaCO}_3$  particles was poor. On the other hand, the dispersion of  $\text{CaCO}_3$  particles in  $\text{CaCO}_3$  suspensions with PAA-g-MPEO was improved markedly because of the electrostatic repulsions and steric hindrance of PAA-g-MPEO adsorbed onto the  $\text{CaCO}_3$  particle surfaces.



**Figure 5.** TEM of  $\text{CaCO}_3$  suspensions (a) and  $\text{CaCO}_3/\text{PAA-g-MPEO}$  suspensions (b).

### Conclusions

The PAA-g-MPEO comb copolymer was used as dispersant to prepare aqueous  $\text{CaCO}_3$  suspensions. The amount of PAA-g-MPEO adsorbed onto  $\text{CaCO}_3$  particle surfaces increased with increasing PAA-g-MPEO content. Compared to that of aqueous  $\text{CaCO}_3$  suspensions, the zeta potential of aqueous  $\text{CaCO}_3$  suspensions with PAA-g-MPEO increased. Addition of 0.5% PAA-g-MPEO, the conductivity of aqueous  $\text{CaCO}_3$  suspensions decrease rapidly, and then the conductivity increased with PAA-g-MPEO content. The viscosity of aqueous  $\text{CaCO}_3$  suspensions containing PAA-g-MPEO was less than that of aqueous  $\text{CaCO}_3$  suspensions, and the fluidity of aqueous  $\text{CaCO}_3/\text{PAA-g-MPEO}$  suspensions was improved. The dispersion of  $\text{CaCO}_3$  particles in aqueous  $\text{CaCO}_3$  suspensions with PAA-g-MPEO was improved due to electrostatic repulsions and steric hindrance.

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