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Dispersion and rheological properties of concentrated kaolin suspensions with polycarboxylate copolymers bearing comb-like side chains

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Abstract

Comb-like polycarboxylate copolymers (PCs) were synthesized and first used as the dispersants for kaolin suspensions. The apparent viscosity, adsorption behavior, zeta potential, rheological behavior, and TEM images of concentrated kaolin slurries deflocculated with these copolymers were systematically investigated. Sodium acrylate homopolymer (SA) was selected as a reference in order to contribute to the knowledge of how the electrostatic interaction and molecular structure of these copolymers influenced the dispersion, adsorption, and rheological properties of colloidal kaolin suspensions. The results showed that the dispersion of kaolin slurries mainly depended on the synergistic effects of electrostatic interaction and steric hindrance for APEG type comb-like copolymers. PC_2 bearing proper carboxylic groups and side chains produced stable dispersion and fluidity in concentrated kaolin slurries. Based on the electrostatic and steric effect of comb-like copolymers, the kaolin slurries displayed a shear thickening behavior, and the Herschel–Bulkley model well described their rheological behaviors.

Keywords: Comb-like copolymer; Kaolin; Dispersants; Absorption; Rheology

1. Introduction

It is well known that polymeric dispersants, owning well properties of controlling the colloidal processing and keeping good adsorption at the solid–liquid interfaces, are of increasing interest in recent years due to the potential applications in many fields.[1,2] Wherein, as one of the most representative polymers, polycarboxylate polymers with the adsorbing backbone and no adsorbing side chains have already been considered as effective dispersants for different applications such as cement and concrete placement, ceramic slurry processing, paints, cosmetics, etc.[3–6] This is the case of concrete, where polycarboxylate polymers have been widely used over the past decades for greatly improving workability, strength, and durability.[7–9] Nevertheless, in ceramic industry, it is well known that successful colloidal processing of ceramics requires careful selection of inorganic or organic plasticizers to provide suitable plasticity, to prevent ceramic green bodies from cracking, and to limit distortions and volume contraction on drying and sintering.[10,11] Now for organic plasticizers, their usages are just the linear polycarboxylate polymers, including polyacrylate salts, polymethacrylates carrying some carboxylic or sulfonic anions with ammonium cations and terpolymers containing acrylic acid, acrylamide, and vinylpyrrolidone.[12–16] Those linear polycarboxylate polymers have significant effect of establishing dispersion–adsorption equilibriums among the ceramic particles and dispersants, enhancing the stability and impeding particles aggregation by electrostatic interactions, and the ceramic pastes show clear homogenous dispersion as well as keep high solid loadings and low viscosities.[3,4]

It is widely accepted that interactions between the dispersants and the particles are not only affected by the properties of particles, but also by the properties of dispersants, such as molecular architecture, degree of polymerization, flexibility of backbone and grafts, etc.[5,10,15] Researchers have already used kinds of polyacrylate salts as effective dispersants to control the stability and fluidity of the ceramic slurries. Marco et al. found that whether in the mobility or stability, linear sodium

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Table 1
Chemical composition (mass%) of the kaolin used.

Kaolin	SiO_2	Al_2O_3	Fe_2O_3	CaO	K_2O	MgO	Na_2O	TiO_2	LOI
Composition (%)	69.18	19.81	0.83	0.07	0.24	0.16	0.65	0.31	9.56

polyacrylate is better than other polyacrylate dispersants, such as sodium poly (alkyl sulfonate), copolymer of sodium acrylate and sodium alkyl sulfonated and non-ionic poly (alkyl acrylate) in raw porcelain gres.[4,6,16] Jiang et al. found sodium poly (acrylicacid-co-maleic anhydride-co-itaconic acid) bearing more charge density in their side chains, produces a more stable dispersion and fluidity in concentrated suspensions.[17] Although Ran et al. first studied the dispersion ability of SMA-g-MPEG comb-like copolymers in the Al_2O_3 suspension, and found SMA-g-MPEG with moderate length of side chain has best dispensability.[18] Nevertheless, the structure–properties correlations for such comb-like ceramic dispersants have been rather less studied up to present, and there is no attention on the dispersion and fluidity effect of comb-like polycarboxylate polymers in the raw porcelain gres.

It has been noticed that polycarboxylate polymers often demonstrate excellent water reducing properties because of their steric hindrance effect of comb-like side chains, and we hypothesized that it might be possible to have the similar effect for ceramics suspensions. Therefore, the objective of this study was to synthesize and characterize series of APEG type polycarboxylate copolymers via aqueous free radical polymerization, and contributed this paper to the knowledge of investigating the dispersion and rheological properties of kaolin suspensions with APEG type comb-like polycarboxylate copolymers which have nonionic polyethylene glycol (PEG) based side chains grafted onto the backbone at frequent intervals but with different carboxylic groups and molecular weight. Meanwhile, the linear sodium acrylate homopolymer (SA) was used as a reference to understand the relationship of molecule structure and dispersion mechanism. To the best of our knowledge, this is the first report about the dispersion ability and rheological properties of APEG type comb-like polycarboxylate copolymers in kaolin suspensions as compared to linear polyacrylate salts.

2. Materials and methods

2.1. Materials

The main chemical compositions of kaolin used in this paper (Hebei, China) are shown in Table 1. The particle size distribution was measured by using laser diffraction (WS5-RODOS laser particle size analyzer, System Partikel Technik, Germany), and the mean particle size was 5.17 μm, with about 50% of the particles larger than 6.20 μm and the 100% of the kaolin particles were below 59.47 μm. The specific surface area was measured by the Brunauer–Emmet–Teller (BET) method (3H-2000PS1 specific surface and pore size analyzer, Beishide Instrument, China), and its value was 20.30 m^2/g.

A common linear sodium acrylate homopolymer (SA) used as dispersing agents broadly in ceramic industry was supplied by Shandong Aona Chemical, China. APEG-AA-MA copolymers were prepared from allyl polyethylene glycol (APEG, Mw 1200, Shanghai Taijie Chemical, China), acrylic acid (AA), and maleic anhydride (MA) through free radical polymerization according to the procedure as follows. Ammoniumpersulfate (APS) was used as the initiator. APEG, AA and MA were dissolved in distilled water, when the temperature rising to 70 °C, APS aqueous solution were added drop wise into the reaction mixture for 2 h, and then retained the temperature for 3 h. After the reaction was completed, the polymer solution was neutralized by alkali solution of 40% sodium hydroxide. The synthetic route of free radical copolymerization between APEG, AA, and MA is represented in Fig. 1.

The crude products were purified by anhydrous ether and dried at 50 °C under vacuum for 2 d. The structure of the APEG type copolymers was verified from the FT-IR and ^{1}H NMR spectra. FT-IR spectra of the copolymers (KBr pellets) were recorded with an FT-IR Nicolet 5100 spectrometer in the fundamental region of 400–4000 cm^{-1}. ^{1}H NMR spectra were recorded with a Bruker DRX-400 Nuclear magnetic resonance spectrometer. APEG-AA-MA copolymers (PC_2): IR (KBr) (wavenumber, cm^{-1}): 1750 cm^{-1}, 1620 cm^{-1} (C=O); 3200–3650 cm^{-1} (COOH). ^{1}H NMR, δ (400 MHz, D_2O, TMS, ppm): δ 4.0 (HO–), 3.5–3.8 (–CH_2–CH_2–O–), 2.27–2.59 (–CH–), 1.75–1.90 (–CH_2–).

The average molecular mass and distribution of the copolymers were determined with gel permeation chromatography (GPC) using an ultrahydrogel 250 columns with a waters 2410 significant differential refractometer detector. The samples were analyzed using 0.1 mol/L $NaSO_4$ aqueous solutions as eluant, at a flow rate of 0.5 mL/min. The physical and chemical structures of copolymers are summarized in Fig. 2 and Table 2.

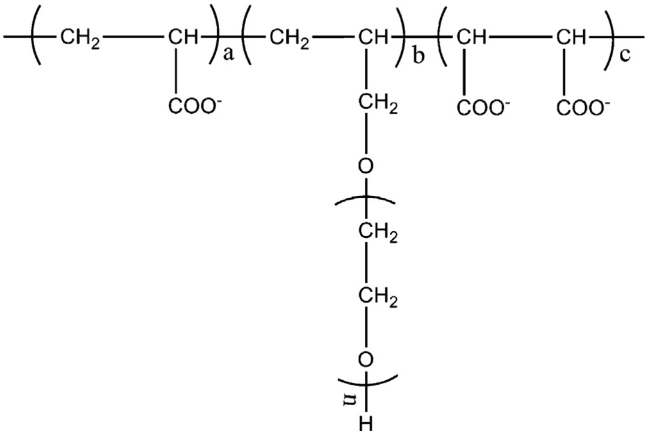

Fig. 1. Free radical copolymerization between APEG, AA and MA.