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ORIGINAL PAPER

Effect of length of branched-chain of PAA-*g*-MPEO on dispersion of $CaCO_3$ aqueous suspensions

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Abstract The viscosity of $CaCO_3$/poly(acrylic acid) grafted methoxyl poly(ethylene oxide) (PAA-*g*-MPEO) aqueous suspensions was influenced by length of the branched-chain and content of PAA-*g*-MPEO. The viscosity of $CaCO_3$/PAA-*g*-MPEO suspensions first decreased and then increased with increasing length of branched-chain of PAA-*g*-MPEO at the same PAA-*g*-MPEO content. The viscosity of $CaCO_3$ suspensions containing PAA-*g*-MPEO with short branched-chain ($\bar{M}_n =$ 200 g/mol and 600 g/mol) decreased with increasing the PAA-*g*-MPEO content. However, the viscosity of $CaCO_3$ suspensions containing PAA-*g*-MPEO with long branched-chain ($\bar{M}_n = 1500$ g/mol) increased with increasing the PAA-*g*-MPEO content. The size distribution of $CaCO_3$ particles in $CaCO_3$ suspensions containing PAA-*g*-MPEO with the short branched-chain became narrower and the average size decreased with increasing length of the branched-chain. This is due to the steric hindrance of branched-chain of the PAA-*g*-MPEO adsorbing on surface of the $CaCO_3$ particles increased with increasing length of the branched-chain. The size distribution of $CaCO_3$ particles in $CaCO_3$ suspensions containing PAA-*g*-MPEO with the long branched-chain had two regions, and the average size increased compared with that of $CaCO_3$ particles in the $CaCO_3$ suspensions containing PAA-*g*-MPEO with the short branched-chain. This is due to the flocculation of fractional $CaCO_3$ particles induced

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by “tangle” between the long branched-chain of PAA-*g*-MPEO adsorbing on surface of $CaCO_3$ particles.

Keywords PAA-*g*-MPEO · Length of branched-chain · $CaCO_3$ aqueous suspensions · Viscosity · Dispersion

Introduction

Polymer species are often added to colloidal suspensions to impart desired dispersion and fluidity by adsorbed on the surface of solid particles and forming electrostatic and steric hindrance to reduce aggregation between particles. The force acting on the surface of cement particles adsorbing sulphonated naphthalene formaldehyde condensate and copolymer of olefin with maleic acid, and the rheological properties of cement, β-dicalcium silicate and γ-dicalcium silicate suspensions prepared with adding the polymer have been reported [1, 2]. Effects of a strong anionic polyelectrolyte, melamine formaldehyde sulfonate (MFS) on the rheological properties of concentrated cement suspensions were investigated [3]. Poly(acrylic acid) (PAA) contained ionizable carboxylic acid (COOH) groups along their backbone. The groups dissociated to form negatively charged carboxylate groups (COO^-). Adsorption behaviour of PAA on the TiO_2 particle surfaces and its dispersion effect had been investigated in aqueous suspensions [4–6]. The dispersion of $CaCO_3$, kaolin and TiO_2 using low-polydispersity PAA were improved [7]. The settling property of barium sulphate suspensions has been systematically investigated as a function of particle volume fraction and dispersant (PAA or polystyrene sulphonate) concentration [8]. The comb copolymers with a backbone and side chains have been designed to optimise the dispersion behaviour and shown great promise as colloid stabilizers [2, 9–11]. The effects of PMAA-*g*-PEO comb copolymer on the electrokinetic and rheological properties of concentrated Si_3N_4 suspensions, and the effects of PAA-*g*-PEO on rheological properties and interparticle forces of aqueous silica suspensions have been discussed [12, 13]. The rheological behaviour of concentrated cement suspensions in the absence and presence of comb polymers PAA-*g*-PEO has been reported [14]. The concentrated cement/PAA-*g*-PEO suspensions exhibited complex rheological behaviour 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 $BaTiO_3$ nanoparticle suspensions have been studied [15]. The presence of PEO teeth effectively shielded the underlying PAA backbone from ion interactions, thereby allowing PAA-*g*-PEO dispersants to impart stability to $BaTiO_3$ nanoparticle suspensions. The comb copolymer poly(acrylic acid) grafted methoxyl poly(ethylene oxide) (PAA-*g*-MPEO) was used in aqueous $CaCO_3$ suspensions and TiO_2 suspensions, and its adsorption behaviour on the particle surfaces and its effect on dispersion and viscosity of the suspensions had been investigated [16–18]. Ran et al. studied the adsorption characteristics of various comb dispersant containing different graft densities on surfaces of cement particle. And they synthesised a series of comb-like copolymer with variation in poly(ethylene oxide) side chain length and anionic group content for detailed interfacial studies [19, 20].

In this article, the effect of length of branched-chain of PAA-*g*-MPEO on dispersion of $CaCO_3$ aqueous suspensions was investigated. Compared with that of $CaCO_3$ aqueous suspensions, the dispersion of $CaCO_3$ particles in $CaCO_3$/PAA-*g*-MPEO suspensions was improved markedly. When the number average molecular weight ($\bar{M}_n$) of branched-chain of PAA-*g*-MPEO was increased from 200 g/mol to 600 g/mol, the average size of $CaCO_3$ particles in $CaCO_3$/PAA-*g*-MPEO suspensions decreased. However, the average size of $CaCO_3$ particles in $CaCO_3$ suspensions containing PAA-*g*-MPEO with long branched-chain ($\bar{M}_n = 1500\,\text{g/mol}$) increased.

Experimental

Materials

Poly(acrylic acid) (PAA, $\bar{M}_n = 3.2 \times 10^3$ g/mol) was provided by Jiangsu Institute of Building Science (China). Methoxy poly (ethylene oxide) (MPEO, $\bar{M}_n = 200$, 600 and 1500 g/mol) 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 Scientifiac Company (China). Chloroform was supplied by Shanghai Lingfeng Chemical Reagent Factrory (China). Acetic ether was supplied by Nanjing Chemical Reagent Factory (China). $CaCO_3$ with an average particle diameter of 0.4 μm and a specific surface area of 7.6 m^2/g was obtained from Nanjing Omya Fine Chemical Ind. Co. LTD (China).

Synthesis of PAA-*g*-MPEO

Poly(acrylic acid), MPEO and THF were added into a reaction flask, forming homogeneous solution by stirring at first, and then DMAP and DCC were added. The mixture was reacted for 168 h at 50 °C under stirring. The mixture was filtrated to remove dicyclohexylurea, and then the filtrate was put into chloroform 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, and the PAA-*g*-MPEO was obtained. The PAA-*g*-MPEO prepared by PAA and MPEO with $\bar{M}_n$ of 200, 600 and 1500 g/mol were marked as PAA-*g*-MPEO200, PAA-*g*-MPEO600 and PAA-*g*-MPEO1500, respectively.

Measurement and characterisation

The viscosities of aqueous $CaCO_3$ suspensions with and without PAA-*g*-MPEO were performed using a HXS-11A rotary viscosimeter. The aqueous $CaCO_3$ suspensions with and without PAA-*g*-MPEO were treated by ultrasonic dispersion for 5 min, and then stirred for 20 min. The size distribution of $CaCO_3$ particles in the suspensions was mensurated by Malvarn Instruments Ltd Mastersizers Laser Hondrometer. The dispersion of the $CaCO_3$ particles was observed by a JEOL JEM-100S transmission electron microscopy.

Results and discussion

Viscosity analysis

The $CaCO_3$ suspensions ($CaCO_3$ content was 38 vol%) and a series of $CaCO_3$/PAA-*g*-MPEO with different length of branched-chain suspensions ($CaCO_3$ content was 38 vol%, PAA-*g*-MPEO content were 0.2, 0.4 and 0.6%) were prepared, respectively.

The apparent viscosity of $CaCO_3$ suspensions decreasing with increasing shear rate (Fig. 1a), was a pseudoplastic fluid. The high viscosity of $CaCO_3$ suspensions showed aggregation of $CaCO_3$ particles in the suspensions. With increasing shear rate, the viscosity of $CaCO_3$/0.2 wt%PAA-*g*-MPEO200 suspensions markedly decreased, however the viscosity of $CaCO_3$ suspensions with 0.4 and 0.6 wt% PAA-*g*-MPEO200 little decreased (Fig. 1b). The change trend of the viscosity of $CaCO_3$/PAA-*g*-MPEO600 suspensions was the same with that of $CaCO_3$/PAA-*g*-MPEO200

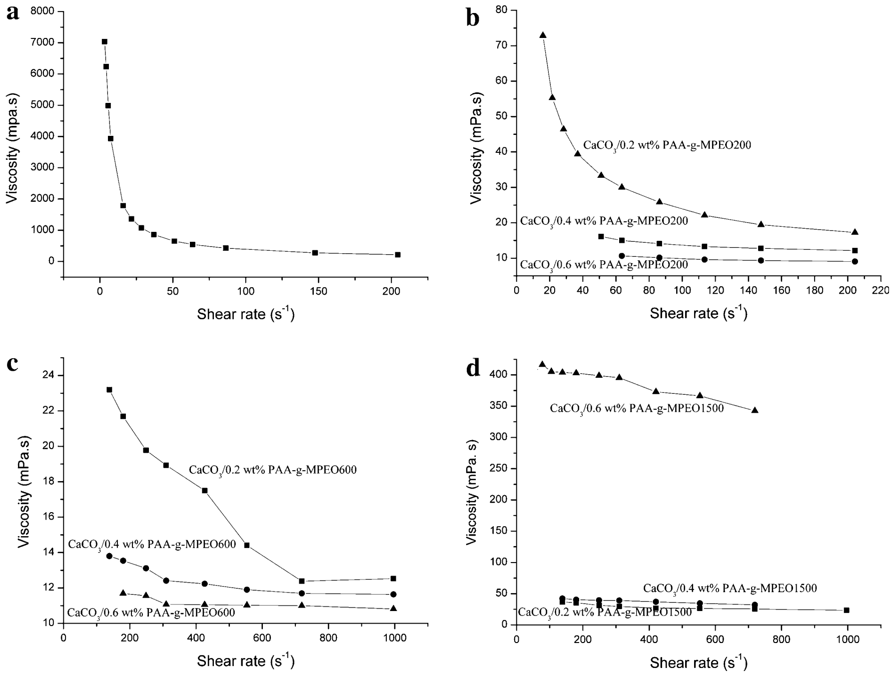

Fig. 1 Apparent viscosity of $CaCO_3$ suspensions (**a**), $CaCO_3$/PAA-*g*-MPEO200 suspensions (**b**), $CaCO_3$/PAA-*g*-MPEO600 suspensions (**c**) and $CaCO_3$/PAA-*g*-MPEO1500 suspensions (**d**)

suspensions (Fig. 1c). The viscosity of $CaCO_3$ with PAA-*g*-MPEO200 or PAA-*g*-MPEO600 suspensions decreased with increasing the PAA-*g*-MPEO content. Compared with that of $CaCO_3$ suspensions, the viscosity of $CaCO_3$/PAA-*g*-MPEO200 suspensions and $CaCO_3$/PAA-*g*-MPEO600 suspensions decreased remarkably, showing the melioration of dispersion of $CaCO_3$ particles in the suspensions. The viscosity of $CaCO_3$/PAA-*g*-MPEO1500 suspensions increased with increasing the PAA-*g*-MPEO content. The viscosity of $CaCO_3$/0.4 wt% PAA-*g*-MPEO1500 suspensions was little higher than that of $CaCO_3$/0.2 wt% PAA-*g*-MPEO1500, and the viscosity markedly increased when PAA-*g*-MPEO1500 content was 0.6 wt% (Fig. 1d). This may be caused by the increase of agglomeration of $CaCO_3$ particle in the suspensions increasing the PAA-*g*-MPEO content. The viscosity of $CaCO_3$/PAA-*g*-MPEO1500 suspensions was higher than that of $CaCO_3$/PAA-*g*-MPEO600 suspensions at the same PAA-*g*-MPEO content, suggesting that the dispersion effect of PAA-*g*-MPEO1500 was less than PAA-*g*-MPEO600.

Size distribution

The size distributions and average sizes of $CaCO_3$ particles in $CaCO_3$ suspensions ($CaCO_3$ content was 3 wt%) and $CaCO_3$/PAA-*g*-MPEO suspensions ($CaCO_3$ content was 3 wt%) are shown in Fig. 2 and Table 1, respectively. The size distribution of

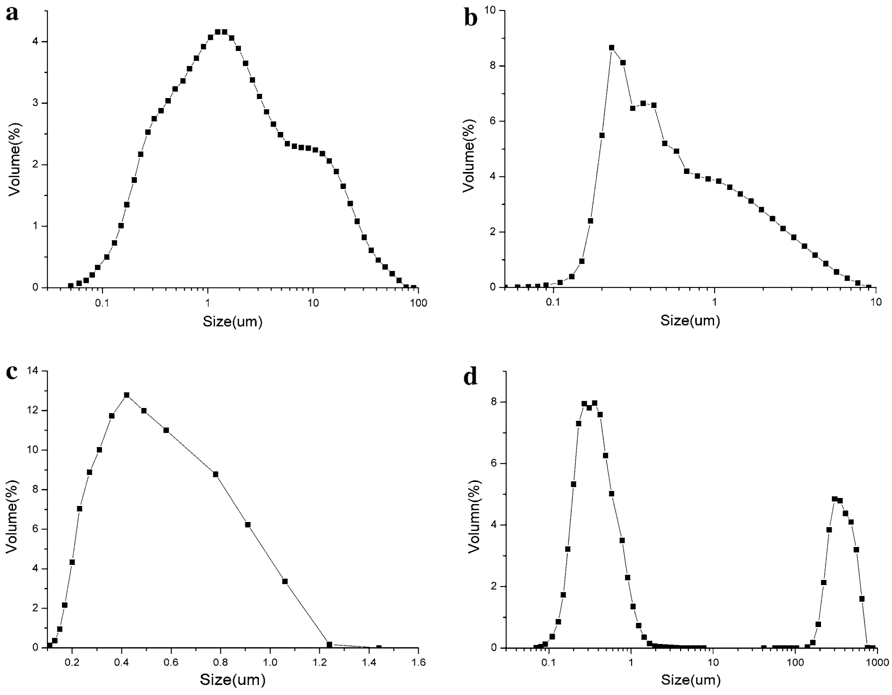

Fig. 2 Size distribution curve of $CaCO_3$ particles from $CaCO_3$ suspensions (**a**), $CaCO_3$/0.4 wt% PAA-*g*-MPEO200 suspensions (**b**), $CaCO_3$/0.4 wt%PAA-*g*-MPEO600 suspensions (**c**) and $CaCO_3$/0.4 wt%PAA-*g*-MPEO1500 suspensions (**d**)

Table 1 Average size of $CaCO_3$ particles from $CaCO_3$ suspensions and $CaCO_3$/0.4 wt% PAA-*g*-MPEO suspensions

Particles	No PAA-*g*-MPEO	PAA-*g*-MPEO200	PAA-*g*-MPEO600	PAA-*g*-MPEO1500
Average size (μm)	2.15	0.55	0.45	0.59

$CaCO_3$ particles in $CaCO_3$ suspensions was wide (0–100 μm, Fig. 2a), and its average size was 2.15 μm. The size distributions of $CaCO_3$ particles in $CaCO_3$/0.6 wt% PAA-*g*-MPEO200 suspensions and $CaCO_3$/0.6 wt% PAA-*g*-MPEO600 suspensions were 0–10 and 0–1.6 μm (Fig. 2b, 2c), respectively, and their corresponding average sizes were 0.55 and 0.45 μm (Table 1), respectively. The size distribution of $CaCO_3$ particles in $CaCO_3$/PAA-*g*-MPEO suspensions became narrower and the average size decreased with increasing the length of branched-chain at the same PAA-*g*-MPEO content. For $CaCO_3$/0.4 wt% PAA-*g*-MPEO1500 suspensions, the size distribution of $CaCO_3$ particles showed two areas: 0–10 μm and 100–1000 μm (Fig. 2d), and the average size increased to 0.59 μm, showing the generation of flocculation of the fractional $CaCO_3$ particles in the suspensions. The tangled action of the long branched-chain of PAA-*g*-MPEO1500 adsorbed on surface of the adjacent $CaCO_3$ particles led to flocculation of the fractional $CaCO_3$ particles, so the viscosity of the suspensions was enhanced. Compared with that of $CaCO_3$ particles in $CaCO_3$ suspensions, the dispersion of $CaCO_3$ particles in $CaCO_3$/PAA-*g*-MPEO suspensions (exception of $CaCO_3$/0.6 wt% PAA-*g*-MPEO suspensions) was improved because of electrostatic repulsion of COO^- on the backbone and steric hindrance of branched-chain of the PAA-*g*-MPEO adsorbed on surface of the $CaCO_3$ particles.

TEM

The $CaCO_3$ particles in $CaCO_3$ suspensions ($CaCO_3$ content was 3 wt%) presented poor dispersion, and were agglomerated (Fig. 3a), so the corresponding suspensions showed high viscosity. After Adding 0.4 wt% PAA-*g*-MPEO200 into $CaCO_3$ suspensions ($CaCO_3$ content was 3 wt%), the dispersion of $CaCO_3$ particles in the $CaCO_3$ suspensions was improved (Fig. 3b), and the dispersion of the $CaCO_3$ particles was further increased when the PAA-*g*-MPEO600 replacing PAA-*g*-MPEO200 (Fig. 3c). Therefore, the $CaCO_3$/PAA-*g*-MPEO600 suspensions showed low viscosity. The melioration of the dispersion of the $CaCO_3$ particles was ascribed to the electrostatic repulsions (COO^- in PAA backbone) and the steric hindrance of branched-chain of the PAA-*g*-MPEO adsorbed on the surfaces of the $CaCO_3$ particles. Moreover, the steric hindrance of the branched-chain was enhanced with increasing the length of the branched-chain. The schematic model of the electrostatic repulsions and steric hindrance branched-chain in PAA-*g*-MPEO adsorbed on the surface of $CaCO_3$ particles is shown in Fig. 4. The dispersion of $CaCO_3$ particles in $CaCO_3$/0.4 wt%PAA-*g*-MPEO1500 suspensions decreased (Fig. 3d) compared with that of $CaCO_3$ particles in $CaCO_3$/0.4 wt%PAA-*g*-MPEO600 suspensions or $CaCO_3$/0.4 wt%PAA-*g*-MPEO200 suspensions. This was

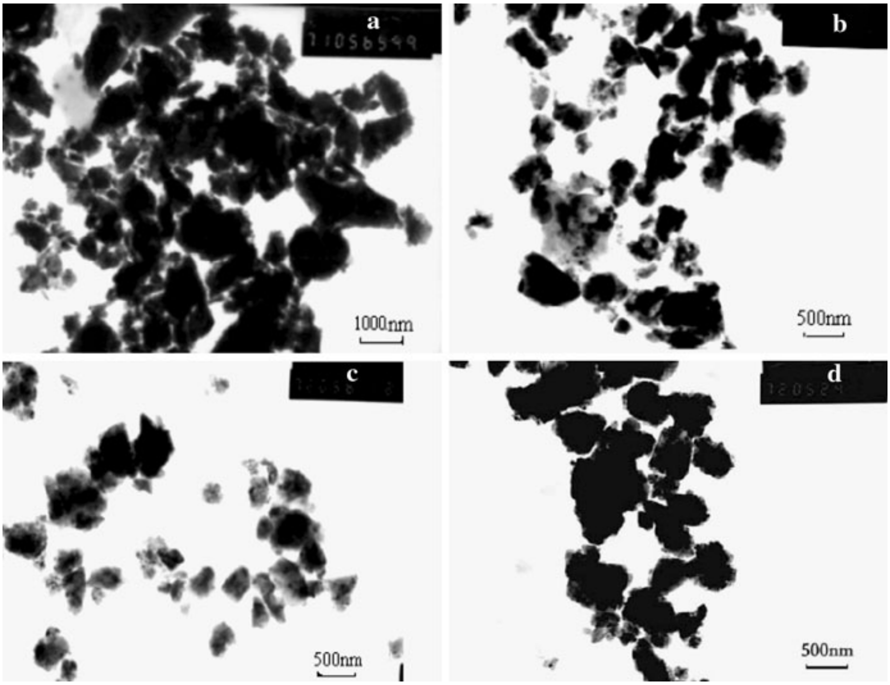

Fig. 3 TEM of $CaCO_3$ from $CaCO_3$ suspension (**a**), $CaCO_3$/PAA-*g*-MPEO200 suspension (**b**), $CaCO_3$/PAA-*g*-MPEO600 suspension (**c**) and $CaCO_3$/PAA-*g*-MPEO1500 suspension (**d**)

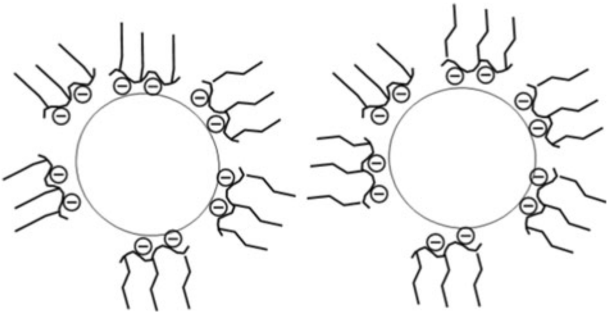

Fig. 4 Schematic model of electrostatic repulsions and steric hindrance branched-chain in PAA-*g*-MPEO adsorbing on surface of $CaCO_3$ particles

due to the flocculation of the fractional $CaCO_3$ particles induced by the tangled action between long branched-chains in PAA-*g*-MPEO1500 adsorbed on the surface of the adjacent $CaCO_3$ particles. The schematic model of the tangle between the long branched-chains in PAA-*g*-MPEO adsorbed on the surface of the adjacent $CaCO_3$ particles in $CaCO_3$/PAA-*g*-MPEO1500 suspensions is shown in Fig. 5.

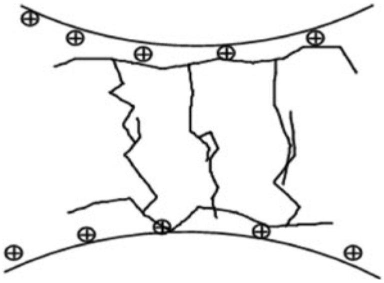

Fig. 5 Schematic model of tangle between long branched-chain in PAA-*g*-MPEO adsorbing on surface of $CaCO_3$ particles

Conclusion

Compared with that of $CaCO_3$ suspensions, the viscosity of $CaCO_3$/PAA-*g*-MPEO suspensions decreased, and its liquidity was improved. The viscosity of $CaCO_3$/PAA-*g*-MPEO suspensions was influenced by PAA-*g*-MPEO content and length of the branched-chain. The viscosity of $CaCO_3$/PAA-*g*-MPEO200 suspensions and $CaCO_3$/PAA-*g*-MPEO600 suspensions decreased with increasing PAA-*g*-MPEO content. However, the viscosity of $CaCO_3$/PAA-*g*-MPEO1500 suspensions increased with increasing PAA-*g*-MPEO content. At the same PAA-*g*-MPEO content, the viscosity of $CaCO_3$/PAA-*g*-MPEO suspensions first decreased and then increased with increasing length of branched-chain of PAA-*g*-MPEO.

Adding 0.4 wt% PAA-*g*-MPEO200 into $CaCO_3$ suspensions, the size distribution of $CaCO_3$ particles in the $CaCO_3$ suspensions became narrower and the average size decreased. The size distribution of $CaCO_3$ particles further became narrower and the average size unceasingly decreased when $\bar{M}_n$ of branched-chain of the PAA-*g*-MPEO increased from 200 to 600 g/mol. The size distribution of $CaCO_3$ particles in the $CaCO_3$ suspensions containing 0.4 wt% PAA-*g*-MPEO1500 presented two regions, and the average size augmented compared with that of $CaCO_3$ particles in $CaCO_3$ suspensions containing 0.4 wt% PAA-*g*-MPEO200 or PAA-*g*-MPEO600. Compared with that of $CaCO_3$ suspensions, the dispersion of $CaCO_3$ suspensions containing PAA-*g*-MPEO was improved. Hereinto, the $CaCO_3$/0.4 wt% PAA-*g*-MPEO600 suspensions showed best dispersion.

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