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A novel associative latex thickener using ethoxylated behenyl methacrylate as functional monomer

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Abstract

Alkali-soluble associative latex thickeners modified with hydrophobic long chain alkyl groups were prepared using common acrylics and varying amount of a functional monomer, ethoxylated behenyl methacrylate (BEM), through emulsion polymerization. It was found that the size of the emulsion particle became larger with addition of BEM. The light transmittance of the thickener latex sharply increased with pH varied from 6 to 7. The associative latex thickener manifested a higher viscosity when solids in the latex thickeners were kept at 0.5 wt% or higher, and the optimal amount of BEM was found to be around 2.5 wt%, or 0.16 mol%. All thickener latexes modified with BEM have better shearing resistance than the BEM-free thickener.

Keywords: Associative thickener; Functional monomer; Ethoxylated behenyl methacrylate; Viscosity

Hydrophobically modified alkali-soluble emulsions (HASEs) polymers generally offer excellent viscosity building, wide formulation latitude, excellent biostability and ease of dosing. At present, excellent results in latex thickening are often obtained using associative thickeners (AT) on the basis of HASEs. It is generally accepted that viscoelastic properties in AT latex/systems are enhanced by building an associative latex particles through hydrophobic associations [1] or through ion–dipole interactions [2].

HASEs are usually obtained by emulsion polymerization [3,4], inverse emulsion polymerization [5], or precipitation polymerization [6]. Typically, HASEs polymers are synthesized using conventional semi-continuous emulsion polymerization. Ji et al. [3] and Jassal et al. [4] discussed the polymerization of methacrylic acid (MAA)–ethyl acrylate (EA)–diallyl phthalate (DAP) using semi-continuous emulsion polymerization. Different functional monomers were used in their preparations of HASEs.

In this work, a hydrophobic comonomer, ethoxylated behenyl methacrylate (BEM), was used to prepare hydrophobically modified polyacrylic acid latex. The structure of BEM is shown in Scheme 1. The effects of BEM contents and latex solids on the viscosity and light transmittance of the latexes at different pH were studied.

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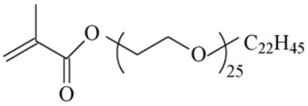

Scheme 1. Structure of BEM.

1. Experimental

Ethyl acrylate (EA), methacrylic acid (MAA) and diallyl phthalate (DAP), all chemical pure, were all domestic chemicals; surfactants OP-21 and OP-9, both industrial grades, were from Tianjin Hongmei Chemicals. Sodium dodecyl benzene sulfonate (SDBS), chemical pure, was from Shanghai Chemical Reagent Supply Association. Ammonium persulfate (APS), of Tianjin Guangfu Technology & Development Ltd., was recrystallized before use. EA and MAA were distilled under reduced pressure before use. Other chemicals were used as received. BEM is a functional monomer from Rhodia, USA. It is an aqueous solution of 50 wt% concentration with 24 wt% of MAA.

The solids of the latexes and monomer conversions were determined by gravimetry. Particle size and its distribution were determined using nano-ZS dynamic light scattering particle sizer (Malvern, UK). The viscosity of the original and diluted thickener latexes were tested using Dynamic viscometer (Anton Paar, Austria) at 30 °C or DV-II+ Pro Viscometer (Brookfield, USA). The light transmittance at different pH was followed by 662 photometer and 808 Titrando (Metrohm, Switzerland).

Emulsion polymerization was used to prepare the thickeners latex. The formula for the latex comprised of 100 g of water, 40 g of monomers including EA, MAA, 0.10 wt% of cross-linker DAP based on all monomers, and BEM at varying levels. SDBS, OP-21 and OP-9 were used as surfactants at levels of 1.0 wt%, 0.5 wt% and 0.5 wt% based on total mass of the monomers. APS was used as initiator. Semi-batch process was employed for the polymerization, in which 1/2 of the water was initially charged into the reactor, and the rest of the water was used to prepare a pre-emulsion, which was fed into the reactor at a constant rate during 3 h. The polymerization temperature was fixed at 85 °C, kept for 1 h after completion of the pre-emulsion addition.

2. Results and discussion

Table 1 shows the basic properties of thickener latexes. It is to note that BEM content was expressed as its pure amount in its mixture with MAA. Namely, an equivalent MAA amount to that in BEM solution was taken out when BEM was used. It can be seen that particle size of these latexes increased with addition of BEM, and that Brookfield viscosity of these latexes increased at first, followed by a decrease when content of BEM exceeded 8.0 wt%. Due to the presence of MAA, pH in all these thickeners was quite low, and a slight increase was observed with BEM content in the latex.

Thickener latexes of different BEM content were diluted to 0.3 wt% and 0.7 wt% solids, and their pH gradually adjusted from 6 to 11. The light transmittance and dynamic viscosity of the diluted latex thickeners during pH adjustment were followed, and the results are shown in Figs. 1 and 2. Because all samples at different solids followed a similar pattern in variation of light transmittance, only the results on latexes with 0.3 wt% solids are displayed in

Table 1
Basic properties of BEM based associative thickener latexes.

Thickener	BEM content (wt%)	Solids (%)	Conversion (%)	Particle size (nm)	PDI[a]	pH	Viscosity[b] (mPa s)
T00	0.0	27.66	97.85	78.40	0.033	2.44	5.0
T05	0.5	28.29	98.89	83.88	0.041	2.87	25.0
T25	2.5	28.48	98.56	89.12	0.017	2.99	26.7
T50	5.0	29.00	99.45	94.45	0.063	3.05	26.7
T80	8.0	29.27	98.32	136.0	0.004	3.26	18.3
T120	12.0	30.11	97.88	140.7	0.024	3.41	18.3

[a] Polydispersity index of the particle size.

[b] Brookfield viscosity done with spindle 3# at 60 rpm.