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Effects of submicron core-shell latexes with different functional groups on the adsorption and cement hydration

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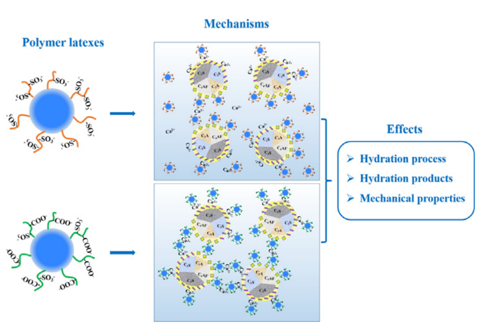
HIGHLIGHTS

- SSBR and CSBR are two polymer latexes separately assembled with $-SO_3^-$ and $-COO^-$.
- CSBR exhibits stronger retardant effect on cement hydration than SSBR.
- CSBR leads to more excellent flexural strength of cement composites.
- The retardation and toughening mechanisms of two latexes are discussed.

GRAPHICAL ABSTRACT



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ABSTRACT

The type of functional groups equipped on surface of colloidal particles is a dominant factor determining the impacts of polymer latexes on the properties of cement-based materials. In this study, two kinds of polymer latexes separately assembled with acrylic acid (AA) and 2-acrylamico-2-methyl propane sulfonic acid (AMPS) were incorporated into oil well cement as chemical additives. Their effects on hydration and mechanical properties of cement-based materials as well as mechanism were investigated and compared. The results show that polymer latexes with different functional groups present different adsorption behaviors and retardation effects in cementitious systems. These two latexes both retard the cement hydration but to different extents. Compared with the polymer latex modified with $-SO_3^-$, the latex assembled with $-COO^-$ exhibits a stronger retardation effect. This phenomenon can be attributed to the higher adsorption capability of $-COO^-$ on mineral surface as well as the stronger chelation effect formed by Ca^{2+} and $-COO^-$.

1. Introduction

As an indispensable additive in cementitious materials, polymer latexes perform amazingly on improving the properties of the cementitious materials, which not only include the anti-channeling performance and permeability of fresh cement pastes, but also contain the mechanical strength, ductility, anti-cracking ability, permeability resistance and durability of hardened cementitious materials [1–4]. Nowadays, the most commonly utilized polymer latex in cement mortar are styrene-butadiene rubber (SBR) latex, styrene-acrylate (SA) latex and ethylene-vinyl acetate (EVA) copolymer etc [5,6]. SBR latex is a large-class of polymer latexes widely used as cement additive on account of its excellent properties such as water-proofing and toughness [7–9]. It is worth noting that the traditional SBR latex faces same problems, such as poor salt tolerance, weak temperature-resistance and inferior dispersibility. Thus, it is usually modified with water-soluble monomers containing $-COO^-$ and $-SO^{3-}$ to improve its comprehensive performance. However, these modified SBR latexes exhibit

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Table 1
Chemical and mineralogical composition of G class oil well cement.

Chemical composition (wt%)									Mineralogical composition (wt%)			
CaO	SiO_2	Al_2O_3	Fe_2O_3	MgO	SO_3	K_2O	Na_2O	L.O.I	C_3S	C_2S	C_3A	C_4AF
69.68	14.51	2.33	6.28	1.01	3.09	0.74	0.40	1.92	54.17	20.29	6.22	9.09

Note: L.O.I is loss on ignition.

various impacts on cement hydration and even affect the composition and morphology of hydration products [10,11]. Furthermore, it has been widely reported that many properties of cement-based materials are closely correlated with their hydration kinetics in the early stages such as their workability, setting time and mechanical strength [12,13]. Therefore, it is of great importance to investigate the action mechanism of modified SBR latex on cement hydration.

It has been widely accepted that the impacts of the polymer latexes on cement hydration are closely associated with their adsorption behaviors on the cement grains surface and their chelation effects with Ca^{2+}. Owing to the heterogeneous charge distribution on cement grains surface, the charged polymer latexes can be considerably adsorbed onto the mineral surface through electrostatic interaction [14,15]. Besides, the strong chelation effect between polymer latexes and the Ca^{2+} adsorbed on the negatively charged mineral surfaces also promote the adsorption of latex particles on cement surface [16,17]. The adsorption of latex particles on the hydrating cement surface will suppress the diffusion of water and ions between the mineral phase and aqueous phase, thus prolong the induction period and depress the hydration rate [18,19]. In addition, polymer latexes could reduce the concentration of free Ca^{2+} in cement pore solution through chelation effect with the Ca^{2+}. In this way, the nucleation rate of calcium silicate hydrates (C-S-H) and the precipitation rate of portlandite (CH) are decelerated [20,21]. Thus, it can be summarized that the adsorption and chelation effect both inhibit cement hydration kinetics and influence the constitution of hydration products to a certain extent.

It has been verified that different polymer latexes usually possess different adsorption behaviors and retardation effects due to their surface characteristics. Winnefeld et al. [22] found that the molecular weight, the side chain density and the side chain length were the main decisive factors for the adsorption amount on cement surface. Kong et al. [23] demonstrated that acrylic based latex particles show significant retardation effect on cement hydration and the retardation effect enhanced gradually with the increase of carboxyl content. Plank and Gretz [24] compared the adsorption capacity of anionic and cationic latex particles via zeta potential and adsorption measurements. They proposed that adsorption amount of anionic latex particles on the surface of cement grains is larger than that of cationic latex particles. Wang et al. [25] investigated the difference of modification mechanism between carboxylated styrene-butadiene latex (XSBR) and SBR. Zingg et al. [26] indicated that the retarding effects of admixtures on cement hydration are closely correlated with the amount of $-COO^-$ existed on the surface of polymer.

Many literatures mainly focused on the impacts of charge characteristics of polymer on their adsorption behaviors and cement hydration. Nonetheless, the correlation between the type of functional groups and their impacts on the adsorption and cement hydration is not clear. In order to elucidate the correlation, two kinds of polymer latexes modified with various functional groups were synthesized by using acrylic acid (AA) and 2-acrylamico-2-methyl propane sulfonic acid (AMPS) as functional monomers. The influences of the two latexes on the cement hydration were characterized by setting time tests, isothermal heat flow calorimetry and XRD. The action mechanism was studied by evaluating their chelation effect with Ca^{2+} and the adsorption behaviors on the cement surface using inductively coupled plasma-optical emission spectrometry (ICP-OES), conductivity measurements, total organic carbon (TOC) tests and zeta potential measurements. Herein, the influences of SBR latexes separately modified with carboxyl and sulfonic groups on the adsorption and cement hydration can be compared. These explorations not only provide the theoretical basis for the application of polymer latexes in cement file, but also be beneficial to the development of a new type polymer latex modified cement composites.

2. Experimental

2.1. Materials

Liquid polybutadiene (LPB, $M_w \approx 1080\ g\ mol^{-1}$) and AMPS ($M_w = 207.24$) were technical grade and obtained from Ruibolong Oil Tech& Development (Beijing, China). Styrene (St, $M_w = 104.15$, AR) and AA ($M_w = 72.06$, AR) were purchased from Yuanli Chemical Tech (Tianjin, China). Sodium dodecyl sulfate (SDS, surfactant, AR), Ammonium persulfate (APS, initiator, AR) and Sodium hydroxide (pH regulator, AR) were obtained from Guangfu Chemical Technology Co., LTD (Tianjin, China). All chemical reagents were utilized as received unless specified.

G class oil well cement supplied by Jiahua Special Cement Co., Ltd. (Sichuan, China) was used in our laboratory. Its chemical and mineralogical composition are presented in Table 1, which were measured by X-ray fluorescence and quantitative X-ray diffraction Rietveld analysis respectively.

2.2. Synthesis and characterization of the styrene-butadiene latexes

2.2.1. Synthesis of the two latexes

The uniform spherical poly (AMPS-co-St-co-LPB) (SSBR) and poly (AA-co-AMPS-co-St-co-LPB) (CSBR) latex particles were prepared by micro-emulsion polymerization using AMPS and AA as the functional monomers, which provides carboxyl groups and sulfonate groups on the surface of latex particles respectively. The schematic diagrams of abovementioned polymer latexes are shown in Fig. 1.

The detailed preparation procedure, taking SSBR for example, can be described as following. The microemulsion was prepared

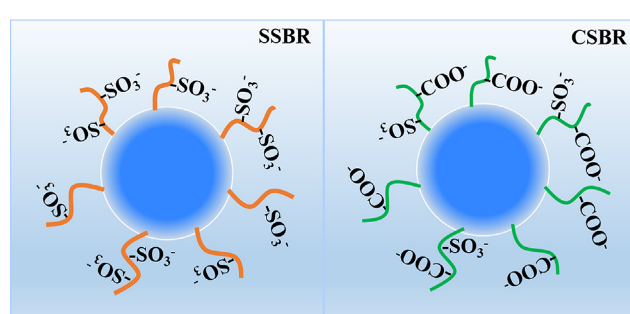

Fig. 1. Schematic diagrams of the synthesized latex particles.