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Development and use of polymer-modified cement for adhesive and repair applications

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HIGHLIGHTS

- Development of specialty cement with improved bond and tensile properties.
- Ready-to-use cement for adhesive, repair, and protective applications.
- Grindability of clinker in presence of elastomer polymeric latexes.

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ABSTRACT

Limited attempts are made to develop speciality cement possessing improved tensile and bond properties resulting from inter-grinding clinker with elastomer polymeric latexes such as styrene-butadiene rubber (SBR) or polyvinyl acetate (PVA). This type of ready-to-use cement can be of particular interest in adhesive applications requiring enhanced bond to substrates (i.e., tile adhesives, patching mortars, waterproofing slurries) as well as repair and injection works necessitating improved durability and adhesion to embedded steel bars. Test results demonstrated that latexes remain efficient after grinding to alter cement properties, including higher workability and improved flexural and pull-off bond strengths. The SBR and PVA addition rates should be limited to less than 0.4% and 0.3% of cement mass, respectively, given that clinker grindability including Blaine fineness and sieve residue could be detrimentally affected. The validity of polymer-modified cement to produce tile adhesives as per EN 12004 standard requirements is discussed.

1. Introduction

Considerable efforts and advances have been made over the past years to develop specialty cements that suit particular applications and satisfy the construction market demand. For instance, it is worth mentioning the high-early strength cement for precast industry, masonry cement for plastering works, expansive cement to compensate the volume decrease due to shrinkage, air-entrained cement for frost resistant applications, and superplasticized cement possessing improved workability and compressive strength [1–3]. The desired properties of specialty cements are achieved by thoroughly controlling the clinker chemical composition and/or incorporating suitable processing additions during the clinker comminution process.

Limited attempts were made to develop specialty cement possessing improved tensile and bond properties resulting from inter-grinding elastomer polymeric latexes during clinker processing. This type of ready-to-use cement can be of interest for adhesive and protective cementitious-based materials requiring enhanced bond to existing substrates such as tile adhesives and grouts, rendering and patching mortars, and waterproofing slurries. Other relevant applications would be for repair and injection works typically associated with stringent stability and durability requirements such as high adhesion to embedded steel bars and parent substrate, controlled shrinkage and permeability, and reduced diffusion of aggressive ions.

Latexes such as styrene-butadiene rubber (SBR) and polyvinyl acetate (PVA) are widely incorporated in cementitious materials intended for adhesive, repair, and protective applications [4–6]. These consist of very small polymer spherical particles (0.05–5 μm) formed by emulsion polymerization and stabilized in water with the aid of surfactants [7]. Earlier studies showed that the inclusion of such polymers remarkably improves workability of cementitious systems due to ball-bearing mechanism resulting form polymers adhered onto cement surfaces, which are released due to shearing action. Concurrently, the adsorption of hydroxyl

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groups and stabilizing surfactants onto cement surfaces could form electrostatic barriers that hinder cement flocculation and act as dispersing mechanism [7–9]. This practically allows reduction in water-to-cement ratio (w/c), for fixed workability, which would decrease porosity and enhance mechanical properties [10,11]. Over hydration time, Silva et al. [12] reported that the polymer acetate groups interact with interstitial aluminum and calcium ions to gradually attenuate the ball-bearing action and increase stickiness of modified system. Issa and Assaad [6] showed that SBR and PVA latexes impart improved stability to highly flowable concrete including reduced bleeding, segregation, and increased thixotropy.

In the hardened state, most studies converged that polymer-modified cementitious materials show noticeable improvement in tensile and flexural strengths with increased polymer-to-cement ratio (p/c), but reduced compressive strength [7,11,13,14]. Ribeiro et al. [13] associated the increase in tensile and flexural strengths to atrophy of hydrated $Ca(OH)_2$ crystals in the paste-aggregate interfaces, which in conjunction with less drying shrinkage, improves resistance against tensile stresses. Additionally, the polymer films are believed to create internal barriers to free water movement, which enhances internal curing (i.e., lowering porosity) and reduces micro-crack propagation inside the matrix [4,9,11]. In contrast, the benefits of polymers become much less significant under compressive forces, given that micro-crack propagation in the paste occurs more easily and at much lower tensile or flexural forces. The decrease in compressive strength has often been attributed to a combination of phenomena including increased air entrainment due to polymer surfactants, delay in cement hydration process, increased closed porosity at cement-aggregate interfaces, reduced elastic modulus, and eventual polymer-cement chemical reactions that create weaker and less stiffer structure in compression than pure hydrated cement [7,9,13,15].

Latexes found particular acceptance in applications requiring enhanced bond properties. Gomes et al. [16] reported 1.5- to 3-folds increase in bond for PVA and SBR-modified pastes at p/c ranging from 0.05 to 0.1 on concrete substrates. The microstructural images of failure interfaces showed distinct diffusion of modified pastes to the bonded concrete substrate, implying the formation of monolithic bond between both materials [17]. During pullout bar testing, Assaad and Daou [14] found that the adhesive component of bond in the local shear stress vs. slip relationships can double when SBR is incorporated at 3% of cement mass, which was attributed to electro-chemically active polymer-cement co-matrixes at the steel interfaces that help relaxing stresses during loading. Mirza et al. [18] reported that SBR and acrylic-modified latexes are indispensible for repair applications subjected to severe climatic and site conditions such as freeze-and-thaw cycles, abrasion, erosion, and permeability.

This paper is part of a comprehensive research program initiated to evaluate feasibility of SBR and PVA additions during clinker processing; tested properties include Blaine fineness, sieve residue, water demand, setting time, flexural/compressive strength, and bond to existing substrates. The effect of reducing w/c to compensate the drop in compressive strength and validation using mortars intended for tile adhesive applications are discussed. Such data can be of interest to cement producers, construction companies, and contractors involved in ready-to-use specialty cementitious binders intended for repair, injection, adhesive, and protective works.

2. Experimental investigation

2.1. Materials

Industrial clinker used for producing ASTM C150 Type I portland cement, ground granulated blast furnace slag meeting ASTM C989 Grade 80 requirements, and gypsum were employed; their chemical compositions are listed in Table 1. The relative hardness of clinker, slag, and gypsum materials determined according to the Mohs hardness scale were around 6, 5, and 2, respectively.

Commercially available SBR and PVA latexes are used. The SBR is general-purpose synthetic rubber produced from a copolymer of 70% styrene and 30% butadiene. The two compounds are copolymerized to form long, multiple-unit molecules arranged in random manner along the polymer chain [7,19]. The polymer chains are cross-linked in the vulcanization process, and stabilized in water using an anionic emulsifying system. This latex contained defoaming agent to reduce risks of air entrainment in cementitious materials; its solid content, specific gravity, pH, viscosity, median particle size, and minimum film forming temperature (MFFT) are 45%, 1.03, 8.5, 180 cP, 0.075 μm, and −5 °C, respectively.

The PVA latex is composed of 80% vinyl acetate monomer (VAM) and 20% vinyl ester of versatic acid (VeoVa). It has a white-colored milky appearance with solid content, specific gravity, pH, viscosity, medium particle size, and MFFT equal to 52%, 1.07, 4.5, 220 cP, 0.18 μm, and 4 °C, respectively. The PVA technical data sheet indicates the presence of non-ionic emulsifying system together with defoaming agent; it is designed for enhancing flexibility and water-impermeability of cement-based products. The grain size distributions of tested SBR and PVA latexes determined using laser particle size diffraction analyzer are shown in Fig. 1 (also, two cement specimens are shown in this figure).

2.2. Production of cement specimens

A 50-liters laboratory-grinding mill connected to electric counter for monitoring the specific energy consumption (Ec) was used for cement production [3,20]. The mill's drum diameter, width, and rotational speed are 400 mm, 400 mm, and 50 rpm, respectively. A total of 80 kg steel balls (36 kg of 20-mm diameter and 44 kg of 30-mm diameter) were used. Prior to grinding, the clinker, gypsum, and slag materials were crushed and sieved so that all particles are smaller than 10 mm. The gypsum and slag were dried to constant mass at 45 and 100 °C, respectively, then allowed to cool down to ambient temperature prior to use. All tests were conducted using 7 kg of mixtures composed by 80% clinker, 15% slag, and 5% gypsum. The grinding tests were performed at fixed Ec of 31.42 kWh/ton (i.e., corresponding to grinding time of 25 mins) to secure Blaine of 3340 ± 75 cm^2/g (i.e., fineness commonly targeted when producing ASTM C150 Type I cement [1]).

The effect of SBR and PVA on cement properties was evaluated by two methods, i.e. inter-grinding with clinker and post-addition to control cement (this would determine whether such polymers preserved efficiency following the grinding process). The latexes were incorporated at increased increment rates corresponding to 0.1% of cement mass; the maximum addition rate was considered being reached when Blaine fineness of polymer-modified cement deviated by ±130 cm^2/g from the fineness of control cement, as per ASTM C465 recommendations for processing additions [21]. Hence, as will be discussed later, the SBR addition rates varied from 0.1% to 0.4%, while the PVA varied from 0.1% to 0.3%; the corresponding p/c varied from 0.045 to 0.18 and from 0.051 to 0.15, respectively.

During the inter-grinding method, the required amount of latex was sprinkled over the dry clinker, vigorously mixed, then introduced in the mill with the slag and gypsum materials for processing. At end of grinding, the temperature of charge was found to increase from ambient to around 32–37 °C. In the post-addition method, the control cement already ground to targeted fineness was considered for testing, while latex was diluted with 10% mixing water prior to batching. The cement properties obtained