Construction and Building Materials 162 (2018) 628–648

Contents lists available at ScienceDirect

Construction and Building Materials

journal homepage: www.elsevier.com/locate/conbuildmat

Photocatalytically active coatings for cement and air lime mortars: Enhancement of the activity by incorporation of superplasticizers

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HIGHLIGHTS

- Polycarboxylated SPs avoided the agglomeration of photocatalysts in water media.
- Coatings of these SPs improved the NO removal rates by 15% (UV) and by 76% (solar)
- The presence of the photocatalyts reduced the static WCA of the mortars.
- SPs enhanced TiO_2 distribution, percolation and formation of thin coating layers.
- Accelerated weathering moderately reduced NO removal supporting long-run activity.

ARTICLE INFO

Article history:
Received 29 June 2017
Received in revised form 5 December 2017
Accepted 9 December 2017

Keywords:
Coating
NO removal
Superplasticizer
Photocatalysis
Polycarboxylate

ABSTRACT

Coatings made with water dispersions of different nano-particles of photocatalytic additives (titania and titania doped with iron and vanadium) were prepared with diverse superplasticizers, SPs, to optimize the atmospheric NO removal efficiency when applied onto cement- and air-lime mortars. The use of different polycarboxylate-based superplasticizers (52IPEG, 23APEG and 45PC6) prevented nano-particles from agglomeration. The steric hindrance, provided by a large density and length of side chains, was ascertained as the most effective repulsion mechanism and 52IPEG was the most efficient SP. In PC- and air-lime mortars, the coatings with polycarboxylate-based SPs improved the NO removal rates as compared with the SP-free coating: an average increase of NO degradation by 15% under UV and by 76% under solar light was found. This finding was related to the drop in the agglomeration of the photocatalysts, with more exposed active sites and a decrease of the electron-hole recombination rates. Capillary water absorption and water vapour permeability values showed that the coatings did not alter the performance of the mortars. SEM examination showed that the use of SPs enhanced the distribution of the photocatalysts yielding thinner coating layers and boosting the percolation of the active material within the mortars. Accelerated weathering showed a moderate reduction of NO removal efficiency. Coating with 52IPEG was the most efficient in preserving the activity. Measurements of Ti content showed a low washout of the TiO_2 nano-particles, supporting the long-run activity of these coatings.

1. Introduction

Current urban environment presents some toxic gases as nitrogen oxides (NO and NO_2, usually noted as NO_x) which are responsible of air pollution. This polluted environment is a problem in our society because harmful gases and airborne particulate worsen human health [1]. Furthermore, the interaction of these compounds with the exposed areas of building materials has a direct detrimental effect on functionality and aesthetic building appearance [2], leading to dirt accumulation that demand spending economic resources in cleaning processes.

In order to decrease the levels of pollutants and, consequently, to reduce their negative impact, the photocatalytic oxidation (PCO) of these substances, their conversion into less or even non-harmful compounds and their final removal have shown to be efficient in different systems [3]. To this aim, building materials have to be modified either by inclusion of photocatalytic agents during their manufacture (bulk incorporation) or by *in situ* coating them with those active agents [4–7].

The excellent characteristics of TiO_2 among the photocatalysts have led to vast research on its applications. Different building

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https://doi.org/10.1016/j.conbuildmat.2017.12.087
0950-0618/

materials, particularly cementing matrices, have been modified by the presence of TiO_2 [4–6]. Good values of gaseous pollutants removal together with the provision of self-cleaning ability to these active materials have been reported [6–8]. To tackle the well-known constricting sensitivity of the titania, which is limited to UV light, different dopant agents of the crystalline lattice of TiO_2 have been tested. Literature reports the use of many different metallic cations as well as p-block elements (individually or in co-doped systems) as dopant elements [9]. This approach reduces the band-gap of the titania lattice, allowing it to absorb visible light photons. Therefore, the photocatalytic compounds, with enlarged sensitivity, can be active under visible irradiation. It should be noted that sunlight shows 60% of visible photons in comparison with a mere 4.5% of UV photons. So far, just very few works have been devoted to the study of these doped photocatalysts when incorporated into cementitious matrices [10].

The coating application of photocatalysts onto building materials is gaining a growing interest owing to several advantages [7]

(i) It allows applying active agents in pre-existing construction structures.
(ii) Active sites are located at the surface of the materials: this fact avoids the inclusion of the photocatalysts in the inner, inaccessible part of the matrices, thus yielding better performance of pollutants removal. Previous works have demonstrated how coatings of TiO_2 reach photocatalytic efficiencies of up to 60% whereas just a maximum of 45% was found for TiO_2 incorporated by mass [11,12]. The fact that PCO requires the adsorption of the pollutant onto the active site of the photocatalytic additive should be kept in mind.
(iii) Coating application requires a lower consumption of photocatalytic additive than bulk addition: in a comparison between mortars coated with TiO_2 and mortars with TiO_2 in bulk, similar photocatalytic performances were found, although coating was loaded with 20 times less TiO_2 [11].
(iv) The presence of the additive on the surface of the materials can lead to changes in their hydrophilicity (photo-induced superhydrophilicity). As a consequence, materials exhibit self-cleaning performance: the reduction of the water contact angle (WCA) allows the water to easily remove the dirt (oily smog, dust, carbonaceous particles ...) [13–15].
The easily washable surfaces would also contribute to the long run activity of the photocatalytic additives, since the final products of the PCO would be expected to be removed by the water sweep.
It has to be noticed, however, that some researchers warn about problems ascribed to the WCA reduction: the increased wettability of the surface of the building materials could give rise to an increase in water absorption that would negatively affect these materials [16]. Therefore, changes in the WCA are not desired to be accompanied by dramatic changes in the water transport phenomena of the treated materials.

Assuming the interest of these active coatings, different factors related to the characteristics of the substrate have a strong influence on the performance of these modified materials: roughness, pore size distribution, chemical and mineralogical composition, which can affect the adhesion of the coating [17,18]. The last point is strongly related to the loss of efficiency of these active coatings after weathering or abrasion phenomena [19]. Substrates with high porosity and roughness have shown better retention of particles of the photocatalysts, thus enhancing the resistance of the materials to different degradation mechanisms [20]. Literature shows successful coating applications onto limestone, bricks, cement and lime mortars [21,22]. Two different strategies have been put forward [23]: dispersion of titania nano-particles in organic carriers with adjuvant water repellent compounds (based, among others, on poly-alkyl-siloxanes, acrylic polymers ...) [24–27] or water dispersions of the active nano-particles [16,28–30]. High color variations and compatibility problems have been mentioned as main concerns referring to the first approach. The second approach, with the use of aqueous dispersions, appears to be much more environmentally friendly and low-cost. However, nano-particles tend to combine forming aggregates, agglomerates, and flocs, some of them with strong bonds, reducing the active sites of the photocatalysts. Conventional methods of stirring cannot guarantee a proper dispersion of the nano-particles [31]. In this line, very limited research has been devoted to the optimization of the aqueous sprayable suspensions in order to achieve better performance of the coatings. Particularly it is very important to reach a good dispersion of the nano-particles of the photocatalysts with the aim of: 1) increasing the number of active sites and 2) enhancing the electron-hole separation in order to prevent their eventual recombination that suppresses the photocatalytic activity [32,33].

The combination of the photocatalysts with superplasticizers, which act as dispersing agents, can thus lead to more efficient coatings and it is precisely the main focus of the current work. Four superplasticizers (SPs), compatible with cement matrices, were chosen as the subject matter of this study: three different polycarboxylate ethers derivatives were synthesized and comparatively studied versus a naphthalene-based superplasticizer. Their interactions in aqueous dispersions with nano-structured titania and Fe- and V-doped titania were studied. Active coatings were applied onto cement and air lime mortars. The effect of the different superplasticizers was assessed by studying the photocatalytic efficiency in NOx removal under different illumination sources (UV, solar and visible light). Studies on the water contact angle modifications due to the presence on the surface of the mortars of the photocatalysts were also carried out to estimate the potential self-cleaning ability of these coatings. The work also reports changes in the water absorption, capillarity and water vapour permeability of the treated mortars and their microstructural examination. Finally, artificial accelerated weathering was applied to the treated mortars to assess the long run performance of these coatings.

1.1. Background on superplasticizers

Superplasticizers are common admixtures used in cementitious matrices in order to improve workability of the plastic mixtures avoiding the excess of mixing water [34]. When added to cement-based systems, these molecules exhibit a dispersing action between cement particles due their electrostatic repulsion and/or steric hindrance effects [35,36] preventing them from agglomeration. The last generation of superplasticizers belongs to the polycarboxylate ethers family which are based on a main backbone with carboxylic groups with side ethylene oxide unit chains. Consequently, at the alkaline pH of the cement media, the carboxylic groups appear deprotonated and negatively charged [37]. By means of these negative charges, polymeric molecules are adsorbed onto the positively charged surfaces of the cement particles. The dispersion effect takes place because of the steric effect induced by the polyethylene lateral chains as the predominant effect [38], and the electrostatic repulsion forces, as a minor contribution [39]. Previous works have studied the influence of the superplasticizer molecular architecture on the properties of the cement mixtures [40,41] and in other binding systems [36]. These works have reported that the parameters with strong influence on the performance of the superplasticizers are the size of the side chains, the number of the carboxylic groups of the main backbone (as determined by their anionic charge density) as well as the pres-