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Silver nanoparticulate enhanced aqueous silane/siloxane exterior facade emulsions and their efficacy against algae and cyanobacteria biofouling

James MacMullen [a,*], Zhongyi Zhang [a], Hom Nath Dhakal [a], Jovana Radulovic [a], Alkistis Karabela [b], Gianluca Tozzi [b], Samuel Hannant [a], Mohammed Ali Alshehri [a], Vincent Buhé [a], Constandinos Herodotou [a], Miltiadis Totomis [a], Nick Bennett [a]

[a] *Advanced Polymer and Composites (APC) Research Group, School of Engineering, University of Portsmouth, Portsmouth, Hampshire PO1 3DJ, UK*

[b] *Mechanical Behaviour of Materials (MBM) Research Group, School of Engineering, University of Portsmouth, Portsmouth, Hampshire PO1 3DJ, UK*

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Silver nanoparticulate enhanced aqueous silane/siloxane emulsions and their efficacy against biofouling mechanisms are presented within this study. Different concentrations of silver nanoparticulates were added into viscous shear-thinning aqueous treatments and key attributes required for facade remedial applications assessed. Water repellence, biofouling resistance, and aesthetical alteration were studied to assess key treatment attributes. In addition, assessment of the porosity, sorptivity, and treatment depth was used to identify penetration and facade protection efficacy and morphological alteration of the masonry substrate. Results showed that silver nanoparticulate incorporation did not impede treatment penetration, better water repellent attributes were achieved with increased concentration while effectively conserving the morphology and aesthetics of the substrate. It was concluded that the reduced bioreceptivity observed primarily stemmed from the silver nanoparticulates ability to sanitise the surface, and that only small concentrations (<0.5%wt) were required to attain significantly beneficial improvements. Treatments were deemed practically and commercially viable for retrofit and heritage projects.

1. Introduction

Silver is one of the most widely used nanomaterials. With the first development of silver vessels around 400 BC the antibacterial nature of silver was found from the outset. Even prior to 1938 colloidal and nanoparticulate forms of silver (particle diameters circa 30 nm) were used in over 650 different applications to treat infectious conditions (Murr, 2009). It has been found that silver nanoparticulates are particularly effective against gram-positive and gram-negative bacteria (Shirakawa et al., 2013). Research by Choi et al. (2010) has shown that Ag ions are effective at penetrating and treating dense biofilms through diffusion while nanosilver aggregates are suitable for the sanitisation of plantonic cultures, where reduced ion/particle diffusion occurs. This is attributed to cytotoxic perturbations created within cells (particle sizes <30 nm) and related to silvers physical–chemical properties (Bottero et al., 2011). In addition, fungal enzyme systems have also been found to become disrupted by Ag ions causing cell death (Murr, 2009). Nanoparticulate suspensions of silver can be theoretically created pure, but in practice are mixtures of silver ions, nanoparticulates, and either sub-nano or larger sized nanoparticulate aggregates (Hadrup and Lam, 2014). Particles of smaller diameters (<25 nm) have been shown to have higher dissolution rates than larger particles, resulting in a much higher release of toxic ions (Bottero et al., 2011). Algae toxicity values for silver in ionic, nano, and micron size ranges in water may be considered as being $1.1 \pm 0.5\ \mu g l^{-1}$, $3.0 \pm 0.7\ \mu g l^{-1}$, and $900–1030\ \mu g l^{-1}$ respectively according to Angel et al. (2013). However, a study by Oukarroum (Oukarroum et al., 2012) suggests that silver nanoparticulate sensitivity varies greatly between algae species due to varying aggregation kinetics and environmental influences. Work conducted by Gutarowska et al. (2012) suggests that silver nanoparticulate efficacy to resist bacterial colonisation after deposition on surfaces may endure for a long time and warrant its use in the protection of historic artefacts.

* Corresponding author. Tel.: +44 2392 842340.
E-mail address: James.MacMullen@port.ac.uk (J. MacMullen).

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These sanitisation mechanisms and material traits therefore make silver nanoparticulates of key interest in many diverse fields and applications; from filters and biofilm membranes to anti-bacterial coatings for medical facilities, although only when the cost can be justified (Shirakawa et al., 2013).

Facade water retention increases with soiling and thus exacerbates the associated degradation mechanisms of exterior masonry walls (Djongyang et al., 2009; MacMullen et al., 2011; Rirsch et al., 2011); which includes further biological colonisation by larger vegetative matter (Barberousse et al., 2007; Tran et al., 2012; Martinez et al., 2014). As energy consumption is detrimentally effected by facade deterioration retrofitting of existing UK housing stock to improve the thermal envelope efficiency of structures has become a key requirement necessary to meet carbon emission targets. One such target includes an 80% CO_2 reduction by 2050 against 1990 CO_2 output levels (Frossel, 2007; Rirsch and Zhang, 2010). Such a large reduction and rising energy demands, driven by population increase and escalating resource demands cannot be achieved by one method alone (Lorenzoni et al., 2007; Odenberger and Johnsson, 2007; Osmani and O'Reilly, 2009; Booth et al., 2012).

Aqueous silane/siloxane water repellent emulsions are the current trend in the facade remediation industry due to their greener credentials compared to traditional solvent based counterparts (Buyl, 2001; Somasundaran et al., 2006). These emulsions exhibit shear-thinning properties allowing for controlled application unlike conventional solvent based solutions and water present in these formulations that act as a carrier may be synergistically used as the catalyst for curing (Council Directive, 1999). Silanes are small molecules that can be used to modify masonry pores without blocking them and have the potential to penetrate deep into a substrate. 3D networks are produced as silanes bond to both the pore and themselves through typically 3 functional sites on each molecule. A coating conversely seals a porous structure and does not penetrate deep (typically 1–2 mm) compared to treatments (typically greater than 10 mm for masonry but highly dependent on substrate morphology) and line pores which allow the substrate to breath and resist compromised protection when chipped. Pore lining treatments allow water vapour to travel through the porous substrate while reducing liquid water ingress through alteration of the pores surface free energy (Radulovic et al., 2013; Zhang et al., 2013). Coatings seal the substrate at the interface stopping the dissipation of internal humidity, this increases the potential for internal biological propagation and structural degradation as relative internal humidity increases (Parnell and Popovic Larsen, 2005; Poel et al., 2007).

The bioreceptivity of treated exterior facade surfaces containing nanosilver in particle/aggregate form is not well established, and although adhesion to substrates for biofilms and marine macro-organisms are believed to be directly linked to micro-topography and interfacial chemistry characteristics (Guezennec et al., 2012) more work in this field is required. Biofilms on facades that cause staining may be composed of a variety of different organisms including algae, cyanobacteria, heterotropic bacteria, protozoa, fungi and even small animal and plant life. Previous work suggests that of these, algae, cyanobacteria and fungi are able to survive under UV conditions to such an extent that some strains even can be repeatedly dried and rehydrated (Gaylard and Gaylard, 2005) and therefore present a challenge to effectively remove. Several interesting studies have been conducted to assess the durability of titanium dioxide and silver nanoparticles in aqueous colloids and coatings for a variety of exterior antifouling applications have been conducted (Graziani et al., 2014; Ruffolo et al., 2013; La Russa et al., 2012; Quagliarini et al., 2012). However, currently almost all work carried out on silver nanoparticulates used for facade protection has been conducted using coatings and not treatments. Current studies on nanoparticulate treatments typically do not deal with external facade building materials and directed around internal structures such as wood or plasterboard which have different bioreceptivity characteristics. Recent studies conducted by the Authors evaluated the biofouling resistance of titanium dioxide and zinc oxide nanoparticulate enhanced silane/siloxane facade treatments against algal colonisation (MacMullen et al., 2012; Zhang et al., 2012, 2013; Radulovic et al., 2013). This study further expands upon nanoparticulate incorporation in such novel viscous shear-thinning emulsions by looking at the influence silver nanoparticles have on the performance of such silane/siloxane treatments to protect and enhance the facade interface. Unlike prior work, sanitisation is not considered here to be limited extensively by environmental conditions and thus may be more effective at sustained sanitisation. Information regarding how well these treatments would perform with variation in concentrations is critical for assessing service life, performance durability, and limiting constraints such as aesthetical impact. The work presented here should help nanoparticulate silane/siloxane emulsions to be developed, optimised and used effectively in future.

2. Experimental

2.1. Emulsion preparation

Silver nanopowder <100 nm 99.5% coated with 0.02 %wt Polyvinylpyrrolidone (PVP) dispersant was purchased from Sigma–Aldrich Co. LLC. n-isooctyltriethoxysilane 95% (ITES) and polydimethylsiloxane (PDMS) was obtained from ABCR Gmbh & Co. KG, while distilled water (0PPM) was sourced from ReAgent Chemical Services Ltd. The emulsions were prepared by high shear mixing with <0.5 %wt of non-ionic polyoxyethylene stearate (POE) used as the emulsifier. This was then followed by the introduction of a nanoparticulate dispersion produced by a technique developed by the Authors volume ratio was maintained at oil 8:2 water. Emulsion details are given in Table 1 and examples of silver emulsions before application are shown in Fig. 1.

2.2. Preparation of mortar samples

Mortar samples (13 cm × 29 cm × 2 cm) containing a 3:1 sand-to-cement ratio were used for testing. A 0.6 water/cement weight ratio was used to create a highly porous substrate allowing them to be theoretically more susceptible to algal retention while aiding morphological scrutiny (Giannantonio et al., 2009). The mortar was put in moulds and left for three days to cure before being removed and left to dry for a further 4 months. Each treated sample had a total of 40 g of emulsion applied using a pre-wetted brush to all exterior surfaces and allowed to cure for a week. Plastic composite rods were attached using epoxy resin to the top rear of each culture streaming sample and left for 24 h to cure before being placed inside the test rig to reduce possible VOC contamination of the system.

Table 1
Emulsion types used during study.

Treatment abbreviation	Treatment description	Nanoparticulate incorporation (%wt)
TC	Mortar control (no treatment)	N/A
EC	Control emulsion (no nanoparticles)	N/A
ES1	Silver emulsion	<0.1
ES3	Silver emulsion	<0.3
ES5	Silver emulsion	<0.5