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Research Article

Proposing a sustainable strategy for the fabrication of robust anti-soiling coatings with enhanced antibacterial attributes for non-absorbent substrates

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Abstract

In this paper, we propose a convenient methodology for fabricating a generic structure toward developing a robust, easy-to-clean transparent coating with inherent antibacterial properties for smooth, non-absorbent surfaces, such as glass and plastics. A two-step coating comprising an organopolysilazane primer and an alkoxysilane topcoat, based on positively charged quaternary ammonium silanes, is proposed. The topcoat is co-condensed with the primer to provide a hybrid structure with high wear strength even on surfaces that lack surface hydroxyl groups. Surfaces examined included glass and PMMA. The coated samples were studied in terms of abrasion resistance as well as anti-soiling and antimicrobial performance. It was found that the quaternary silane compound could covalently graft onto the primer acting both as an antibacterial, anti fungicidal, and hydrophobizing agent. The utility of amphoteric surfactants within the coating's solution was also examined. The resulting structure was transparent and exhibited pronounced self-disinfecting properties with remarkable sustainability. These attributes suggested a dual functionality of the coating, i.e., both anti-soiling and antimicrobial, thus rendering it a potential candidate for numerous industrial and commercial applications.

Introduction

Common smooth, non-absorbent surfaces are constantly exposed to various pollutants and microbes. Humidity, limescale, stains, and germs can easily penetrate into the surface's micro-pores promoting gradual surface degradation. Easy-to-clean hydrophobic coatings have found a plethora of applications in scientific and industrial fields [1-3]. By modifying a surface with an easy-to-clean coating, new functionalities, including anti-corrosion, anti-scratch, ice-phobic, non-stick, and most importantly, antimicrobial [4,5], can be adapted. Concerning antimicrobial properties especially, it has been shown [6] that microbial adhesion decreases on increasing hydrophobicity due to the decrease in interaction and contact area. Therefore, antisoiling attributes may give rise to passive antimicrobial protection mechanisms as well. Over time though, the strength of this effect is reduced, due to the degradation of non-adhesive properties, which eventually leads to biofilm formation. On the other hand, active antimicrobial coatings are usually highly efficient in killing the microbes, but after a certain period, significant amounts of debris or dead microbes start accumulating on the surface, thus affecting its functionality. A coating that could effectively combine both antisoiling and antimicrobial attributes is of utmost importance.

The performance of a coating however is strongly affected by the chemical and physical characteristics of the chosen materials, techniques and methods applied, and most importantly, the nature of the substrate. Hence, features such as wettability and critical surface tension are principal indicators that affect crosslinking reactions between the substrate and the coating, either reinforcing or inhibiting them [7]. Inorganic substrates can easily be modified and coated due to their high surface energies, whereas polymeric materials, such as polyethylene (PE), polyvinyl chloride (PVC), or painted

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surfaces, yield very low surface energies, thus preventing their proper and efficient processing [8,9], ultimately leading to poor mechanical and chemical stability [10]. This results in limited applicability, especially in high-touch surfaces and public facilities where painted surfaces are dominating.

In recent years, sol-gel especially has emerged as a promising technology in the fabrication of functional coatings since it can provide flexibility along with broad spectrum capabilities in the design of thin film nanostructures. In this article, a robust sol-gel polysiloxane/siloxane coating system is presented. The aim was to combine in a facile way hydrophobic properties with active antibacterial attributes within a single coating, capable of attaining a sustainable dual functionality, i.e. antisoiling and biocidal, for a variety of surfaces, especially those of low surface energies.

Experimental section

Materials: A propyltriethoxysilyl-substituted polymethyl (hydro)/polydimethylsiloxane was used as the organopolysilazane (Durazane 1500 rapid cure, Merck KGaA). Tetraethyl orthosilicate (Dynasylan A, Evonik Operations GmbH) was used as a silane coupling agent. The biocide octadecyl dimethyl (3-triethoxysilyl propyl) ammonium chloride (42% in ethanol) from Sigma-Aldrich was employed to impart antibacterial properties [11-13] to the coating. Glacial acetic acid, butyl acetate (anhydrous, 99%), and ethanol (99,8%) were all purchased from Sigma-Aldrich. Finally, an acrylic-modified betaine copolymer (Polyquart Ampho 149, BASF Corporation) was used as an amphoteric surfactant, in order to improve wetting and drying time.

Preparation of the coating

A two-step coating scheme was followed. First, durazane 1500 RC was dissolved in butyl acetate at 1% w/w and vigorously stirred to produce a homogenous primer solution. Meanwhile, in a separate beaker a silane blend of 3g tetraethoxysilane and 2.4 g octadecyl dimethyl (3-triethoxysilyl propyl) ammonium chloride was dissolved in an ethanol/water mixture (70:30 v/v), acidified with glacial acetic acid at pH~3. The mixture was vigorously stirred for 1 hour and left to age at ambient conditions for at least 24 hours. Then the amphoteric surfactant was introduced at 0.1 wt% concentration, to yield the final top-coat solution.

The primer was applied on clean glass and PMMA samples (each 20 x 20cm^2) by HVLP spraying (Sata Minijet 4400B) and was left to dry at ambient conditions for about 10 min. The top coat was subsequently applied to the primer layer with the aid of a microfiber towel. The coated substrates were left to dry at room temperature for 7 days. Then they were studied in terms of antisoiling behavior, abrasion resistance, and antibacterial efficacy.

Results and discussion

The prepared coatings were transparent and hydrophobic with water contact angles exceeding 90°. Generally speaking, the observed compositions seemed to exhibit most of the required properties of any functional coating, such as good adhesion, scratch resistance (mostly on PMMA samples), hydrophobicity, and mechanical and chemical resistance.

The organopolysilazane comprised alternating silicon and nitrogen atoms, ≡N-S-N≡ on its backbone which provided adhesion, and mechanical and chemical stability to the coating even on non-hydroxylated surfaces. Surface energy was found to be in the order of 30mN/m. Transamination, hydrolysis, and polycondensation reactions of the organopolysilazane probably led to the creation of reactive ≡Si-N, ≡Si-H, and ≡Si-OH groups [14-17] which reacted with hydrolyzed species of tetraethoxysilane and with residual silanol groups resulting from the hydrolysis of ethoxy groups. Enhanced crosslinking between the primer and the top coat provided a three-dimensional network with multiple anchor sites where grafting of the quaternary silane was facilitated. It was assumed that due to the increased density of active anchor groups and thickness of the polymer matrix (about 1 μm) only a part of quat molecules were available to interact with the substrate through covalent bonding. The rest were probably trapped in the bulk phase of the siloxane-silazane copolymer, with their long aliphatic chains extending beyond the three-dimensional network. Hence, the coating's antimicrobial activity was not affected by the substrate's nature. The addition of the amphoteric surfactant offered good wettability and pronounced adhesion, especially to non-polar substrates. It was also assumed that the surfactant domains which were not adsorbed on the substrate may exhibit synergy with the quaternarized silanes by exposing positively charged ammonium groups, thus enhancing antimicrobial activity. The possible structure of the proposed coating is shown below (Figure 1).

The coating's antisoiling behavior was evaluated by correlating hydrophobicity alterations to optical transmission losses evaluated by UV-VIS spectrophotometry after cyclic soiling testing on glass substrates. More specifically, the

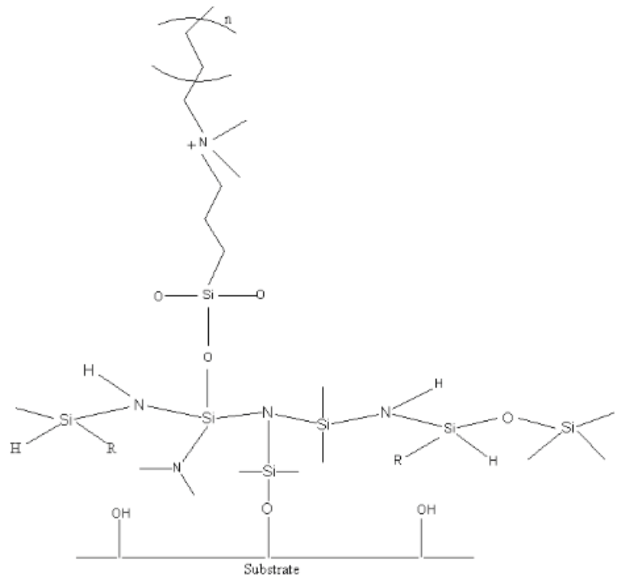

Figure 1: Hybrid siloxane-silazane copolymer modified with quaternary ammonium silanes.

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proposed coating and four commercial glass coatings with WCA values ranging from 30° to 105° were subjected to 5 cycles of soiling test. Each test followed a specific soiling sequence: First the sample was immersed for 5 min in distilled water. Then dust was applied by blowing air. Drying for 24 hours followed. The 1st and 5th cycle additionally included a final step of washing with distilled water for 30 sec. The proposed anti-soiling & anti-static coating demonstrated values of WCAs in the order of 105° (dark blue line in Figure 2). In general, hydrophobic coatings with high contact angles performed best. It was also proven that soil accumulation, transmittance, and surface energy were strongly correlated. Furthermore, the soiling test cycles revealed antistatic functions of the proposed coating. It was assumed that the long aliphatic chain of the Si-QUAT promoted lubricity, while, at the same time the N^+R_3 polar group allowed strong interactions with moisture, thus increasing the conductivity of the coating's surface. As a result, the coating's tendency to accumulate static electricity was dramatically reduced.

Adhesion strength, especially on surfaces that lack free hydroxyl groups was evaluated by conducting wet scrub abrasion tests on glass and PMMA, the latter being either primed or non-primed. Testing was performed according to standard EN ISO 11998. As expected, coated glass sampled revealed an excellent abrasion resistance (Figure 3). The more important finding however was the significant improvement in abrasion resistance of coated PMMA after priming compared to the non-primed sample, thus highlighting the role of polysilazane in increasing interfacial adhesion, due to enhanced crosslinking reactions.

The antibacterial performance of the coating was performed on coated Leneta-Foil according to the Japan Industrial Standard JIS Z 2801:2010 Antimicrobial products-Test for antimicrobial activity and efficacy. The test bacteria used were *S.aureus* Gram-positive bacteria and *E.coli* Gram-negative bacteria. It was found that the coating exhibited strong germicidal efficacy, even 10 min after application, on both bacteria types (Figure 4). After 24 h bacterial colonies were reduced by more than 99.9%.

Curing time and synergism with cationic groups of the amphoteric surfactant seemed to further strengthen antibacterial efficacy. The latter was, to a large extent, maintained, even after abrasion. It was assumed that the polysilazane-siloxane network provided a hard matrix that encapsulated antibacterial functions. Moreover, a small residual amount of quaternized silanes seemed to be enough to enable effective self-disinfection through a contact-killing mechanism.

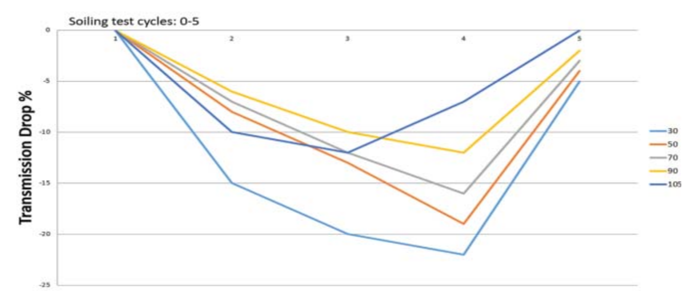

Figure 2: Anti-soiling properties vs Optical transmission loss.

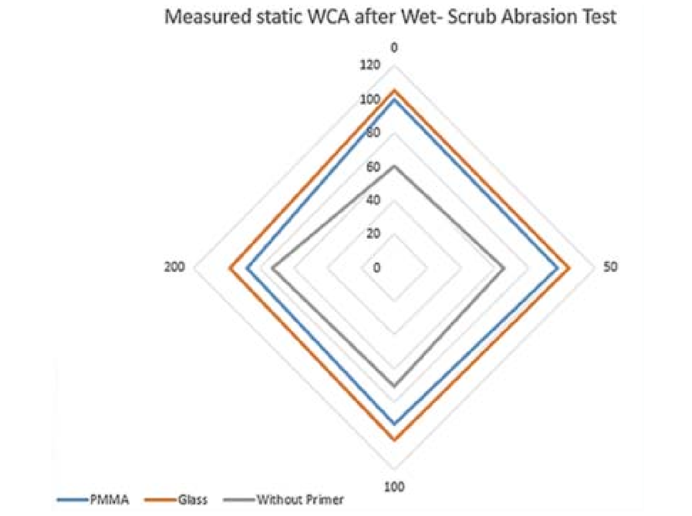

Figure 3: Abrasion resistance of the coating on glass, PMMA substrate, and PMMA substrate without primer.

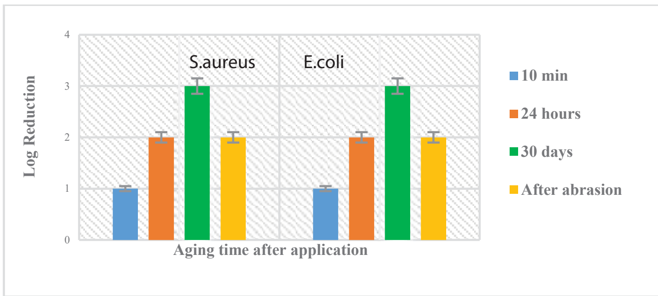

Figure 4: JIS Z 2801:2012: Antimicrobial activity on coated Leneta-Foil.

Conclusion

The methodology for formulating in a facile way a permanent anti-soiling barrier with sustained antimicrobial activity is hereby proposed. Curing takes place at room temperature with atmospheric humidity, through the use of silane-based precursors and a quaternary ammonium coupling agent, which can sufficiently interact with the organic-inorganic composition. The incorporation of an amphoteric surfactant aids further in antimicrobial effectiveness. The hybrid coating composition thus produced, can be easily applied to a variety of substrates, even non-hydroxylated ones. Possible applications include permanent easy to clean or self-cleaning coatings for architectural glass, glazed tiles, sinks, toilets, plastic apertures, touch screens, keypads, door handles, etc. of various sectors, such as medicine, pharma, household, sanitary, gastronomy, public transport and so on. Formulation and application flexibility promise scaling up capabilities in an industrial environment. Further work needs to be conducted, especially with regard to the correlation of the coating's chemical composition with mechanical and physical properties. Towards this end, a systematic study of its microstructure with the aid of analytical techniques is underway.

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