

Smart antimicrobial coating with endless applications

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ABSTRACT

The global demand of antimicrobial coatings is increasing in leaps and bounds following a CAGR of 13.4%. In spite of huge demand in several industrial sectors, only few antimicrobial products are available for the effective protection against invasive pathogens. This article describes an innovative smart quasi bioceramic coating technology that shows potential of imparting long term microbial protection to the coated articles. The coating is single component ready to use, environmental friendly, transparent, hard yet flexible new silicone quasi-bioceramic material that can adhere strongly to numerous substrates such as metals, textiles, papers, woods, plastics, ceramics, concretes, paints, glass etc. The liquid precursor to coating can be applied by spray, dip, brush, roller or wiping technique and dries in an ambient condition without the need of external heating. The coating becomes invisible after it is completely dry and does not hide the appearance of the underlying surface. The nominal thickness of the dry coating is between 500 nm to one micron and possesses high scratch resistance. Coating shows high thermal and environmental stability along with high mechanical properties. The atomic force microscopic analysis of the dry coated surface indicates that the material binds with individual grains of the substrate at a nanoscopic level and shows significantly low coefficient of friction. The coated substrates when tested as per ASTM showed 99.99% reduction of pathogens.

Keywords: antimicrobial coatings, thermal stability, scratch resistance, low coefficient of friction, nanoscale morphology

1.0 INTRODUCTION

The world has witnessed unprecedented growth in infectious diseases in past few decades. Do you know that more than eighty percent of infectious diseases are transmitted through touch? As per the World Health Organization report, nearly 50,000 men, women and children die of the infectious disease every day. The antibiotics and other lifesaving drugs are losing their effectiveness as microbes are becoming stronger and resistance to such drugs. Exponentially growing population and rapid urbanization is forcing people to live in overcrowded places with low level of hygiene. Moreover, significant increase in air travel could rapidly transmit infectious disease from one place to another [1].

The medical device related infection is the second biggest cause of worry for the health sector [2]. In USA alone, nearly one million cases of nosocomial infections are recorded every year. About 95% of such infection cases are related to catheter. About 5% of central venous catheters inserted in USA each year results into complications due to blood stream infection. Similarly, infections of surgically placed intravascular devices such as cardiac pacemaker, vascular grafts, heart valves etc., pose life threatening conditions with risk of mortality exceeding 25% [3]. Unfortunately, treatment of the surgical device related infections are expensive and could cost as high as \$50,000 [4]. It is therefore eminent that strategies to prevent device related infections should be the priority for the healthcare sector.

It has been discovered that bacterial colonization of the indwelling device is the primary factor associated with infections and malfunctioning of devices [2]. Several approaches of using antimicrobial agents to combat infection due to bacteria adhesion has been proposed. Coating of surgical implants with antimicrobial agents has shown several advantages over other methods [5]. As per a recent market analysis report, the antimicrobial coating market in year 2015 was estimated to about US\$2.1 billion and is expected to reach US\$4.2 billion in year 2021 with a CAGR of 13.4%. While medical and indoor air quality management were the major application areas, silver was the dominant ingredient in such antimicrobial coatings. Although, silver is an important metal that could impart antimicrobial properties yet the use in biomedical devices has been regulated due to safety reasons related to building of high level of silver in serum. Additionally, it is crucial to use silver in a size smaller than 10 nm for the best antimicrobial activities [6]. The use of silver in improper manner could have adverse effect and develop stronger drug resistance pathogens.

Although the demand of antimicrobial coatings is high yet few effective materials are available due to lengthy regulatory approval process. The U.S. Environmental Protection Agency (EPA) regulates the use of antimicrobial products as pesticides and U.S. Food and Drug Administration (FDA) regulates the antimicrobial products as drugs.

1.1 Background of Coating Development

Typically an antimicrobial surface or coating contains an antimicrobial agent that inhibits the ability of

microorganisms to grow on the surface of a material [7]. The nature of such can be varied in their composition and mechanism of action. Greater interest is being currently evinced on the use of such surfaces and their possible use in various settings including clinics, industry, and even at home.

1.2 Classification of Antimicrobial Coatings

The antimicrobial coatings can be classified into different categories such as inorganic (heavy metal based), organic (organosilanes), nanomaterials and antimicrobial peptides.

(a) *Inorganic and metal based:* Among the inorganic types, silver and copper tend to be popularly used ingredients. Besides this there also exist other metal based coatings. The uses of these types have been well documented. Despite their advantages, there are toxicity concerns over a period of time due to leaching. Long term dosage effects are not well documented.

(b) *Organic compounds and derivatives:* Apart from these metal based approaches there are also coatings that are based on organo-compounds. For example, organosilanes are a popularly adopted solution since they present a virtually hydrophobic surface incapable of hosting any colonization properties. Their applicability on rough as well as smooth surfaces gives an advantage of being over a wide range of products from clothing and room walls to biomedical equipment. Their non-reactive nature makes them less prone to leaching and hence interaction upon human contact [8].

(c) *Nanomaterials:* Nanoparticles have also entered the domain of antimicrobial applications due to their extraordinary properties and behavior. There are more studies being carried out on the ability of nanomaterials to be utilized for antimicrobial coatings due to their highly reactive nature.

(d) *Anti-microbial Peptides (AMPs):* This is a totally biological based application that is gaining considerable attention. The AMPs can be functionalized onto a surface by either chemical or physical attachment. Further, can be physically attached by using oppositely charged polymeric layers and sandwiching the polypeptide between them. This may be repeated to achieve multiple layers of AMPs for the recurring antibacterial activity [9].

Flora Coatings has developed a global patent pending INVESIL™, a thin silicone based smart quasi-bioceramic coating that can adhere strongly to most surfaces including metals, textiles, wood, plastic, concrete etc., and effectively impart significant antimicrobial characteristics to the coated substrate. The application of INVESIL™ could be in household items (such as countertops, refrigerators, cooking stoves, toys, etc.), transportation (such as airplane cabins, rideshare cars, trains, buses etc.) shopping malls (shopping carts, table, chairs, handrails etc.), schools,

public restrooms, restaurants, electronic gadgets, hospitals, medical equipments and countless others that still need to be explored. The following sections describes the **key parameters** (such as stability, mechanical properties, surface features and antimicrobial efficacy) required to assess the properties of an effective and robust antimicrobial coating.

2.0 MATERIALS AND METHODS

2.1 Coating Development

The INVESIL™ is an environmental and user friendly transparent quasi-bioceramic flexible ready to use product. This coating acts as robust barrier against microbial activities. For the first time, we have achieved a stable solution of TRION™ (i.e., silver, tantalum and zirconium) nanoparticles of desired sizes in an exempted environmental friendly solvent along with a blend of effective antimicrobial compounds. Our coating is easy to apply and does not require extensive surface preparation. The coating material reacts with the substrate to form a permanent protective layer. The INVESIL is a high performance coating, scratch proof with hardness exceeding 200 MPa and thickness below 1/10th of human hair.

2.2 Thermal Analysis of INVESIL

To assess the stability of the materials, thermogravimetric analysis was performed on the solid INVESIL containing inadvertently entrapped volatile solvent (Figure 1).

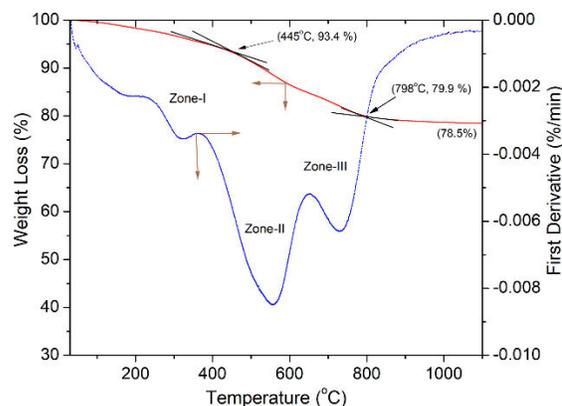


Figure 1: Thermogravimetric analysis (TGA) of solid INVESIL. Inert atmosphere thermogram showing weight loss in the solid coating as a function of temperature. First derivative of the curve has suggested that degradation phenomenon took place in three steps. Exceptionally, high thermal stability is achieved as a result of stable residual structure.

The heating rate of 10 °C/min was adopted to check the stability of the solidified INVESIL. After heating to 100 °C, approximately 2 wt.% of volatile components including solvent, and free and bound water evaporated. After all the volatile components had evaporated, the gel transformed to a rigid solid mass and lost some weight during the

subsequent heating steps as the temperature increased. In an inert condition (flowing nitrogen gas), the INVESIL lost about 7 wt.% (of transformed solid) at 445 °C and retained approximately 80 wt.% of its solid content at 1100 °C. Noticeably, no weight loss was observed after 800 °C heating.

2.3 Mechanical Analysis of INVESIL

The second important property of the coating is to withstand mechanical stress. The loading and unloading curves demonstrated the elastic recovery of the coating with negligible plastic deformation. The loading and unloading curves also indicated that residual deformation was low, suggesting that the coating is elastic. A close observation of loading/unloading curves and low standard deviation data suggests that the coating has smooth surface morphology. The nanomechanical properties (i.e., nanoscale hardness and modulus) of INVESIL on aluminum surface were evaluated using nanoindentation and nano-scratch experiments (Figure 2a, 2b). These results are useful in evaluating the ability of the coating to withstand wear and tear. At least twelve tests were performed to draw a good representation of coating property. The properties were evaluated using standard testing protocols that dictate the derivation of results before the appearance of substrate effect. The INVESIL on aluminum showed high hardness value of approximately 0.20 GPa, while the modulus was 2.47 GPa.

The scratch resistant of INVESIL is demonstrated in Figure 2b. The original and residual surface morphology is plotted along with penetration curve as a function of scratch distance. The critical load to failure in INVESIL was 12 mN. The elastic deformation recorded during the nanoscratch test was 95.2 % while the remaining 4.8 % was plastic deformation. The critical load and deformation values confirmed that INVESIL can withstand periodic service load without failure. The solvent rub test was also conducted as per ASTM and did not show any sign of wear. Another INVESIL coated panel was subjected to cross hatch test as per ASTM and no coating delamination was noticed. These tests clearly demonstrate that INVESIL is a durable coating technology that holds promise to become a leading high performance antimicrobial coating product. A coefficient of friction value lower than 0.2 was obtained on INVESIL suggesting the lack of surface roughness for microbes to adhere.

2.4 Surface Features of INVESIL

It is important to know about the surface features that are formed after full curing of the coating. The surface appearance and homogeneity of the coating was studied with the help of atomic force microscopy (AFM). Small volume of INVESIL (without silver nanoparticles) was spin coated on a polished silicon wafer and dried in ambient condition for seven days. Coated sample was analyzed using tapping mode and force spectroscopy. Figure 3a,

shows 2D surface scan of area 1x1 micron². The surface morphology displays very smooth coating (<1 nm roughness) with equally distributed single Gaussian population of elastic modulus proving a single material (non-blended) coating. This clearly demonstrates that all the components in the INVESIL were reactive and forms a single phase material rather than phase separated domains existing in most commercial coatings. The Figure 3b, shows 3D surface topography of 500x500 nm² scanned area along with phase channel overlay. No surface defect or excessive surface roughness has been seen in the image. The coating lacks of any relatively large contrast, as well as any contrast independent of topography for the phase channel across coating. This suggests that on coating INVESIL, surfaces would remain unchanged and coating remains undetectable.

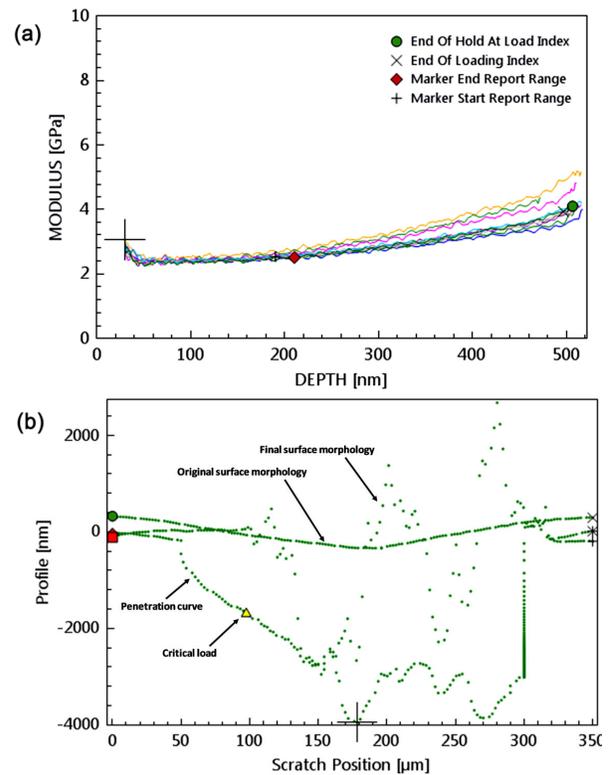


Figure 2: The mechanical analysis and surface morphology of coated aluminum alloys. Modulus value of INVESIL hardened over aluminum as a function of displacement into the surface. Load was applied on the 12 areas of INVESIL (containing Ta, Zr and Ag nanoparticles) cured on polished aluminum surface. Similar results were obtained in each case. (a) Stable modulus values seen in each case; (b) Scratch test on INVESIL to demonstrate the scratch resistance and low coefficient of friction value.

2.5 Evaluation of Antimicrobial Activity of INVESIL

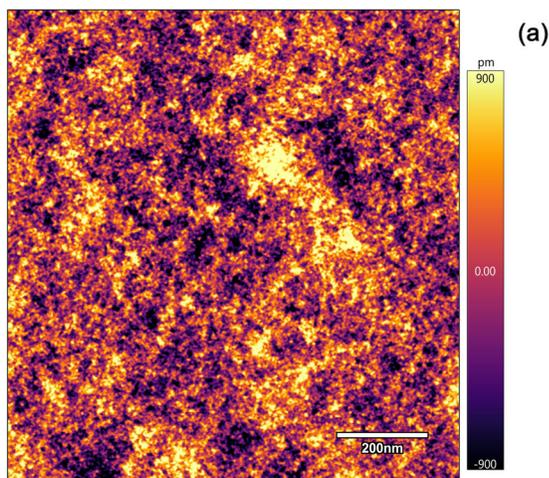
The INVESIL has been evaluated by a third party facility for antimicrobial activity. Coated fiber filters were dried in ambient conditions for seven days and tested as per ASTM

E2149 and ASTM E2180. The Gram-negative bacterium *Escherichia Coli* (E-Coli), *Klebsiella pneumoniae*, *Pseudomonas aeruginosa* as well as Gram positive bacteria bacterium *Staphylococcus Aureus* (S. Aureus) were selected for the test. The INVESIL coating showed more than 60% reduction in bacterial activity within an hour of exposure as per ASTM E2149 and 99.99% reduction in bacterial activity within 24 hours as per ASTM E2180.

and excellent reduction in pathogen activities. This thin and transparent coating could provide significantly long term antimicrobial protection to the coated objects. The chemical ingredients used in this coating have already been approved by the regulating agencies. We anticipate that INVESIL could achieve good market success in a short time.

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1- μ m Scan



500nm Scan

Figure 3: AFM scan of the INVESIL (without silver nanoparticles) coated silicon substrate. Data was acquired in tapping and force microscopy mode. (a) 1 micron scanned 2D image showing homogeneous surface topography; (b) 500 nm scanned 3D surface topography. Phase channel was overlaid on rendered 3D topography.

3.0 CONCLUSION

We have developed and demonstrated a single component ready to use effective antimicrobial smart quasi-bioceramic coating that can adhere to numerous surfaces tested so far. Coating has shown good adhesion to surfaces and high mechanical properties along with low coefficient of friction