DEVELOPMENT OF SOL GEL FOR UV AND ANTIBACTERIAL PROTECTION

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Abstract

The current trend in coating industry is toward functional coating. The concept of functional building and even now the term ‘smart building’ have been the guide line for architects to diligently consider especially in high rise building. One particular fact considered is the maximum amount of light that enters the building. Thus, most high rise buildings incorporate glass panels that allow maximum amount of sunlight into the building. Whilst sunlight is free, the Ultra Violet (UV) can be hazardous. Thin film UV protective layer are regularly used on cars and glass panels are effective to block the unwanted UV rays but they have drawbacks. The films cling to the glass panels by adhesive between the plastic films and the glass and it will lose its functionality over some time and bubbles start to appear. The films need to be removed once these happened. Thus, films are definitely not an option to block unwanted UV rays in high rise building. Therefore, a clear coating that can bind to glass chemically is the best option for higher durability.

In this research work, low temperature curing sol gel coating was developed for UV protective coatings. Glycidoxypropyl trimethoxy silane and amino propyl triethoxy silane were used as binders for high clarity with functionality of UV absorber coatings. Benzophenone has been used as the main UV absorber material in the coating layer and boron triflouride piperidine was used as the catalyst. It managed to block more than 99% of UV penetrating through the coating sample when coated on the blank float glass.

Antibacterial or antimicrobial coatings also have created major demands in coating technology. In this research work, the antibacterial coating has been developed as the top coat of the coating that consists of low molecular weight methyl trimethoxy silane (136.22 g/mol) as the binder, N-propanol as the solvent and nano silver for antimicrobial agent. Nano silver was synthesised via precipitation method of silver nitrate and hydrazine hydrate as the reducing agent. The silver precipitates were added into the coating formulation and grinded using the ball milling. Nitric acid was added as a catalyst in the coating system. The coating was tested according to JIS Z 2801:2000 Antimicrobial product-Test for antimicrobial activity and Efficacy by SIRIM QAS Sdn Bhd. The antibacterial test result clearly shows the antimicrobial activity of the coated samples against *Pseudomonas Aeruginosa*, *Staphylococcus Aureus* and *E-Coli*.

Abstrak

Trend semasa industri bahan penyalut adalah ke arah penyalutan yang mempunyai pelbagai fungsi. Konsep dan istilah 'bangunan pintar' telah menjadi garis panduan untuk arkitek dengan bersungguh-sungguh mempertimbangkan faktor ini terutamanya di bangunan tinggi.

Satu fakta yang dianggap penting adalah jumlah maksimum cahaya yang memasuki bangunan tersebut. Oleh itu, kebanyakan bangunan tinggi menggunakan panel kaca yang membolehkan amaun maksimum cahaya matahari memasuki bangunan. Walaupun cahaya matahari adalah percuma, sinaran lembayung (UV) boleh memerbahayakan kesihatan. Filem lapisan pelindung UV kerap digunakan pada cermin kereta dan panel kaca. Walaupun filem ini berkesan untuk menyekat sinaran UV yang tidak diingini, ia mempunyai banyak kelemahan. Filem yang dilekatkan pada panel kaca oleh bahan perekat antara lapisan plastik dan kaca akan kehilangan fungsinya dari masa ke semasa dan gelembung udara mula muncul. Filem-filem perlu diganti sebaik sahaja fenomena ini berlaku. Ini menjadikan filem-filem terdahulu tidak menjadi pilihan utama untuk menghalang UV di bangunan tinggi.

Oleh itu, lapisan yang boleh boleh merekat secara kimia adalah pilihan terbaik untuk ketahanan yang lebih tinggi. Dalam penyelidikan ini, lapisan gel sol di dalam suhu rendah telah dihasilkan untuk lapisan pelindung UV. *Glycidoxypropyl trimethoxy silane* dan *amino propyl triethoxy silane* telah digunakan sebagai bahan pengikat di dalam formulasi bahan penglitup dengan fungsi penyerapan UV. *Benzophenone* telah digunakan sebagai bahan utama penyerapan UV dan *boron triflouride piperidine* telah

digunakan sebagai bahan pemangkin. Ia berjaya menyekat lebih daripada 99% UV menembusi sampel salutan apabila diaplikasikan pada kaca yang kosong.

Lapisan penglitup anti-bakteria atau antimikrobial juga telah mewujudkan permintaan dalam teknologi penglitup. Dalam penyelidikan ini, lapisan anti-bakteria telah dihasilkan menggunakan bahan pengikat yang mempunyai berat molekul yang rendah iaitu methyl trimethoxy silane (136.22 g/mol) dan N-propanol sebagai pelarut. ‘Nano silver’ telah digunakan dalam penghasilan formulasi ini.‘Nano silver’ dihasilkan melalui kaedah pemendakkan silver nitrat dan hydrazine hydrate sebagai agen penurunan. Mendakkan yang terhasil telah ditambah ke dalam formulasi bahan penyalut dan dikisar menggunakan pengisar bebola. Asid nitrik ditambah sebagai pemangkin dalam system penyalut ini. Penyalut ini telah diuji mengikut JIS Z 2801:2000 ujian-produk antimikrobial untuk aktiviti antimikrobial dan keberkesanan oleh SIRIM QAS Sdn Bhd. Ujian antibakteria jelas menunjukkan keberkesanan fungsi antibakteria sampel ke atas bakteria *Pseudomonas Aeruginosa*, *Staphylococcus Aureus* dan *E-Coli*.

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LIST OF ABBREVIATION

DNA	Deoxyribonucleic acid
EDX	Energy Dispersive X-Rays Spectroscopy
FESEM	Field Effect Scanning Electron Microscope
NASA	The National Aeronautics and Space Administration
NPs	Nanoparticles
ROS	Reactive Oxygen Species
RTA	Road and Traffic Authority
SEER	Surveillance, Epidemiology and End Results Programme
SIRIM	Standards and Industrial Research Institute of Malaysia
SSSS	Staphylococcal Scalded Skin Syndrome
UV	Ultraviolet
WPCIA	World Paint and Coating Industry Association
XRD	X-Ray Diffraction
XPS	X-Ray Photoelectron Spectroscopy

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Appendix 1: Test report of JIS Z 2801:2000 Antimicrobial product-Test for antimicrobial activity and efficacy from SIRIM QAS International Sdn Bhd

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Appendix 3: Publication in Journal of Nanomaterial, Volume 2013 (2013), Article ID 901452, 6 pages “Transparent Nanocrystallite Silver for Antibacterial Coating”

Appendix 4: Publication in Journal of Nanomaterial, Volume 2014, Article ID 523530, 6 pages “Antibacterial coating for elimination of *Pseudomonas aeruginosa* and *Eschericia coli*”

Appendix 5: Patent submission

CHAPTER 1

1.0 INTRODUCTION:

“Traditional Coatings” was described by W. W. Zeno, in his book ‘Organic Coatings: Science and Technology’ as “material (usually liquid) that is applied to a substrate that involves certain application and dries on the substrate”. However, coating is generally described as paint in layman’s terms. There is not much difference between coating and paint. The terms are often used interchangeably. Still, another common term that is essentially a synonym for coating and paint is ‘finish’. In this particular research, the term ‘coating’ will be used throughout the thesis and we will limit our discussion in this research to the functional coatings with Ultraviolet (UV) protection and antibacterial protection.

The multibillion coating industry has consistently risen its annual turnover with value of around 35 billion U.S. dollars in the 1990s to a staggering value of $127.3 billion by year 2013. Global consumption of coatings in 2012 is reported to be around $120 billion (Kusumgar, Nerlfi & Growney, 2013). The significant leaps in the annual turnover for the past 2 decades were not only due to the volume demand, but also due to many new functionalities of coating in the industry.

Basically, coatings are used for one or more of three reasons:

- For decorations
- For protection
- For different functionality

Coatings can be classified by their appearance (clear, pigmented, metallic, glossy, etc.) and also by their functionality (e.g. anti-corrosion, anti-abrasion, skid-resistant, photosensitive, antibacterial, etc.). Figure 1.1 below shows the world consumption of paints and coatings divided by various technologies in 2012.

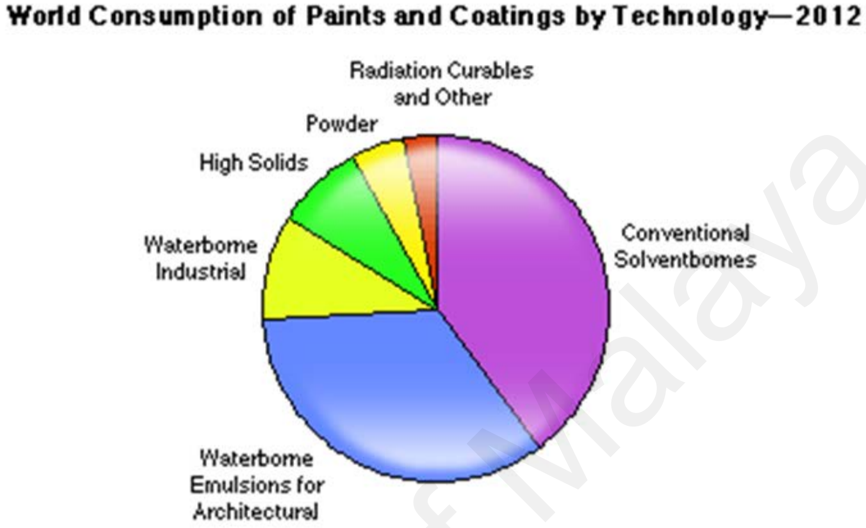


Figure 1.1: World consumption of paints and coatings by technology in 2012 (Global Markets and Advanced Technologies for Paints and Coatings Publish Date: December 2012)

Based on the figure above, conventional solventbornes coatings is still the largest category of the coatings being consumed globally, followed by waterborne, high solids, powder coatings and radiation curable etc. However, the trend is changing due to various factors eg: advancement in material research, rules and regulation production cost etc.

Traditionally, coatings have changed as a response to the new performance requirements, new findings in raw materials, and competitive pressures. Since 1965, a major driving force for change was on the need to reduce the VOC (volatile organic compound) emissions because of their detrimental effect on air pollution. The Environmental Protection Agency published the architectural coatings rule on 11th September 1998 under the authority of Section 183(e) of the Clean Air Act. This rule limits the amount of volatile organic compounds (VOC) that manufacturers and importers of architectural coatings can put into their products. This situation has resulted in increasingly stringent regulatory controls on such emissions. The drive to reduce VOC emission has also been fueled by the rising cost of organic solvents. Other important factors have also accelerated the rate of change in coatings. The improvements in the conventional solvent borne to water borne, powder and radiation curable coatings are the result of increasing concern about toxic hazards in the coating formulation.

The next challenge for the coating formulators is not only to provide the conventional usage of coatings according to the restrictions of certain chemicals in the raw material as a result of increasing awareness in environmental and health issue, but they also expand their findings in terms of functionality of the coatings.

Functional coatings or “special purpose coatings” are designated to satisfy certain requirements in the coating industry. For instance, the low gloss paint on the ceiling of a room fills the decorative needs, but it also has a function of reflecting and diffusing the light to help provide even illumination. The coating on the outside of an automobile adds beauty to the car and also protects it from corrosion. Other coatings reduce the algae growth and barnacles on ships’ bottoms (Danqing Zhu, Wim J. van Ooij, 2002);(Donald R. Baer, Paul E. Burrows and Anter A. El-Azab, 2003).

One of the major concerns among consumers is the method of protecting the interior of the building from the harmful rays of ultraviolet (UV). UV rays can affect the health of human and it not only harms the living people but also harms non-living items; for instance, colour-fading, and degradation of furniture, paints and textiles both indoor and outdoor. The increase of health awareness globally has rapidly expanded the market demand for this functional coating. Various elements and compounds such as zinc oxide, titanium dioxide and benzophenone have been tested and claimed to improve the UV protection functionality. The ability to increase the durability of outdoor products, that coated layers can withstand solar radiation for months or years, by a factor of 14 or more, makes the protective coatings very attractive for use in commercial applications (B. Mahltig, H. Böttcher, K. Rauch, U. Dieckmann, R. Nitsche and T. Fritz, 2005).

For all types of substrates, UV protection is critical to the long-term performance of the substrate and the coating that protects. Highly efficient UV-absorbing coatings that can be applied and cured at room temperature is an added advantage that allows the application of these coatings in a very wide variety of materials possible, especially on heat-sensitive materials. In this study, we develop a clear UV protection coating that can be coated on bare or painted substrates both indoor and outdoor in order to protect the substrates from color fastness and degradation.

In the present era of nanotechnology, the coating industry has witnessed various benefits. The usage of nanostructured materials in coating systems not only poses a diverse effect to the exterior appearance but also tends to behave differently in the coating system. The ability of creating, designing and modeling the nano systems of many shapes and properties will allow new types of materials with new properties to be created. Many applications require uniform coating and this significant degree of uniformity could be achieved with highly-localized nano-sized variation in material composition or structure. The ability to model, formulate, create and characterize materials systems with nanostructures gives us the ability to think about materials in new ways and will lead to the development of coatings with novel and highly desirable properties. In the area of coatings, new approaches utilizing nanoscale effects can be used to create coatings with significantly optimized or enhanced properties. The ultimate impact of nanoscience and nanotechnology in the area of coatings will depend on the ability to direct the assembly of hierarchical systems that includes nanostructures.

Nanoparticles in coating industry are one of the biggest contributions in nanotechnology that has created great interest. Particles in the nano-sized range have been present on earth for millions of years and have been used by mankind for thousands of years. As reported by Kelly J. Higgins, Heejung Jung, David B. Kittelson, Jeffrey T. Roberts and Michael R. Zachariah in 2002, soot for instance, as part of the Black Carbon continuum, is a product of the incomplete combustion of fossil fuels and vegetation; it has a particle size in the nanometer–micrometer range and therefore falls partially within the “nanoparticle” domain. Recently, however, nanoparticles (NP) have attracted a lot of attention because of our increasing ability to synthesize and manipulate such materials.

One of the well-known nanoparticles is silver. Silver nanoparticles have become the promising antimicrobial material in a variety of applications because they can damage bacterial cells by destroying the enzymes that transport cell nutrient and thus weaken the cell membrane or cell wall and cytoplasm (Y. Li, P. Leung, L. Yao, Q.W. Song and E. Newton, 2006). Silver has been employed to fight infections and control spoilage since the times of ancient Greece and Rome. Silver has been used to sterilize recycled water aboard the MIR space station and on the NASA space shuttle. Silver is also a health additive in traditional Chinese and Indian Ayurvedic medicine (Kim, Soo-Hwan, Hyeong-Seon Lee, Deok-Seon Ryu, Soo-Jae Choi, and Dong-Seok Lee, 2011).

It is generally believed that silver ions (Ag^+) can bind to bacterial cell wall membrane (slightly negative), damage it, and later alter its functionality. Ag^+ can interact with thiol groups in proteins, resulting in inactivation of respiratory enzymes leading to the production of reactive oxygen species. In addition to that, because of the interaction between the Ag^+ and DNA structure of bacteria, their multiplication may be prevented. Ag particles of less than 10 nm are more toxic to bacteria such as Escherichia coli. Researchers strongly aim to revive the bactericidal applications especially of nanoparticles due to evolution of new resistant bacteria against the common antibiotics (Akhavan, 2009; Kim. et al.,2011).

1.1 OBJECTIVES:

Functional coating has created a great interest among researchers especially UV protection and antibacterial coating. Various methods and formulations have been used to achieve the best protection against the harmful UV and bacteria. However, the current coating formulation not only complicated in coating procedures which involves high temperatures and costly apparatus, it also change the original appearance of the substrate in terms of colour, clarity, hardness etc. Due to that reason, the application of this type of coatings becomes limited especially on the substrate that need to maintain the clarity such as glass windows, containers etc. A high clarity functional coating formulation and simple coating method is needed to meet that particular demand.

Therefore, the objective of this research is to develop functional coating formulations with high protection and also high transparency with minimum changes to the substrate. It also has to be a simple coating procedure with minimum apparatus needed. Functionalities in this research can be divided into two parts which is UV protection coatings and antibacterial/antimicrobial coatings. UV absorbers will be incorporated into the formulations for UV protection coating and nanosilver will be added into antibacterial coating as the antibacterial agent. The binders that have been developed are supposed to hold the functional materials such as UV absorbers and nanosilver for antibacterial purpose. The coatings formulations need to be able to be coated and cured at room temperature.

Glass substrate was chosen as substrates because of the challenges in maintaining the clarity and transparency of the glass yet with additional values such as protection from the harmful ultraviolet rays and antibacterial properties. The clear coating with UV protection can be coated on the glass windows to protect the interior of the building and it can also be coated on other coated substrates as a protection without disturbing the original appearance of the substrates.

1.2 THESIS LAYOUT:

Chapter 1is the introduction of the topics involved in this research and the objectives of the study. Chapter 2 details the literature review on the trend in coating industry, particularly on functional coatings of UV protection and antibacterial. This chapter will also present the current state of nanotechnology in coatings and a brief review on nanoparticles specifically on silver nanoparticles. At the end of the chapter would be the focus of the study in this research work. Chapter 3 will have discussions mainly on the experimental procedures starting with synthesizing silver nanocrystals and its characterization. This chapter includes the sample preparation method for UV protection coating and antibacterial coating. The instruments and testing methods that have been used for characterization of the nanocrystals, wet coating and dry coating are also presented in this particular chapter. Chapter 4 will focus specifically on development of UV absorber coating and briefly discuss the solar irradiance. Chapter 5 is on synthesizing silver nanocrystals and development of antibacterial coatings. The results and discussion for the efficiency of antibacterial coating will be presented in the last part of this chapter. Chapter 6 would be the conclusion of the findings and the recommendations for further rese

CHAPTER 2

2.0 LITERATURE REVIEW:

2.1 TREND IN COATING INDUSTRY:

According to the analysis that was published by WPCIA (World Paint & Coatings Industry Association) in its annual report in 2014, it was reported that in the past decades, the global paints and coating demand grew steadily. In 2014, sales of global increased 3.9%, reached to 43.38 million tons, with total sales of 85 billion pounds. There were 14 companies with total sales excess $1 billion in 2014 and three companies had sales over $10 billion. Increased demands for paints and coatings are mainly due to the continued recovery of the global economy and rapid industrialization, and depend largely on the end user industries they serve such as automobile, steel, furniture and construction industries. In addition, increasing stringent regulations as well as unique formulation, technology and product development will continue to stimulate growth in the global market.

Geographically, Asia pacific is the largest consumer for paints and coatings, followed by Europe, North America and Latin America. China has the highest sales in Asia pacific region accounted for 58% of Asia Pacific coatings market. Globally, Europe is the second largest paint consumption areas, accounting of 24% of total global sales. Paint manufacturer all over the world are constantly introducing new technologically advanced products in the market, and formulating products for specific customer applications.

Demand for paints and coatings were highest from residential buildings, accounting for around 33.1% of global demand in 2014. Increasing application scope of green coatings and nanocoatings market coupled with growing Middle East and North America paints and coatings market are expected to open opportunities for the growth on the market in the future.

BCC research in 'Global Markets and advanced technology for paints and coatings' has reported that the total market value is expected to reach $141 billion in 2018. According to BCC research, the segment made up of solvent-borne technologies should reach $35.2 billion by 2013 and decrease to $32.1 billion in 2018, a CAGR of -1.8%.The segment made up of waterborne coatings technologies is expected to reach $31.1 billion in 2013 and nearly $40.1 billion in 2018, a CAGR of 5.2%. As a segment, a high solids/radiation cure technology is expected to total $25 billion in 2013 and nearly $33 billion in 2018, a CAGR of 5.7%. The powder/emerging coating technologies segment should reach a value of nearly $25.6 billion in 2013 and $35.9 billion in 2018, a CAGR of 7%. Due to environmental and health issue, higher demand is expected for the coating formulations with minimum or without solvent. As a result, the market for solvent-borne coating will decrease. Bigger market value is expected for water borne, high solids/radiation cure and powder coating which considered more environmental friendly due to the low Volatile Organic Compound (VOC). Figure 2.1 shows the summary figures and estimation in the market for paint and coatings from year 2011 till 2018 according to the segments.

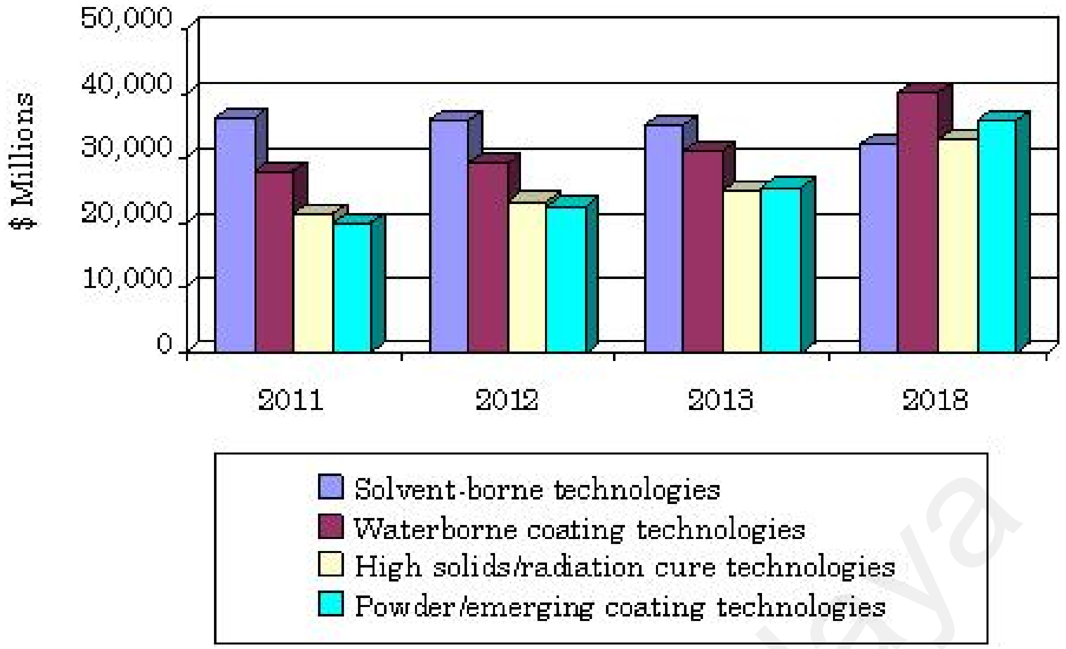


Figure 2.1: The summary figures and estimation in the market for paints and coatings, 2011-2018 (BCC research, 2011) (Market value is calculated according to end-user prices).

The market for coatings and paints includes liquid- and powder-based paints, varnishes and related products used in architectural and decorative, industrial and specialty product segments. Interior and exterior paints, primers, sealers and varnishes are part of the architectural and decorative segment, which are used in homes and buildings. Products that are factory applied to manufactured goods as part of the production process form part of the industrial products segment. Aerosol paints, marine paints, high-performance maintenance coatings, and automotive refinish paints form the specialty products segment.

As predicted, there is a major shift in the global paints and coatings production, which is moving away from the developed regions, such as Europe and the U.S., to the developing economies, such as Asia, mainly China and India. Continued increasing demand from the developed countries, in addition to the demand from the developing countries, contributes to the overall expansion of the worldwide coatings market. Industrial growth in developing economies is a major driver for growth in the coatings industry. In most regions of the world, the coatings industry has matured and the growth of coatings industry is dependent on a number of factors including the level of economic activity and the state of the construction industry which remains a major consumer of paints and coatings.

Coatings market is growing steadily and facing challenges at the same time. Main challenges include the threat of environmental regulations and the additional functionalities of the coatings other than the conventional purposes. Conventional coatings have been through a great leap in the technology advancement due to the great findings in the material science.

More functions have been added up to the coatings system to match with the market demand and to fulfil the awareness in the society. Coatings not only serve corrosion protection and decoration purposes but also improves air pollution and promotes healthy living. The technology not only improved in the coating formulations but also the coating techniques and methods. More coating methods that are friendlier to the end user have been developed (Philippe Belleville, 2010 and H. M. Hawthorne, A. Neville, T. Troczynski, X. Hu, M. Thammachart, Y. Xie J. Fu and Q. Yang, 2004).

2.2 FUNCTIONAL COATINGS:

Traditionally, a coating was supposed to function as a decoration purpose. Paints and lacquer are the earliest coating system that has been developed to satisfy those purposes. Advancement in technology however managed to widen the purpose of the material. More purposes of coating have been developed for different functionalities and also to improve the original condition of substrate.

Below are examples of the functionalities in the coatings technology.

1. Optical coatings
    - Reflective coatings for mirrors
    - Anti-reflective coatings e.g. on spectacles
    - UV- absorbent coatings for protection of eyes or increasing the life of the substrate
    - Tinted as used in some coloured lighting, tinted glazing, or sunglasses
2. Catalytic e.g. some self-cleaning glass
3. Light-sensitive as previously used to make photographic film
4. Protective
    - Most paints are to some extent protecting the substrate
    - Hard anti-scratch coating on plastics and other materials e.g. of titanium nitride to reduce scratching, improve wear resistance, etc.
    - Anti-microbial surface coating

- Anti-corrosion
    - Underbody sealant for cars
    - Many plating products
    - Waterproof fabric and waterproof paper

5. Magnetic properties such as for magnetic media like cassette tapes and floppy disks
6. Electrical or electronic properties
    - Conductive coatings e.g. to manufacture some types of resistors
    - Insulating coatings e.g. on magnet wires used in transformers
7. Scent properties such as scratch and sniff stickers and labels

In this research, we will be focusing on glass coatings. The common reason for applying coatings on glass is to modify the functional behaviour of the glass, i.e., to introduce an anti-glare, anti-reflex, or anti-static layer, or to realize changes in dielectric or transmission properties. The second reason is to strengthen the glass substrate and protect it from environmental influences such as particle impact or moisture. For these purposes, inorganic or hybrid, i.e., combined inorganic/organic coatings can be used (With, 2000).

In this research work, we will narrow down the functionality of the coatings to UV protection coatings and antibacterial coatings on the substrate. Therefore, normal float glass will be used as the substrate. We will add the functionality to the clear substrate with minimum changes to the original appearance of the substrate.

Various coating systems have been studied worldwide to provide the optimum coating system that can be used in functional coatings. In this research work, we will be discussing and applying the sol gel coating system. Sol–gel coatings are widely used for different purposes, especially those related to optical, semiconductor, protective and sensing applications. This kind of coatings show several advantages: low-temperature processing; good adherence to different substrates (metals, alloys, polymers, ceramics, composites, glasses, etc.); several application procedures (dipping, spinning or spraying) at atmospheric pressure; possibility to prepare multi-layered coatings; low-cost equipment and more (C. Gil, 2005; Philippe Belleville, 2010; G. Bräuer, 1999).

C. Gil and M. A. Villegas, in 2005 have developed a silver-containing sol-gel coating for superficial colouring on lead crystal glass. It is an alternative for a simpler and cheaper method compared to the conventional glass colouring which is the ion exchange. A direct chemical bond between the coating and the substrate is realized in the sol–gel process (With, 2000). However, this process requires a final curing which results in shrinkage of the coating and can produce a tensile stress and cracking of the coating. Non-cracked coatings have a critical thickness since the probability of cracking usually increases with thickness. Therefore, in this research, we will develop a sol-gel coating formulation that will eliminate the issue of cracking after the final curing.

The conventional organic coatings are complex mixtures of chemical substances that can be grouped into four broad categories:

- Binders
- Volatile components
- Pigments
- Additives

Binders are considered the most important material since it can form the continuous films that adhere to the substrate (the material that being coated), bind together the other substances in the coating to form a film, and give an adequately hard outer surface. The binders of coating within the scope of this research are silicone-based resins, better known as silane binders. In most cases, these binders were used as the coupling agents in a wide range of fields including the electronics and machinery, chemical, textile and construction. Silicones are materials with diverse properties and great potential (Masayuki Yamane, 2006).

Compounds containing a silicon atom are described as silanes, and it depends on the number of silicon atoms present, they are termed as di- or trisilanes respectively. If the molecule contains two or more silicon atoms separated by another atom, the name reflects the nature of the heteroatom (e.g. sicarbane, silazane, silthiane, siloxane, etc.). Most of the silicone resins used in the coatings belongs to the category of siloxanes. Silazanes and sithiane have not become commercially important because they normally react with the atmospheric moisture. Compounds containing siloxane bonds occupy a position of special importance and constitute the vast majority of commercially available silicone polymers. The presence of the siloxane bonds in the polymer imparts the following properties (Paul, 1997):

- They retain property over a wider temperature range and their properties change more slowly with the temperature
- Improved water repellence
- Impart unique flexibility to the backbone chain and intrinsic surface properties
- Low Toxicity

Siloxane bonds (-Si-O-Si-) form the basic backbone of silicone. Siloxane bonds have a high bonding energy, and this backbone is the same structure which makes up inorganic materials including glass and quartz. Siloxanes are thus chemically stable and exhibit outstanding heat and weather resistance. The molecular structure is helical and highly flexible. This quality is what gives silicone its high compressibility and cold resistant properties. There is little temperature dependence of the physical properties of silicone. Furthermore, the organic groups (CH_3) located on the outside of the coil structure can rotate freely. This results in good and water repellence.

Since any silane that enhances the adhesion of polymer is often termed as coupling agent, regardless of whether or not a covalent bond is formed, the definition became vague. Silane coupling agent finds their largest application in the area of polymers and it has the ability to form a durable bond between organic and inorganic materials. Encounter between dissimilar materials often involve at least one member that has siliceous properties; silicates, aluminates, borates, etc. are the principal components of the Earth's crust.

$$R – (CH_2)_n – Si – X_3$$

R = Organofunctional Group

- (CH_2) - = linker

Si = Silicon atom

X_3 = Hydrolyzable Groups

The general formula for a silane coupling agent typically shows two classes of functionality. X is a hydrolyzable group; typically alkoxy, acyloxy, halogen or amine. Following hydrolysis, a reactive silanol group is formed which can condense with other silanol groups. Stable condensation products are also formed with other oxides such as those of aluminium, zirconium, tin, titanium and nickel. Less stable bonds are formed with oxides of boron, iron and carbon. Alkali metal oxides and carbonates do not form stable bonds with Si-O. The R group is a non-hydrolyzable organic radical that may possess a functionality that imparts desired characteristics.

The ability of the resin to undergo curing in place rendered engineers a new degree of freedom. Moisture curing one or two part silicone coatings is used as a final outer weather-proofing membrane in a roofing system (Paul, 1997). Philippe Belleville in 2010 has discussed the potential of sol-gel silane in the functional coatings especially the optical coatings such as the anti-reflective and mirror coatings. His findings led to more functional coatings applications using silane in sol-gel technology for solar cell, microelectronic devices and gas sensors.

Therefore, silane is used as a binder in this research work to maintain the transparency and increase the adhesion of the coatings incorporated with nanoparticles and UV absorbers for antibacterial coating and UV protection coating.

2.2.1 UV PROTECTION COATING:

The Sun produces a whole spectrum of different energy; the intensity of light from the Sun, for each wavelength (nm) is given in figure 2.2. The Sun's radiation can be divided into three categories which are:

- Visible region (46%)
- Ultraviolet region (5%)
- Infrared region (49%)

Although UV region is of the lowest percentage in the sunlight spectrum, it is considered as the most harmful radiation due to its highest energy that can induce certain chemical reactions.

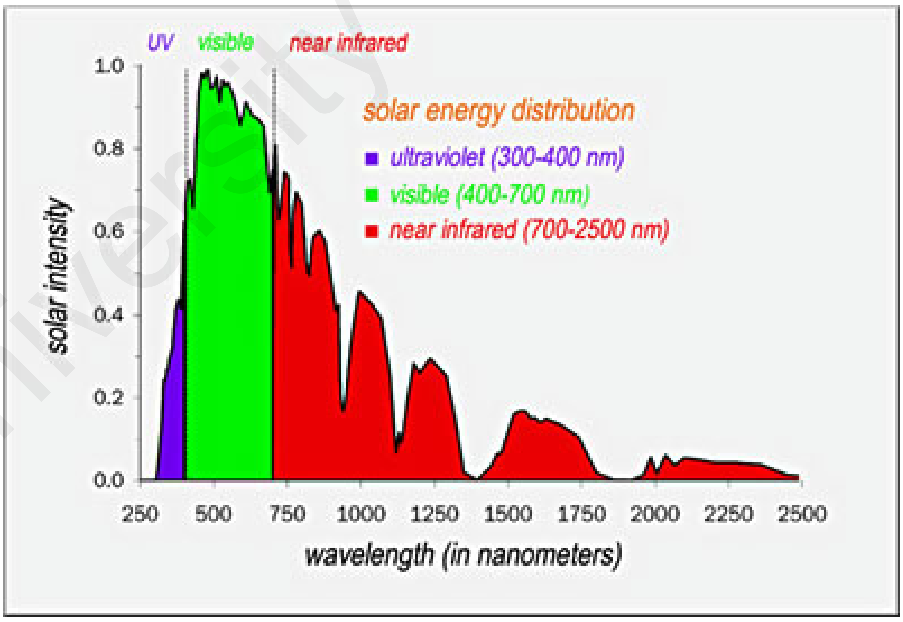


Figure 2.2: Global solar spectrum (Allen C. 2004)

With the progress in knowledge and technology, the increasing awareness has created great potential and demands in the field of UV protection functional coatings. UV radiation is part of the electromagnetic (light) spectrum that reaches the Earth from the Sun. It has wavelengths shorter than visible light, making it invisible to the naked eye. These wavelengths are classified as UV A, UV B, or UV C; UV A is the longest of the three at 320-400 nanometers (nm). UV A is further divided into two wave ranges; UV A I which measures 340-400 nm and UV A II which extends from 320 to 340 nm. UV B ranges from 290 to 320 nm. With even shorter rays, most UV C is absorbed by the ozone layer and does not reach the Earth. Figure 2.3 shows the spectrum of visible light, UV A and UV B.

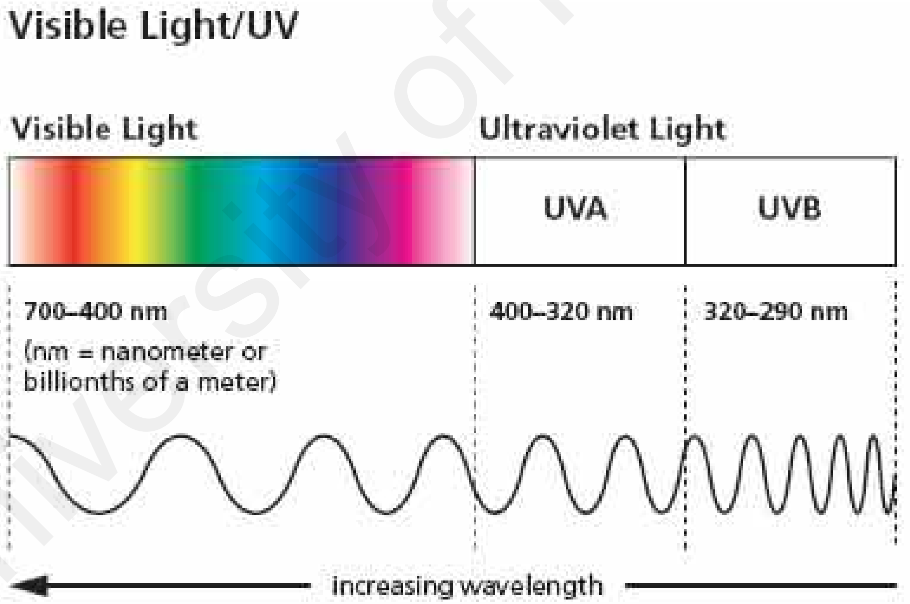


Figure 2.3: The spectrum of visible light, UVA and UVB (Matthew J. Hayat, et al. 2006)

Both UV A and UV B, however, penetrate the atmosphere and play an important role in conditions such as premature skin aging, eye damage (including cataracts), and skin cancers. They also suppress the immune system, reducing our ability to fight off these maladies and others alike. The harmful effects from exposure to ultraviolet (UV) radiation can be classified as acute or chronic. The acute effects of UV-A and UV-B exposure are both short-lived and reversible. These effects include mainly sunburn (or erythema) and tanning (or pigment darkening). The chronic effects of UV exposure can be much more serious, life-threatening even, and include premature aging of the skin, suppression of the immune system, damage to the eyes, and skin cancer. The health factor is one of the major reasons that have created great interest in this field of functional coatings. The incidence of all types of skin cancers is increasing. Figure 2.4 shows graph with data from nine SEER registries showing the increasing incidence of age-adjusted rates of melanoma in men and women from 1973 to 2000.

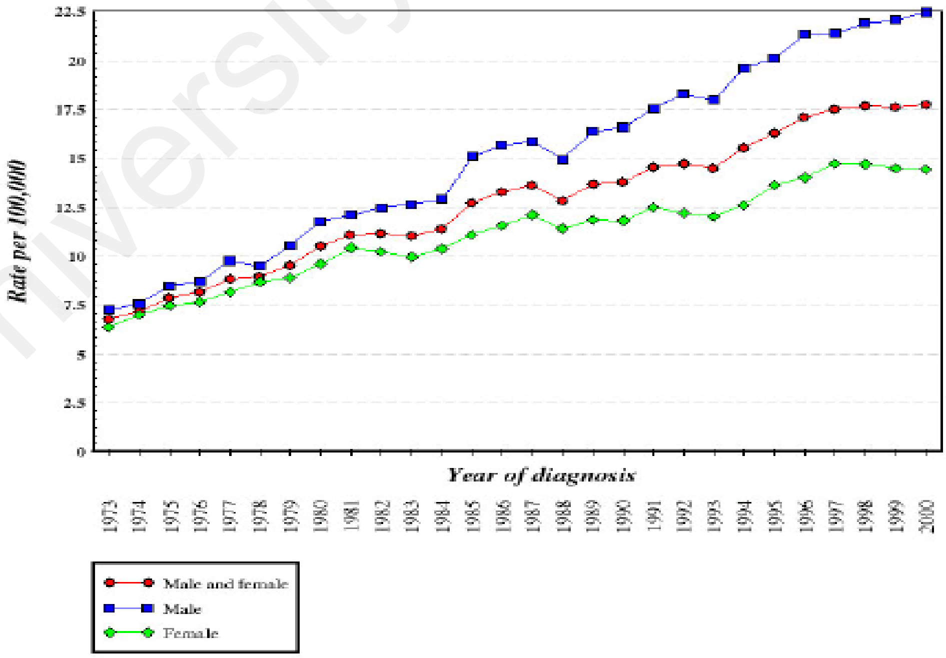


Figure 2.4: The increasing incidence of age-adjusted rates of melanoma in men and women 1973 – 2000, (Matthew J. Hayat, et al. 2006)

Besides health issues, the effect of the harmful UV rays to non-living things has also created great demands in this field of technology. Exterior coatings of the building are designed to provide protection from the harsh environment of outdoor weathering, especially the paint deterioration caused by UV radiation. For all types of substrates, UV protection is critical to the long-term performance of the substrate and the coating that protects it. UV radiation is known to contribute to the chemical modification of exposed paint surfaces resulting in loss of gloss, colour change, chalking, flaking and eventually the destruction of the film.

As previously affirmed by Clive H. Hare in1992, as the wavelength gets shorter, the energy of the radiation increases to the point at which it is energetic enough to cleave the bonds of the chemical substances and produce profound changes in any material on which the radiation falls. UV rays have sufficient energy to disrupt and break the covalent bonds in the organic substances, consequently inducing the degradation process of the material.

Glass and plastic can also be coated with UV protection coating to diminish the amount of ultraviolet radiation that passes through and slow down the aging or degradation process of the materials. Common uses of such coating include eyeglasses and automotive windows. Photographic filters remove ultraviolet to prevent exposure of the film or sensor by invisible light. In fact, any surface is protected but the enclosure will be free of the hazardous rays.

2.2.2 ANTIBACTERIAL COATING:

Other than UV protection coatings, antibacterial is one of the major interests in functional coatings. The fight against bacterial infection represents one of the highest points of modern medicine. The development of antibiotics in the 1940s offered physicians a powerful tool against bacterial infections that has saved the lives of millions of people. However, because of the widespread and sometimes inappropriate use of antibiotics, strains of bacteria have begun to emerge that are antibiotic-resistant. These new, stronger bacteria pose a significant threat to general health and welfare – and a challenge to researchers.

Bacterial infections can be caused by a wide range of bacteria, resulting in mild to life-threatening illnesses (such as bacterial meningitis) that require immediate intervention. In the United States, bacterial infections are a leading cause of death in children and the elderly (Guy, 2009). Hospitalized patients and those with chronic diseases are at an especially high risk of bacterial infection. Common bacterial infections include pneumonia, ear infections, diarrhoea, urinary tract infections, and skin disorders (Immai S, 2005).

Therefore, antibacterial coating is one of the contributions from the material science advancement to the medical aspect. In this research work, silver nanoparticles would be the antibacterial agent that will be incorporated into the sol-gel coating system.

2.3 SILVER NANOPARTICLES:

Nanotechnology is defined as the understanding and control of matter at dimensions of roughly 1–100 nm, where unique physical properties make novel applications possible. Nanoparticles (NPs) are therefore considered as substances that are less than 100 nm in size in more than one dimension. They can be spherical, tubular, or irregularly-shaped and can exist in fused, aggregated or agglomerated forms (Bucheli, 2007).

Unlike soluble salts of metals, the elements contained in nanoparticles normally occur in a non-ionized form, and in the case of noble metals, often in the zero oxidation state. Although the main component of nanoparticles is often not ionized, the groups attached to their surface may dissociate. The physical and chemical characteristics of nano-sized materials differ substantially from those of bulk materials (Grazyna Bystrzejewska-Piotrowskaa 2009).

The design of novel NPs has been the basis of many advances in technology for the last decade. In general, manufactured NPs can be classified according to their chemical compositions and properties. They can be produced by a huge range of procedures which can be grouped into top-down and bottom-up strategies (Figure 2.5). Top-down approaches are defined as those by which NPs or well-organized assemblies are directly generated from bulk materials via the generation of isolated atoms using various distribution techniques. The majority of the top-down strategies involve physical methods such as milling or attrition, repeated quenching and photolithography. Bottom-up strategies involve molecular components as starting materials linked with chemical reactions, nucleation and growth process to promote the formation of something more complex (Lead, 2008).

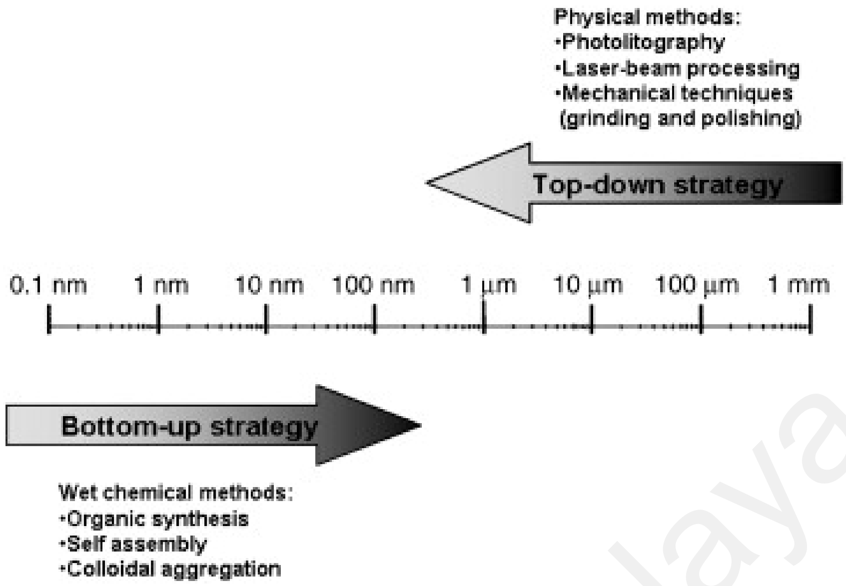


Figure 2.5: Top Down and Bottom up strategies (Lead, August 2008)

Silver has been used as a medicine and preservative by many cultures throughout history. Back in the Middle Ages, placing a silver coin on the tongue was said to ward off the plague. Settlers in the Australian outback still suspend silverwares in their water tanks to retard spoilage. Today, the precious metal acts against many different kinds of germs in a much smaller form. Silver nanoparticles in wall paint prevent the formation of mould inside buildings and the growth of algae on the walls outside.

The antibacterial property of silver has been known for thousands of years with the ancient Greeks cooking from silver pots. The anti-microbial properties of silver were utilized as early as 1000 BC to keep water safe. The Greeks and others used silver vessels for drinking water and other liquids. Alexander the Great used to drink only from silver vessels. This is recently attributed to the anti-microbial activities of released Ag^+ ions. The first recorded medicinal use of silver goes back to the 8th century. In 980 AD, Avicenna used silver as a blood purifier, for bad breath and for heart palpitations. Silver nitrate was used to treat ulcers in 17th and 18th centuries.

In medical history, Dr J. N. Rust was one of the first to use dilute silver nitrate solution for fresh burns. The use of silver for burn patients completely disappeared around World War II. At present, the use of silver is re-emerging as a viable treatment for infections encountered in burns. More recently, silver is used as a biocide to prevent infection in burns, traumatic wounds and diabetic ulcers. Other uses include the coating of catheters and other medical devices implanted on/within the body. It is also used as a water disinfectant. Most of the silver products available in the market today are to counter infections in burns, open wounds and chronic ulcers, and are mainly characterized by the presence of Ag^+ ions. The gold standard in topical burn treatment is silver sulfadiazine (Flammazine™, Smith and Nephew Health care Limited, Hull, Canada), silver sulfadiazine/chlorhexidine (Silverex™, Motiff Laboratories Pvt. Ltd. Kare Health Specialities, Verna, Goa), silver sulfadiazine with cerium nitrate (FlammaceriumR, Solvay, Brussels, Belgium), and silver sulfadiazine impregnated lipidocolloid wound dressing Urgotul SSD (Laboratories, Chenova, France). Researches have shown that impregnating other materials with silver nanoparticles is a practical way to exploit the germ-fighting properties of silver. Different silver products that are used to treat infections can be broadly classified into two categories depending on the presence of either (1) silver ions or (2) silver nanoparticles (Mukherjee, 2008).

The needs of antibacterial apparatus in the health industry have encouraged researchers to study the usage of silver nanoparticles and on incorporating this nanoparticle into the polymer matrix. (Y. Li et al. 2004) conducted studies on incorporating the silver nanoparticles into face mask coatings. Nanoparticles were promising when applied as a coating to the surface of protective clothing in reducing the risk of transmission of infectious agents.

In the anodizing technology, silver was deposited into the pores to form an antibacterial anodized surface (G. J. Chia 2002). The antibacterial activity of anodized aluminium with deposited Ag is directly related to Ag. For the antibacterial mechanism of Ag, there are two theories. The first one holds that metal silver can react with water and release silver ions, and silver ions combine with sulfhydryl groups of the respiratory enzymes or the nucleic acids in bacteria, resulting in the blocking of breathing and finally the death of the bacterium. The other theory advocates that silver can react with the oxygen dissolved in the water and generate activated oxygen O* which can decompose the bacterium. The anodic oxide aluminium films with electrodeposited Ag have an antibacterial activity of over 95% against the growth of E. coli, P. aeruginosa, S. faecalis and S. Aureus (G. J. Chia, 2002).

Bacterial cell wall damage was observed (Kim, Soo-Hwan et al, 2011) on gram positive bacteria (Staphylococcus Aureus) and gram negative bacteria (E.Coli) when exposed to the silver nanoparticles. It was reported that the antibacterial activity of Ag-Nano particles is related to the formation of free radicals (ROS). Under certain conditions, high levels of ROS can increase oxidative stress in cells. Oxidative stress not only causes damage to the cell membrane, but can also cause damage to the proteins, DNA, and intracellular systems such as the respiratory system.

As shown in figure 2.6, it is generally believed that Ag^+ can bind to bacterial cell wall membrane (slightly negative), damage it and so alter its functionality. Ag^+ can also interact with thiol groups in proteins, resulting in inactivation of respiratory enzymes and leading to the production of reactive oxygen species. In addition, because of the interaction between the Ag^+ and the DNA structure of bacteria, their multiplication may be prevented. Ag particles of less than 10 nm are more toxic to bacteria such as

Escherichia coli. Therefore, researchers strongly aim to revive the bactericidal applications of silver (especially silver nanoparticles), due to the evolution of new resistant bacteria against the common antibiotics. In practical applications, both high antibacterial activity and low silver release are two important characteristics for silver-based materials. High release level of silver, especially for silver-based bulk materials, leads to shortening the effective life of antibacterial activity. If Ag nanoparticles and nanostructures with high antibacterial activities are immobilized on porous matrixes, the release time of silver can be delayed for a long time so that these kinds of silver-supported materials will be of great potential for bactericidal application (Akhavan, 2009).

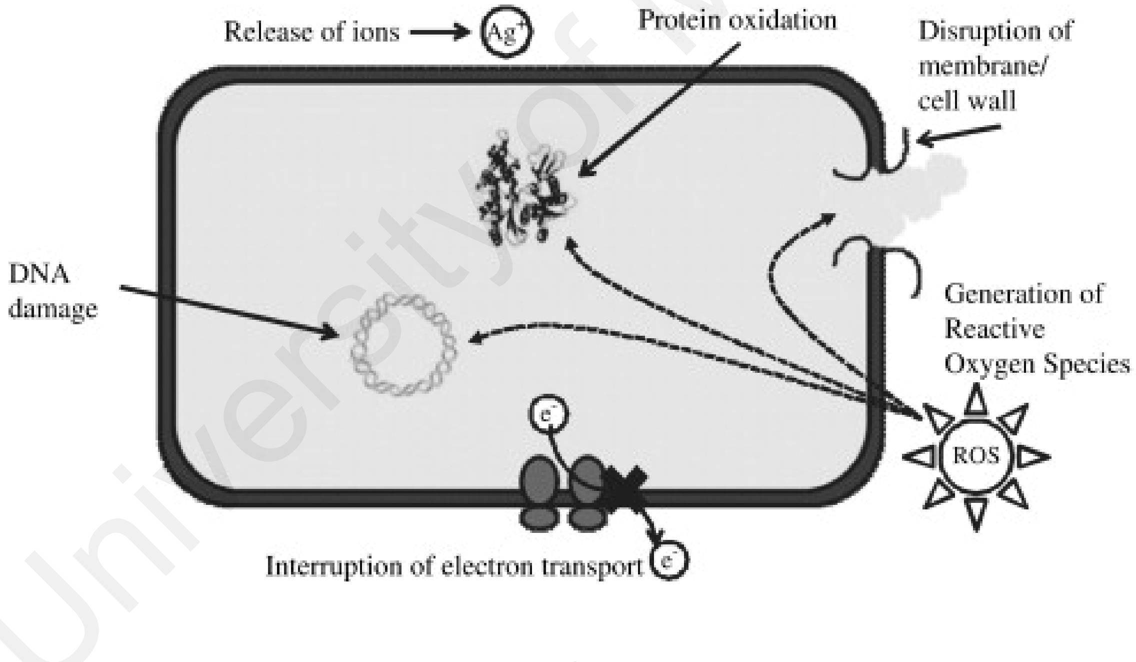


Figure 2.6: Various mechanisms of antimicrobial activities exerted by nanomaterials (Qilin Li, November 2008)

Among all antimicrobial nanomaterials, Ag is probably the most widely used. It is used as an antimicrobial agent in over 100 consumer products, ranging from nutrition supplements to surface coating of kitchen appliances. Commercial home water purification systems such as Aquapure®, Kinetico®, and QSI-Nano®, which are reported to remove 99.99% pathogens, use membranes impregnated with silver or surfaces coated with silver (Qilin Li 2008).

2.3 FOCUS OF THE STUDY IN THIS RESEARCH WORK:

This study attempts to produce dual function coatings that will act as a protective layer on a bare substrate or painted substrate. The coatings will add UV protection and antibacterial function to the substrate. The coatings have to be very clear with acceptable transparency in order to maintain the original appearance of the substrate. The applications of these coatings will be for indoor and outdoor usage. For outdoor, it will provide UV protection to the painted walls and roofs to maintain the colour and reduce the degradation of the paint due to harmful rays, thus extending the life span of the outdoor paint. For indoor usage, especially on the windows, it will provide the UV filtration that comes through the windows into the building and at the same time, provides the antibacterial effect to the indoor environment. Indoor walls with paint can also be coated with this clear coating of UV absorption and antibacterial functions to add protection to the indoor environment without interfering with the original looks of the paint underneath.

The first part of the research would be the development of the UV protection coatings that are very clear and high in transparency. The coatings should be able to block the harmful UV rays (UV A and UV B) at least 99% onwards and should be compatible to top the layer protection which is the antibacterial layer.

The second part of the research is to synthesise silver nanoparticles in the laboratory scale using bottom to top method by precipitation route. The characterization of the nanoparticles will give us a clearer view of the effects of the variables in the precipitation method. The nanoparticles obtained from the experiment will be incorporated into the coating formulation that can adhere to the substrate in an ambient temperature. The coating will be tested against 3 types of bacteria *(Pseudomonas Aeruginosa*, *Staphylococcus Aureus, E-Coli*). The antibacterial test will be conducted by the Chemical Testing Section at SIRIM QAS Sdn. Bhd.

The coating is supposed to bind the nanoparticles together on the substrate and at the same time, provide the added value to the coatings and substrate by providing the UV protection and the antibacterial properties. The physical properties of the coatings with the added functionalities will be studied.

CHAPTER 3

3.0 EXPERIMENTAL PROCEDURES:

3.1 INTRODUCTION:

This chapter deals with the method of synthesizing nanoparticles and coating preparation. Physical properties testing of the wet and dry films that have been utilized throughout the study will also be presented in this chapter.

3.2 SYNTHESIZING NANOPARTICLES

There are four fundamental routes to prepare nanomaterials (Malvern Nanotechnology).

- **Mechanical**

  This is a ‘top-down’ method that reduces the size of particles by attrition, for example, ball milling or planetary grinding.
- **Gas phase synthesis**

  These include plasma vaporization, chemical vapour synthesis and laser ablation.
- **Wet chemistry**

  These are fundamentally ‘bottom-up’ techniques, i.e., they start with ions or molecules and build these up into larger structures.

Wet chemistry method was used as the route for synthesizing nanoparticles in this research work. These wet chemistry techniques currently offer the best quality nanoparticles from a number of points of view.

- Nanoparticles that are already dispersed, hence high inter-particle forces can be reduced to prevent agglomeration.
- The formation of aggregates can be reduced or eliminated.
- The nanoparticles can be made to be very monodisperse, i.e., all the same size to within small tolerances.
- The chemical composition and morphology can be closely controlled. This is especially important for research purposes where the quality of the material must be very high to ensure repeatable and meaningful results.

3.2.1 SYNTHESIZING SILVER NANOPARTICLES

Wet chemical method was used in synthesizing silver nanoparticles. 20 ml of silver nitrate was used as the precursor. 0.1ml of ethylene diamine was added to change the pH to 10. 0.05 g of cetyl trimethyl ammonium bromide (CTAB) was added into the solution to act as a dispersing agent. The solution was stirred for 15 minutes. 5 ml of hydrazine hydrate was added dropwise to the solution while it was stirred. Keep stirring the solution for 5 minutes. The solution was kept at room temperature for 15 minutes before centrifuging at 2500 rpm for 20 minutes. The particles were washed with deionised water for a few times and the collected silver particles were dried in a desiccator for 24 hours.

3.3 CHARACTERIZATION OF NANOPARTICLES

3.3.1 FIELD EFFECT SCANNING ELECTRON MICROSCOPE (FESEM) AND ENERGY DISPERSIVE X-RAYS SPECROSCOPY (EDX)

FESEM was used to study the morphology and the microstructures of the silver nanocrystal formed via precipitation method. FESEM has a large depth of field, which allows a large amount of the sample to be in focus at one time. The FESEM also produces images of high resolution, which means that closely spaced features can be examined at high magnification. Sample preparation was relatively easy because FESEM only needs the sample to be conductive. The combination of higher magnification, larger depth of field, greater resolution, and ease of sample preparation makes the FESEM the obvious choice of instruments for surface study. EDX analysis of the samples was carried out to identify the element that exists in the bulk of the samples.

3.3.2 X-RAY DIFFRACTION (XRD)

X-ray Diffractions method provides information about the arrangement and the spacing of atoms in crystalline materials. Such studies have led to a much clearer understanding of the physical properties of metals, polymeric materials and other solids. X-ray Diffraction also provides a convenient and practical means for the qualitative identification of crystalline compound (Skoog, 1997). Diffraction is the result of radiations being scattered by a regular array of scattering centres that are about the same as the wavelength of the radiation. For X-rays, atoms are the scattering centres. The specific mechanism of scattering is the interaction between a photon of electromagnetic radiation and an orbital electron in the atom (Shackelford, 2000).

3.3.3 X-RAY PHOTOELECTRON SPECTROSCOPY (XPS)

X-ray photoelectron spectroscopy (XPS) is a surface analytical technique, which is based upon the photoelectric effect. Each atom in the surface has a core electron with the characteristic-binding energy that is conceptually, not strictly, equal to the ionization energy of that electron. When an X-ray beam directs to the sample surface, the energy of the X-ray photon is adsorbed completely by the core electron of an atom. If the photon energy, $h\nu$, is large enough, the core electron will then escape from the atom and emit out of the surface. The emitted electron with the kinetic energy of E_k is referred to as the photoelectron. The binding energy of the core electron is given by the Einstein relationship:

$$E_b = h\nu - E_k - \phi$$

Where $h\nu$ is the X-ray photon energy (for monochromatic Al Ka, $h\nu$ = 1486.6eV); E_k is the kinetic energy of photoelectron, which can be measured by the energy analyzer; and $\phi$is the work function induced by the analyzer, about 4~5eV. Since the work function, ϕ , can be compensated artificially, it is eliminated, giving the binding energy as follows:

$$E_b = h\nu - E_k$$

For insulating samples, once the photoelectrons are emitted out of the sample surface, a positive charge zone will establish quickly in the sample surface. As a result, the sample surface acquires a positive potential (varying typically from several volts to tens of volts) and the kinetic energies of core electrons are reduced by the same amount, *C*.

$$E_b = h\nu - (E_k - C)$$

It can be seen that the surface charging results in the shift of the XPS peaks to higher binding energy. In this case, the binding energy has to be calibrated with an internal reference peak. The C 1s peak from the adventitious carbon-based contaminant, with the binding energy of 284.8 eV, is commonly used as the reference for calibration. In order to neutralize the surface charge during data acquisition, a low-energy electron flood gun is used to deliver the electrons to the sample surface. The electron flood gun can be tuned to provide the right current to push the XPS peaks back to the real position.

The core electron of an element has a unique binding energy, which seems like a "fingerprint". Therefore, almost all elements except for hydrogen and helium can be identified *via* measuring the binding energy of its core electron. Furthermore, the binding energy of the core electron is very sensitive to the chemical environment of an element. The same atom is bonded to the different chemical species, leading to the change in the binding energy of its core electron. The variation of binding energy results in the shift of the corresponding XPS peak, ranging from 0.1 eV to 10 eV. This effect is termed as "chemical shift", which can be applied to studying the chemical status of an element in the surface. Therefore, XPS is also known as electron spectroscopy for chemical analysis (ESCA).

XPS is used to measure:

- elemental composition of the surface (top 1– 10 nm usually)
- empirical formula of pure materials
- elements that contaminate a surface
- chemical or electronic state of each element in the surface

- uniformity of elemental composition across the top surface (or line profiling or mapping)
- uniformity of elemental composition as a function of ion beam etching (or depth profiling)

3.3.4 AUGER SPECTROSCOPY

Auger spectroscopy (AES) is one of the most common methods to analyse the chemical composition on the surface of the solid material. Auger Electron Spectroscopy (AES) is an analytical technique that uses a primary electron beam to probe the surface of a solid material. Secondary electrons that are emitted as a result of the Auger process are analyzed and their kinetic energy is determined. The identity and quantity of the elements are determined from the kinetic energy and intensity of the Auger peaks. The nature of the Auger surface analysis process is such that Auger electrons can only escape from the outer 5-50 Å of a solid surface at their characteristic energy. This effect makes AES an extremely surface-sensitive technique. A finely focused electron beam can be scanned to create secondary electron and Auger images, or the beam can be positioned to perform microanalysis of specific sample features. Applications include materials characterization, failure analysis, thin film analysis, particle identification for semiconductor, and thin film head manufacturing.

The Auger effect is named for its discoverer, Pierre Auger, who observed radiationless relaxation of excited ions in a cloud chamber, during the 1920s. Auger electrons are emitted at discrete energies that allow the atom of origin to be identified. The Auger process involves three steps:

- Excitation of the atom causing emission of an electron; this is Step 1
- An electron drops down to fill the vacancy created in Step 1
- The energy released in Step 2 causes the emission of an Auger electron.

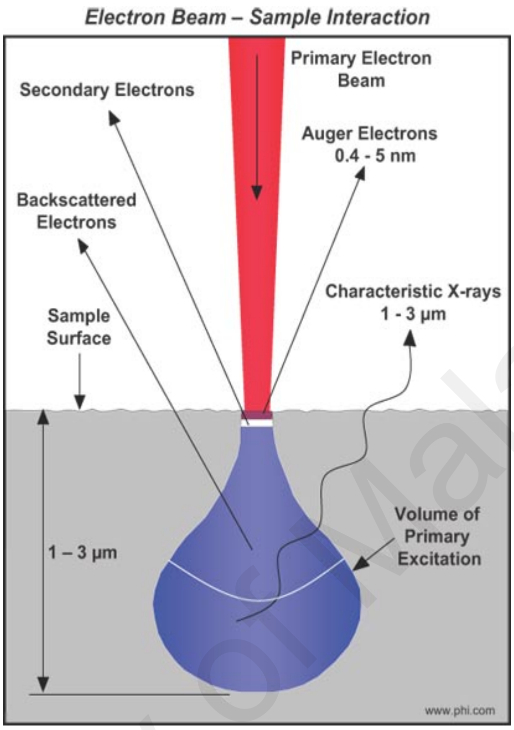


Figure 3.1: Comparison of AES and EDX analysis (www.phi.com)

3.4 PREPARATION OF THE COATING SYSTEM

Silane coupling agents are organosilicon compounds that are widely used to bond organic materials and inorganic materials. In many cases, these are materials that might otherwise be considered too dissimilar to form strong interactions. As a result, silane coupling agents are extensively used to greatly improve the interfacial adhesion in composites and other materials systems, significantly improving desirable qualities such as mechanical strength, moisture or chemical resistance, electrical properties, etc. In general, silane coupling agents are used to tailor the composition, functionality, compatibility, and reactivity of a given system, enhancing its desirable properties while minimizing the disadvantages that may be inherent. This typically includes the direct modification of resins, other organic components, and/or inorganic surfaces, and it is accomplished by adding one or more specific functional group(s) via one or more organosilane coupling agent(s) (Shinetsu Chemical).

3.5 SPECIMEN PREPARATION

3.5.1 UV PROTECTION COATING

In this research, two types of sol-gel coatings wereprepared. The first type is the inner layer that would be the UV protection layer which consists of silane binder, UV absorber and catalyst. The first stage was the reacting process of epoxy organosilane which is 3-glycidoxypropyltrimethoxysilane with the amine organosilane which is 3-aminopropyltriethoxysilane with the ratio of 1:1 mole. These 2 silanes were mixed in a glass bottle and cured in a room temperature of 25°C and humidity 40% ± 5% and the viscosity of the mixture were monitored every day to get to the stable point that shows the completion of the amine-epoxy reaction. The reaction is an exothermic reaction, therefore the surrounding temperature needs to be controlled in order to prevent the incidents involving the sudden temperature changes and overheating of the chemicals. Once the viscosity shows stable readings, 2,4 dihydroxyl benzophenone was added 5% wt into the binder mixture and let to dissolve. The last stage would be the addition of the boron triflouride piperidine 10% wt was already dissolved in N-propanol with the ratio of 1:9 as catalyst. 2 ml of coating was used to coat the 5 cm x 10 cm glass float glass substrate with a thickness of 6 mm. Melamine sponge was cut 2 cm x 2 cm and used as the coating applicator. The coating was left to dry at room temperature. Table 1 shows the coating formulation for UV protection layer.

Table 1: Coating system formulation for Ultra violet protection layer

Chemicals	Weight (g)
3-glycidoxypropyltrimethoxysilane	43.88
3-aminopropyltriethoxysilane	41.12
2,4 dihydroxyl benzophenone	5
Boron triflouride piperydine	1
N-propanol	9
Total	100

3.5.2 ANTIBACTERIAL COATING

The second type of sol gel coating would be the antibacterial coating as the outer layer or the top layer. 2.5% wt of silver nanocrystal was added into the binder system that consists of 50% methyl trimethoxy silane and 50% N-propanol. The mixture was grinded in the ball mill for 1 hour. 10% wt nitric acid (5%) was added to function as a catalyst. The coating mixture was coated on samples that were already being coated with UV protection sol-gel coatings after more than 7 days as a substrate. The coating process was carried out at room temperature of 25 °C and absolute humidity of 30%. Dehumidifier was used throughout the experiment to control the humidity in the room. Table 2 shows the composition of the antibacterial layer.

Table 2: Coating system formulation for antibacterial layer

Chemicals	Weight (g)
Methyl trimethoxy silane	43.75
N-propanol	43.75
Nitric Acid 5%	10
Silver nanocrystal	2.5
Total	100

3.6 WET FILM TESTING

Wet film testing is a set of testing that has been conducted on the wet coating systems before the drying process. This testing is an essential evaluation in order to assess the coat ability of the coating system and at the same time, to find the relation between wet coating systems and the properties of the dried coatings. Controlling the quality of the wet films is the most appropriate as it permits correction and adjustment of the film by the applicator at the time of application. Correction of the film after it has dried or chemically cured requires costly extra labour time, may lead to contamination of the film, and may introduce problems of adhesion and integrity of the coating system. In a coating process, measurement of the wet paint often provides the first opportunity to check the quality of the work. Measuring coatings before they have cured can predict the final properties of the film. In this research work, the wet coating measurements involve the viscosity and the tack free time.

3.6.1 VISCOSITY

Rheology is the study of fluid dynamics. The flow rate of any liquid is an important measure of the behaviour of fluid. Viscosity is a principal parameter when any flow measurements of fluids, such as liquids, semi-solids, gases and even solids, are made.

It is the measure of the internal friction of a fluid. This friction becomes apparent when a layer of fluid is made to move in relation to another layer. The greater the friction, the greater the amount of force required causing this movement; this is called *shear*. Shearing occurs whenever the fluid is physically moved or distributed, as in pouring, spreading, spraying, mixing, etc. Highly viscous fluids, therefore, require more force to move than less viscous materials.

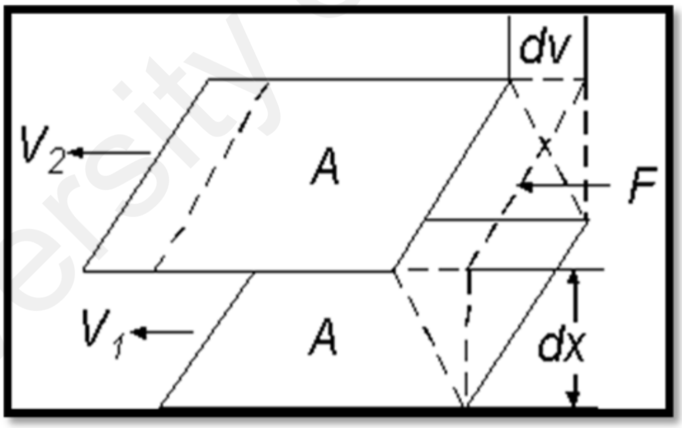


Figure 3.2: Model of viscosity by Isaac Newton (www.brookfield engineering.com)

Viscosity defined by considering the model represented in the figure 3.2. Two parallel planes of fluid of equal area *A* are separated by a distance *dx* and are moving in the same direction at different velocities *V1* and *V2*. Newton assumed that the force required in maintaining this difference in speed was proportional to the difference in speed through the liquid, or the velocity gradient. To express this, Newton wrote: where h is a constant for a given material and is called its viscosity. The velocity gradient, dv/dx, is a measure of the change in speed at which the intermediate layers move with respect to each other. It describes the shearing the liquid experiences and is thus called *shear rate*. This will be symbolized as S in subsequent discussions. Its unit of measurement is known as the *reciprocal second* (sec^{-1}). Using these simplified terms, viscosity may be defined mathematically using this formula (www.brookfield engineering.com):

$$n = Viscosity = \frac{F}{S} = \frac{Shear\ Stress}{Shear\ Rate}$$

The fundamental unit of viscosity measurement is *poise*. A material requiring a shear stress of one dyne per square centimetre to produce a shear rate of one reciprocal second has a viscosity of 1 poise, or 100 centipoise. Viscosity measurements can be expressed in *Pascal-seconds* (Pa·s) or *milli-Pascal-seconds* (mPa·s); these are units of the International System and are sometimes used in preference to the Metric designations. One Pascal-second equals ten poise; one milli-Pascal-second equals one centipoise.

3.6.2 ‘DRY TO TOUCH TIME’ (TACK FREE)

When developing a coating system, it is often important to know the exact time it takes for the coating to dry or cure. There are many stages to the coating’s drying time. Once a coating has been applied, the first stage is that the coating levels off under gravity. Once a coating begins to cure, a thin dry film appears on the surface. The coating then continues to dry and finally, after a period of time, the coating is totally cured.

The coating film is considered tack-free or dry to touch when no mark is left on the coatings when they are touched. In this research, dry to touch time was measured by touching the surface of the coatings with an index finger with moderate pressure. The determination of the ’dry to touch’ time is required because it has to be long enough for the coatings to level, but not too long that all the dust can stick on the wet coatings as this will interfere with the clarity of the coatings and affect the visibility of the samples.

3.7 DRY FILM TESTING

Dry film testing is a set of testing that has been conducted on the dried coating systems after being applied on the particular substrate (glass). This testing is very important in order to assess the performance of the coating system that has been developed. The data can act as an affirmative data to the claims in this research work. The dry film testing will give us the real performance of the coatings especially to the end user. In this part of the research, the dried films will undergo the testing of hardness using pencil scratch, UV transmittance by UV spectrophotometer, and optical measurements by haze meter.

3.7.1 HARDNESS (PENCIL) ASTM D3363

Coating hardness is the ability to resist permanent indentation, scratching, cutting, and penetration by a hard object. A widely used method to measure this property is the ‘Pencil Hardness Test’. The “lead” is actually made of graphite and clay and it is not sharpened as for writing, but it is squared off by rubbing it perpendicularly on an abrasive paper. The sharpened lead point is then held at a 90° angle to horizontal on No.

400 grit abrasive paper and rubbed until a smooth, flat, circular cross-section is obtained. To carry out the test, the coated panel is firmly held on a level surface and the hardest, sharpened pencil is held on the coating at a 45° angle. The pencil is then pushed away from the operator while using sufficient downward pressure to either cut through (gouge) or scratch the film, or to crumple the edge of the lead. This procedure is repeated with softer leads until a pencil is found that will not cut through or scratch the coating. The gouge hardness is reported as the hardest pencil that will leave the coating uncut for a push stroke of at least 3 mm. Determining hardness by gouging or scratching the coating with drawing leads or wood pencils of different hardness (from 6B to 6H) is simple and inexpensive; it is widely used in laboratory development work and production control testing. Testing will be conducted on the coated substrate after 7 days. This is to make sure that all of the reactants and wet coating have dried and have reached their maximum hardness.

3.7.2 UV TRANSMITTANCE

The coated samples that were cured for 7 days at room temperature were used for UV transmittance measurement. UV-Vis-NIR spectrophotometer (SHIMADZU UV 3150) was used in this testing. The transmittance of the UV was measured from 280 nm to 400 nm. The data will give the performance of the coatings in shielding the UV rays from penetrating through the coating layer on the substrate. The original UV transmittance of the blank glass substrate was measured as the reference data.

3.7.3 OPTICAL MEASUREMENT

Optical measurement can be divided into two categories which are:

- Transparency
- Haze

The quantitative assessment of transparency is just as important as that of haze in a clear coating formulation. Transparency refers to the optical distinctness with which an object can be seen when viewed through the samples. Haze meter was used to measure the transparency and the haze level of the coated samples in this research. The instruments give the exact quantification that directly relate to the transparency.

Transparency is not colour-related, but rather relates to the loss of clarity due to the effect of suspended particulate, colloidal material, or both; a lack of clarity or clearness because it is, in part, the effect of these various suspended materials on light passing through liquid or dried coatings. Small deflections of the light, caused by scattering centres of the material, bring about a deterioration of the image. These deflections are much smaller than those registered in haze measurements. While haze measurements depend on wide angle scattering, clarity is determined by small angle scattering. Technically, haze is the percentage of light that is deflected more than 2.5 degree from the incoming light direction. Wide and small angle scattering are not directly related to each other. By this, it means that haze measurements cannot provide information about the clarity of the specimen and vice versa. An object's transparency is measured by its total transmittance. Total transmittance is the ratio of transmitted light to the incident light.

Other than transparency, surface haze can be problematic in most coating applications including automotive manufacturer, powder coating applications and other high gloss coatings. It can be attributed to a number of causes including incompatible materials in the formulation, difficulties in application, and problems encountered during drying/curing/stoving.

$$\% \, Haze = \frac{T \, diffuse \, X \, 100\%}{T \, Total}$$

T = % Transmittance

The haze meter was used to measure the clarity of the samples including the total light diffused and transmitted, and the haze values of the coated samples. D65 illumination light was used as the light source in this instrument. Light may be scattered or diffused due to many factors such as contaminants, unevenness of the coating, agglomeration of the particles in the coatings, etc as shown in figure 3.3. The ideal functional coatings in this research work would be the ones with the lowest light diffused and haze values which will not disturb the appearance of the original substrate.

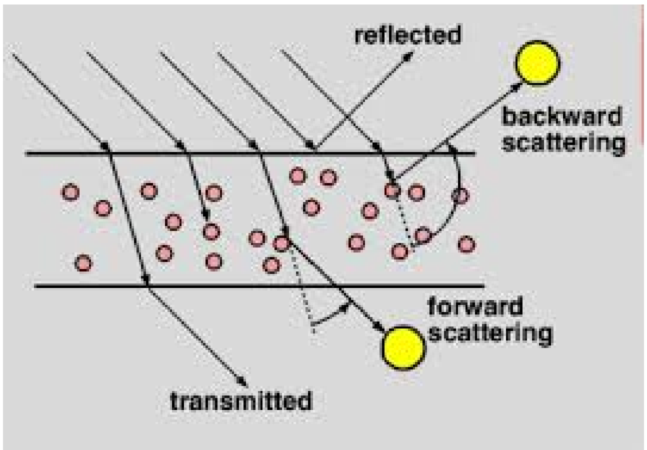


Figure 3.3: Light scattering (http://www.cs.cornell.edu/)

CHAPTER 4

4.0 DEVELOPMENT OF UV ABSORBER COATING:

4.1 UV RADIATION

Ultra violet protective coatings have created an interest among researchers recently. The health issues have been one of the major factors that contributed to the growth of research in this area. The sun radiates energy in a wide range of wavelengths, most of which are invisible to human eyes. The shorter the wavelength, the more energetic the radiation, and thus more hazardous. Ultraviolet (UV) radiation that reaches the Earth's surface is of wavelengths between 290 and 400 nm (nanometers). This is shorter than wavelengths of visible light, which are between 400 to 700 nm.

UV radiation from the Sun has always played important roles in our environment and affects nearly all living organisms. UV radiation at different wavelengths differs in its effects. Radiation of longer UV wavelengths of 320-400 nm, called UV A, plays a helpful and essential role in the formation of Vitamin D by the skin, but plays a harmful role in that it causes skin cancer on human skin and cataracts in our eyes. The shorter UV wavelength, 290-320 nm, falls within the UV B part of the spectrum. (UV B includes light with wavelengths down to 280 nm, but little to no radiation below 290 nm reaches the Earth's surface). UV-B causes damage at the molecular level to the fundamental building block of life — deoxyribonucleic acid (DNA) (Charlotte Young, 2009).

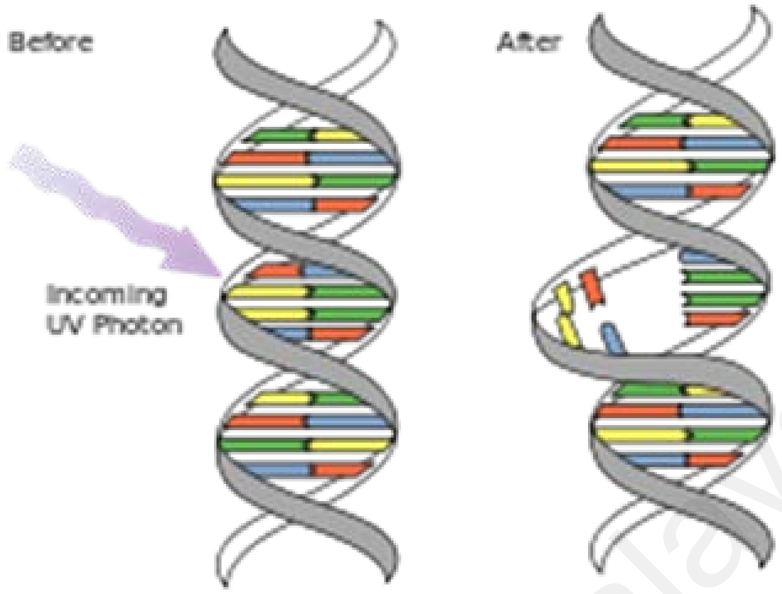


Figure 4.1: The Mutation of DNA after over exposure to UV rays (David Herring, 2006, http://www.onclive.com/)

DNA readily absorbs UV-B radiation, which commonly changes the shape of the molecule in one of several ways. Changes in the DNA molecule often means that protein-building enzymes cannot "read" the DNA code at that point on the molecule. As a result, distorted proteins can be made, or cells can die. Ultraviolet (UV) photons harm the DNA molecules of living organisms in different ways. In one common damage event, adjacent bases bond with each other, instead of across the "ladder." This forms a bulge, and the distorted DNA molecule does not function properly (David S. Goodsell, 2001; Charlotte Young, 2009).

A layer of ozone in the upper atmosphere absorbs UV radiation and prevents most of it from reaching the Earth. However, since the mid-1970s, human activities have been changing the chemistry of the atmosphere in a way that reduces the amount of ozone in the stratosphere (the layer of atmosphere ranging from about 11 to 50 km in altitude). This means that more ultraviolet radiation can pass through the atmosphere to the Earth's surface, particularly at the poles and the nearby regions during certain times of the year. Without the layer of ozone in the stratosphere to protect us from excessive amounts of UV-B radiation, life as we know it would not exist. Scientific concern over ozone depletion in the upper atmosphere has prompted extensive efforts to assess the potential damage to life on Earth due to increased levels of UV-B radiation. Some effects have been studied, but much remains to be learned.

Due to health awareness, many researchers have conducted studies regarding the effect of UV exposure to living organisms. A study was conducted of the Sun safety measures among the construction workers in Britain because the high incidence of skin cancer is attributable to the Sun exposure; this was relatively higher among them compared to other occupational groups (P. Madgwick, J. Houdmont and R. Randal, 2011). In 2005, an estimated 58% of occupational cancer deaths and 55% of occupational cancer registrations are attributed to Sun exposure.

The electromagnetic spectrum of ultraviolet light can be subdivided in a number of ways. The ISO standard on determining solar irradiances (ISO-21348) describes the following ranges in table 3:

Table 3: Solar Irradiances

Name	Abbreviation	Wavelength range	Energy per photon
Ultraviolet	UV	400 – 100 nm	3.10 – 12.4 eV
Ultraviolet A	UVA	400 – 315 nm	3.10 – 3.94 eV
Ultraviolet B	UVB	315 – 280 nm	3.94 – 4.43 eV
Ultraviolet C	UVC	280 – 100 nm	4.43 – 12.4 eV
Near Ultraviolet	NUV	400 – 300 nm	3.10 – 4.13 eV
Middle Ultraviolet	MUV	300 – 200 nm	4.13 – 6.20 eV
Far Ultraviolet	FUV	200 – 122 nm	6.20 – 10.16 eV
Hydrogen Lyman-alpha	H Lyman-α	122 – 121 nm	10.16– 10.25 eV
Extreme Ultraviolet	EUV	121 – 10 nm	10.25 – 124 eV
Vacuum Ultraviolet	VUV	200 – 10 nm	6.20 – 124 eV

On April 2011, the International Agency for Research on Cancer of the World Health Organization classified all categories and wavelengths of ultraviolet radiation as a Group 1 carcinogen. This is the highest level designation for carcinogens and means that there is enough evidence to conclude that it can cause cancer in humans.

It was stated that UV A, UV B, and UV C can all damage collagen fibres and, therefore, accelerate aging of the skin (P. Madgwick, J. Houdmont and R. Randal, 2011). Both UV A and UV B destroy vitamin A in skin, which may cause further damage. In the past, UV A was considered not harmful or less harmful, but today it is known to be able to contribute to skin cancer via indirect DNA damage (free radicals and reactive oxygen species). UV A does not damage the DNA directly like UV B and UV C, but it can generate highly reactive chemical intermediates, such as hydroxyl and oxygen radicals, which in turn can damage the DNA. Accordingly, the DNA damage caused indirectly to the skin by UV A consists mostly of single-strand breaks in the DNA, while the damage caused by UV B includes direct formation of thymine dimers or other pyrimidine dimers, and double-strand DNA breakage. UV A is immunosuppressive for the entire body (accounting for a large part of the immunosuppressive effects of sunlight exposure), and UV A is mutagenic for basal cell keratinocytes in skin.

UV B light can also cause direct DNA damage. As noted above, UV B radiation excites DNA molecules in skin cells, causing aberrant covalent bonds to form between adjacent pyrimidine bases, producing a dimer. Most UV-induced pyrimidine dimers in DNA are removed by the process known as nucleotide excision repair that employs about 30 different proteins. Those pyrimidine dimers that escape this repair process can induce a form of programmed cell death called apoptosis or can cause DNA replication errors leading to mutation.

When DNA polymerase comes along to replicate a strand of DNA with an unrepaired pyrimidine dimer, it reads a "CC" dimer as "AA" and not the original "CC". This causes the DNA replication mechanism to add a "TT" on the growing strand. This mutation can result in cancerous growths, and is known as a "classical C-T mutation". The mutations caused by the direct DNA damage carry a UV signature mutation that is commonly seen in skin cancers. This cancer connection is one reason for concern about ozone depletion and the ozone hole.

As a defence against UV radiation, the type and amount of the brown pigment melanin in the skin increases when exposed to moderate (depending on skin type) levels of radiation; this is commonly known as a sun tan. The purpose of melanin is to absorb UV radiation and dissipate the energy as harmless heat, blocking the UV from damaging skin tissues. UV A gives a quick tan that lasts for days by oxidizing melanin that is already present and it triggers the release of melanin from melanocytes. However, because this process does not increase the total amount of melanin, a UV A produced tan is largely cosmetic and does not protect against either sunburn, or UV B produced DNA damage or cancer.

By contrast, UV B yields a slower tanning that requires roughly two days to develop, because the mechanism of UV B tanning is to stimulate the body to produce more melanin. However, the production of melanin by UV, called melanogenesis, requires direct DNA damage by UV B to initiate. The photochemical properties of melanin make it an excellent photo protectant from both UV A and UV B. Older and more widespread sunscreen chemicals cannot dissipate the energy of the excited state as efficiently as melanin, and, therefore, the penetration of these sunscreen ingredients into the lower layers of the skin may increase the amount of free radicals and reactive oxygen species (ROS). In recent years, improved filtering substances have come into use in commercial sunscreen lotions that do not significantly degrade or lose their capacity to protect the skin as the exposure time increases (photostable substances).

UV rays can also cause harmful effects to the eyes. UV light is absorbed by molecules known as chromophores, which are present in the eye cells and tissues. Chromophores absorb light energy from various wavelengths at different rates – a pattern known as absorption spectrum. If too much UV light is absorbed, eye structures such as the cornea, the lens and the retina can be damaged.

Many polymers used in consumer products are degraded by UV light, and need an addition of UV absorbers to inhibit attack, especially if the products are exposed to sunlight. The problem appears as discoloration or fading, cracking, and sometimes, total product disintegration if cracking has proceeded sufficiently. The rate of attack increases with exposure time and sunlight intensity. Sensitive polymers include thermoplastics, such as polypropylene, polyethylene, and poly (methyl methacrylate) as well as speciality fibres like aramids. UV absorption leads to chain degradation and loss of strength at sensitive points in the chain structure.

Many pigments and dyes absorb UV and change colour, so paintings and textiles may need extra protection both from sunlight and fluorescent bulbs, two common sources of UV radiation. Old and antique paintings such as watercolour paintings, for example, must usually be placed away from direct sunlight. Many museums place black curtains over watercolour paintings and ancient textiles, for example. Since watercolours can have very low pigment levels, they need extra protection from UV light. Tinted glasses, such as sunglasses, also provide protection from UV rays.

In this research study, benzophenone has been used in the UV protection coating system to provide the protection to the substrates. Benzophenone is an organic compound that absorbs ultraviolet (UV) light and are incorporated into the coating system.

Benzophenone is also used as a photo initiator in UV-curing applications such as inks, imaging, and clear coatings in the printing industry. In personal care products, benzophenone prevents UV light from damaging scents and colours in perfumes and soaps. It can also be added to the plastic packaging as a UV blocker. Its use allows manufacturers to package products in clear glass or plastic. Without it, opaque or dark packaging would be required instead of clear glass or plastic.

In UV protection coating, 2,4 dihydroxyl benzophenone (Figure 4.2) was used as a UV blocker that will be mixed into the sol-gel coatings. The coatings must be a clear coating with UV protection and should not change the appearance of the original substrate. Benzophenone was chosen in this experiment due to its solubility in the binder itself and the strong absorption curve of the material. These characteristics are very important because no particular solvent will be used in the sample preparation to dissolve the material. The benzophenone will only be dissolved in the oligomers which are the mixture of amino propyl triethoxy silane and glycidoxyl trimethoxy silane with a stoichiometric ratio of amine hydrogen to epoxide group of 1:1 (mole) at room temperature. The chemicals need to have fully reacted to ensure maximum stability of the product.

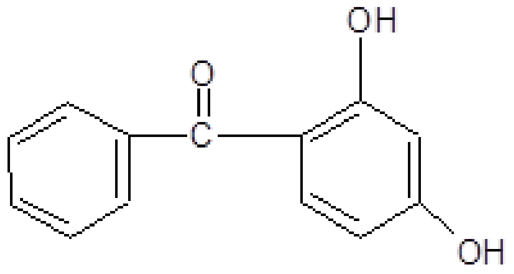


Figure 4.2: 2,4 dihydroxyl benzophenone

4.2 SOL GEL COATINGS

4.2.1 INTRODUCTION:

Glass coatings create interest among researchers due to the needs of modifying its functional behavior. Properties such as anti-glare, anti-reflex, anti-static or modification in dielectric and transmission properties are some of many functional modifications that enhanced value added applications to glass. Protective coatings on glass have many different applications. Self-cleaning, anti-bacterial, ultra violet and heat shielding are some functionality presently of great interest**.**

Presently, the sol-gel method has been increasingly employed in the glass coating industry. In some examples, sols or gels can be used as end products. The current applications of ceramics as finished products in the sol state concern essentially the ferrofluids, commercially by the Ferrofluid Corporation. These products were developed in the year 1960 by NASA to control the rocket fluids in zero gravity environments (Pierre, 1998).

Sol-gel coatings are widely used for different purposes, especially in those related with optical semiconductor, protective and sensing applications. Other than that, sol–gel processes provide an excellent pathway for synthesis of many non-toxic, transparent, crack-free, and photosensitive protective coatings, which add to modern technological enhancement in all spheres.

Sol-gel promotes a simple technique in glass coatings. The most frequent ones are optical functions because oxides are transparent to visible light wavelengths. They can also be used to protect substrate against corrosion, abrasion, scratch, be chemically and thermally stable, or even stable against some radiation. This technique has also been applied to produce coating with high optical transparency and low thermal conductivity, and is presently widely used in an architectural window. Typically, sol-gel coated surfaces need a separate curing treatment by heating at temperatures between 100 and 200°C. This treatment, however, increases the manufacturing costs, especially when sol-gel coating is applied to existing production chains. Another drawback of the high temperature sol-gel processing other than its cost is the shrinkage that accompanies drying and sintering, and processing time.

In order to overcome the drawbacks in the high temperature sol-gel, low temperature sol gel method was invented ((Walid A. Daoud and John H. Xin, 2004) and (V.I. Kondratiev, I. Kink, A.E. Romanov, 2013)). Low temperature sol-gel film is cheaper but more importantly, it can be applied on site to glass surface. Sol-gel coatings of low temperature processing has shown good adherence to the substrates (glass, ceramics composites, etc.), hence posing a possibility to prepare multi layered coatings due to its low viscosity. The possible application for this type of coating system is to have a value added function when functioning agents are mixed to the coating system without interfering with the original appearance of the substrate. The coating should appear very transparent with an acceptable tack-free time.

The basic compositions of the coatings are as follows:

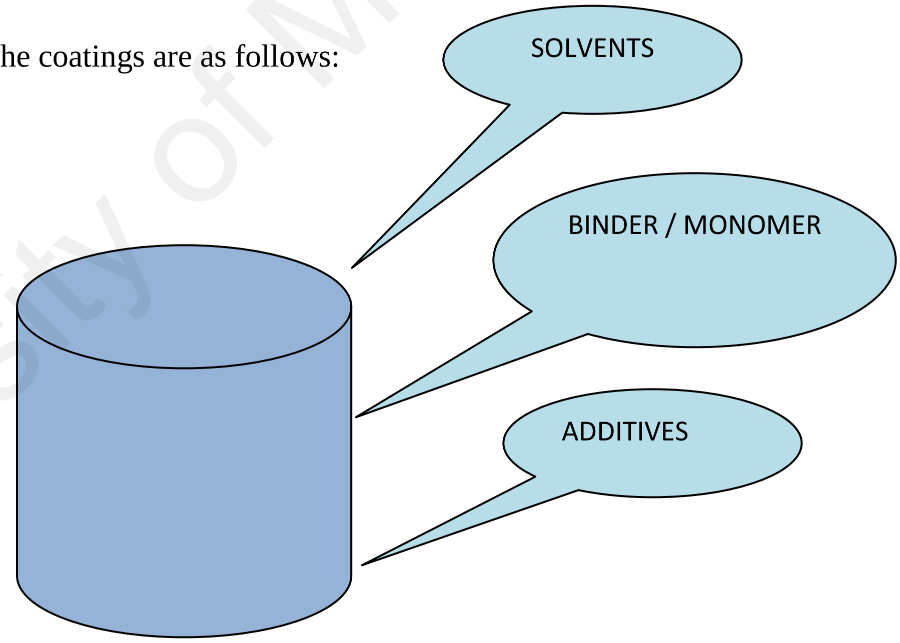


Figure 4.3: Coatings composition

Silane coupling agents have the ability to form a durable bond between organic and inorganic materials. Materials often involve at least one siliceous or have chemistry with siliceous properties; silicates, aluminates, borates, etc.

$$R – (CH2)_n – Si – X_3$$

R = Organofunctional Group

$– (CH2)_n$ = Linker

Si = Silicon Atom

X_3 = Hydrolyzable group

The general formula of the silane coupling agent consists of two classes of functionality. X is a hydrolysable group; typically alkoxy, acyloxy, halogen or amine. Following hydrolysis, a reactive silanol group is formed which can condense with other silanols groups to form siloxane linkages. The R group is a non-hydrolyzable organic functional group that can impart desired characteristics. Significantly, it includes the ability to affect a covalent bond between organic and inorganic materials.

Alkoxides react directly with silanols or with water to produce silanols. The newly formed silanols can react with other alkoxides or self-condense to produce a siloxane bond and water. The by-product of the reaction is an alcohol. Figure 4.4 shows the condensation reaction between the hydroxyl groups in the silane and the hydroxyls group on the surface of inorganic material. Through this method, the hydrogen bond was formed between the silane binder and the substrate.

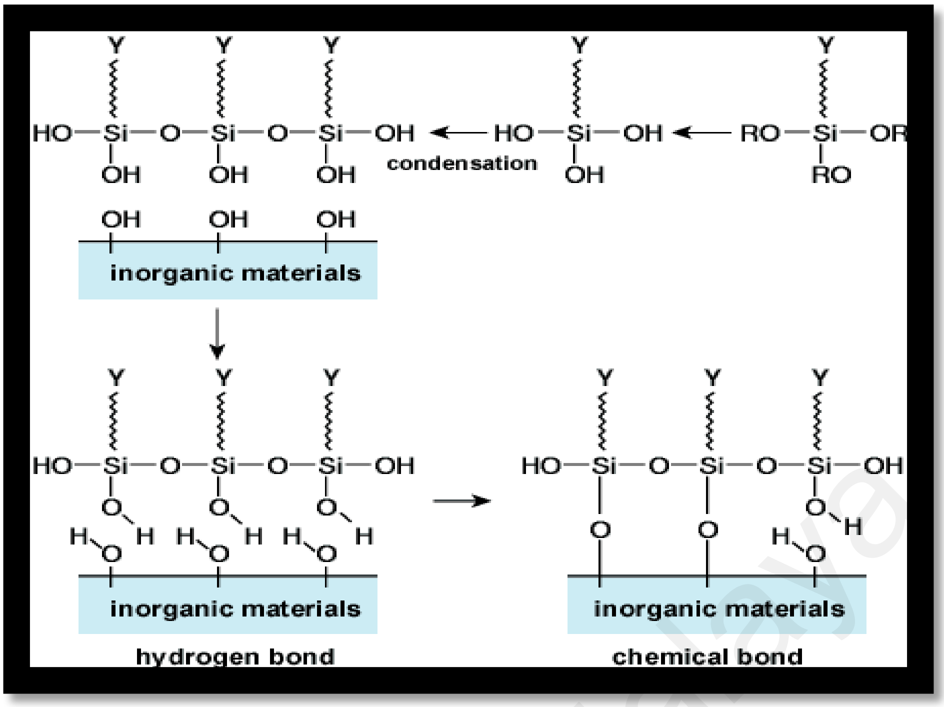


Figure 4.4: Reaction mechanism of the Silane binder

In this study, the suggested reaction of the silanes follows four major steps. Raw material which is methyl trimethoxy silane: CH_3 – Si – $(OCH_3)_{3,}$ will undergo the hydrolysis stage when silane reacts with water molecules, forming silanols with methanols as the side products. Water molecules for the reaction may come from various resources; it may be added, it may be present on the substrate surface, or it may come from the atmosphere. In this study, the water molecule was assumed from the nitric acid and the moisture in the environment.

Condensation to oligomers followed. The oligomers then formed the hydrogen bond with the OH groups of the substrate. Hydroxyl containing substrates vary widely in concentration of hydroxyl groups presents. Fresh substrates stored under a neutral condition have a minimum number of hydroxyls. Hydrolytically derived oxides aged in moist air have significant amounts of physically adsorbed water which can assist in coupling for coating adhesion to the substrate. Finally, during drying or curing, a covalent linkage is formed with the substrate with loss of water molecule.

4.2.2 REACTION OF 3-GLYCIDOXYPROPYL TRIMETHOXYSILANE AND 3-AMINOPROPYL TRIETHOXYSILANE

In general, uncured epoxy resins have only poor mechanical, chemical and heat resistance properties. However, good properties are obtained by the reactions of the linear epoxy resin with suitable curatives to form three-dimensional cross-linked thermoset structures. This process is commonly referred to as curing. Curing of epoxy resins is an exothermic reaction and in some cases, produces sufficient heat to cause thermal degradation if not controlled.

Curing may be achieved by the reactions of an epoxy with itself (homopolymerisation) or by forming a copolymer with polyfunctional curatives or hardeners. In principle, any molecule containing reactive hydrogen may react with the epoxide groups of the epoxy resin. Common classes of hardeners for epoxy resins include amines, acids, acid anhydrides, phenols, alcohols and thiols. Relative reactivity (lowest first) is approximately in the order: phenol < anhydride < aromatic amine < cycloaliphatic amine < aliphatic amine < thiol.

In this study, 3-glycidoxypropyl trimethoxysilane which contains epoxy group will be reacted with 3-aminopropyl trimethoxysilane which contains the primary amines that will become the hardener for the epoxy group in the coating system. As shown in figure 4.5, the primary amine will open the epoxy rings which lead to the formation of strongly hydrophilic hydroxyl groups (-OH). For non-stoichiometric formulations with excess epoxy monomer, the epoxy ring can react with hydroxyls groups, leading to the formation of ether groups according to the reaction as shown in figure 4.6.

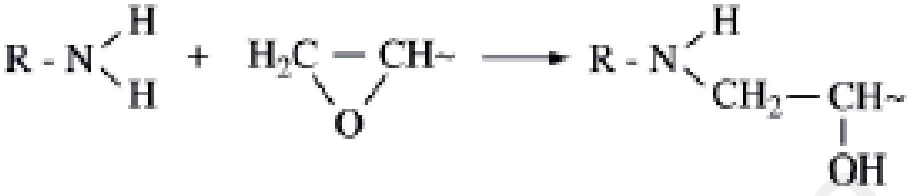


Figure 4.5: The epoxy ring opening by primary amine

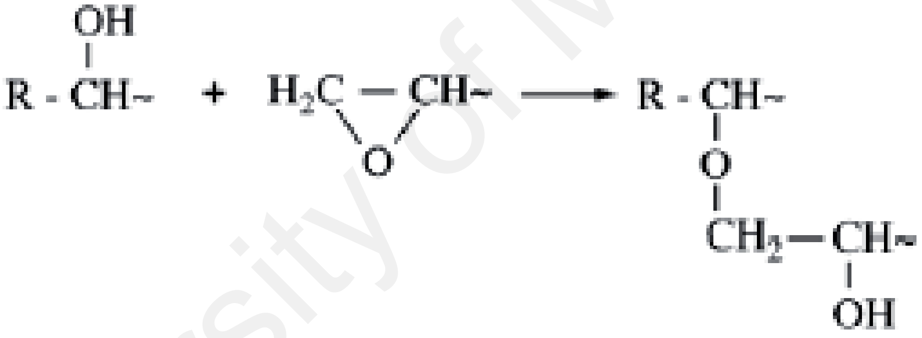


Figure 4.6: The hydroxyl reaction with epoxy ring

Table 4: Chemical properties of 3-Glycidoxypropyltrimethoxysilane

CAS No.	**2530-83-8**
Chemical Name:	**3-Glycidoxypropyltrimethoxysilane**
Synonyms:	GLYMO;A 187;CG6720;Y 4087;Z 6040;DZ 6040;KBM 403;KBM 430;NUCA 187;Pivadorm
Molecular Formula:	$C_9H_{20}O_5Si$
Formula Weight:	236.34

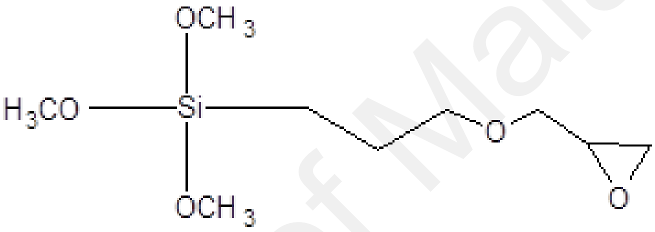


Figure 4.7: 3-Glycidoxypropyl trimethoxysilane

Table 5: Chemical properties of 3-Aminopropyltriethoxysilane

CAS No.	**919-30-2**
Chemical Name:	**3-Aminopropyltriethoxysilane**
Synonyms:	agm9;AMEO;AGM 9;a1112;a1100;agm-9;APTES;CA750;A 1112;A 1100
Molecular Formula:	C9H23NO3Si
Formula Weight:	221.37

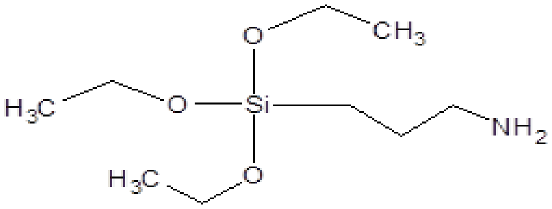


Figure 4.8: 3-Aminopropyl triethoxysilane

4.2.3 EXPERIMENTAL METHOD:

A mixture of amino propyl triethoxy silane and glycidoxyl trimethoxy silane from Shinetsu.co.jp was prepared with the mole ratio of 1:1. The mixture was cured at room temperature for 14 days and the viscosity of the mixture was monitored daily to get the stable readings of viscosity. 2,4 dihydroxy benzophenone from Everlight UV A was added then from 0.5% wt until 5% wt to get the optimum amount of UV absorber needed in the coating system. Boron triflouride piperydine that has been dissolved with N-propanol with the ratio of 1:9 was added into the mixture 10% wt. The coating mixture was stirred vigorously until all the benzophenone powder has dissolved. The viscosity of the wet coating was measured using Brookfield viscometer. Table 6 shows the samples' name based on the amount of benzophenone that was added. The coating was coated on the glass substrate 50 mm x 50 mm x 6 mm using a sponge and dried at room temperature. The dried coating was analysed using a UV spectrophotometer for UV transmittance and a Haze meter for the clarity and haze values.

Table 6: Samples with different amount of 2,4 dihydroxyl benzophenone

Label	S1	S2	S3	S4	S5	S6
% of benzophenone	0.5	1.0	2.0	3.0	4.0	5.0

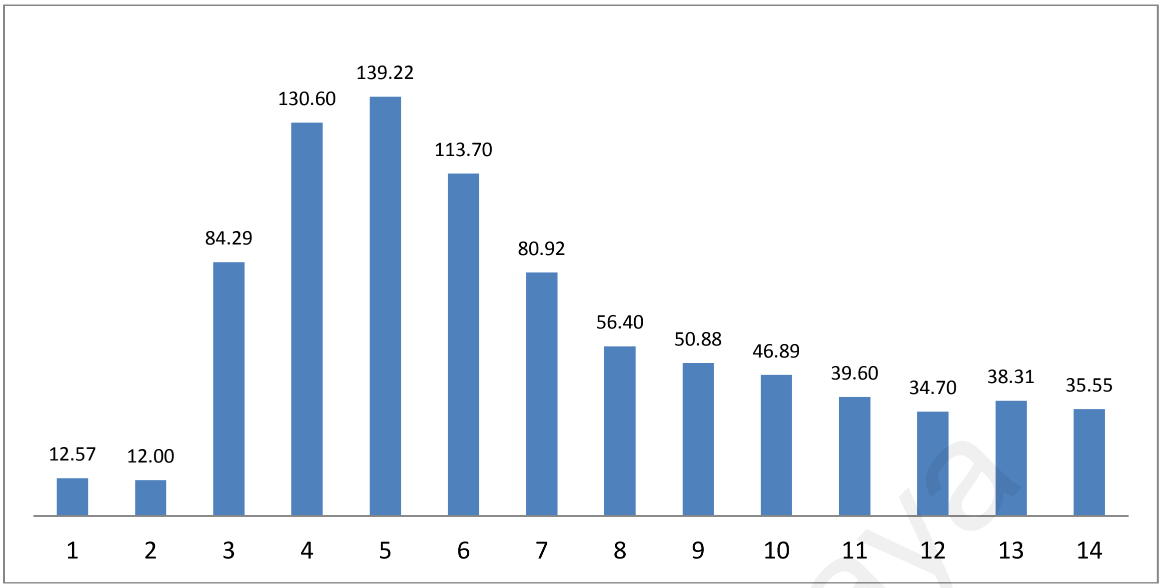


Figure 4.9: The daily readings of viscosity of binder (mixture of amino propyl triethoxy silane and glycidoxyl trimethoxy silane) during curing from Day 1 to Day 14

Figure 4.9 shows that the 2 monomers started to react on Day 3 based on the rapid increment of the viscosity values. Day 5 recorded the highest reading which is 139.22 cp; this was believed to be the peak of the reaction. On Day 6, the viscosity of the binder started to decrease and stabilize from Day 11 to Day 14. Therefore, the binder will only be used on Day 14 onwards.

4.2.4 EFFECT OF THE AMOUNT OF BENZOPHENONE TO THE VISCOSITY OF THE COATING SYSTEM

Viscosity is the liquid’s internal resistance to flow. Coat ability of the coatings depends on the viscosity of the coating formulation. In order for the coating to be coated using a sponge, the viscosity cannot be too high because the liquid need to be absorbed into the sponge and released on the glass substrate during the coating process. Therefore, the viscosity test is important to determine the suitable coating method.

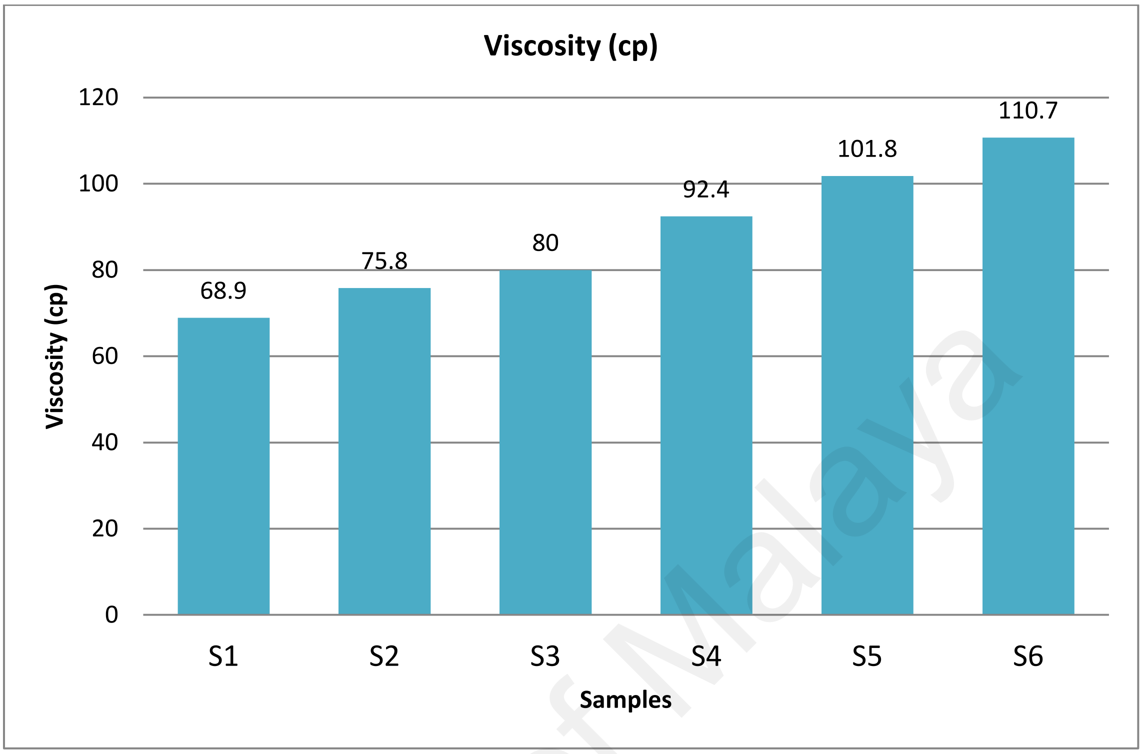


Figure 4.10: Viscosity of the coating system

Figure 4.10 shows the viscosity of the coating formulation with different amounts of benzophenone in the mixture. The viscosity increased as the amount of benzophenone was increased. This is due to the increase in the amount of solute in the solutions but it is still coat-able, and the coating has managed to level after the application.

4.2.5 THE EFFECT OF THE AMOUNT OF BENZOPHENONE TO THE 'TACK FREE TIME'

Tack-free time is the length of time required for a coating to lose its surface tackiness. This is determined by touching the samples with an index finger with minimum pressure. The period at which there is no finger mark appearing on the samples is determined as the tack-free time. Catalyst and moisture are the factors that affect this property. The tack-free time test was conducted as the catalyst amount and moisture remained constant.

Figure 4.11 shows the tack-free time of samples with different amounts of benzophenone in the coating mixture. There are no significant changes in the tack-free time of the coating. The tack-free time is between 3 and 5 minutes, which are still in an acceptable range. It can be concluded that the amount of benzophenone from 0.5% to 6% in the coating does not affect the tack-free time.

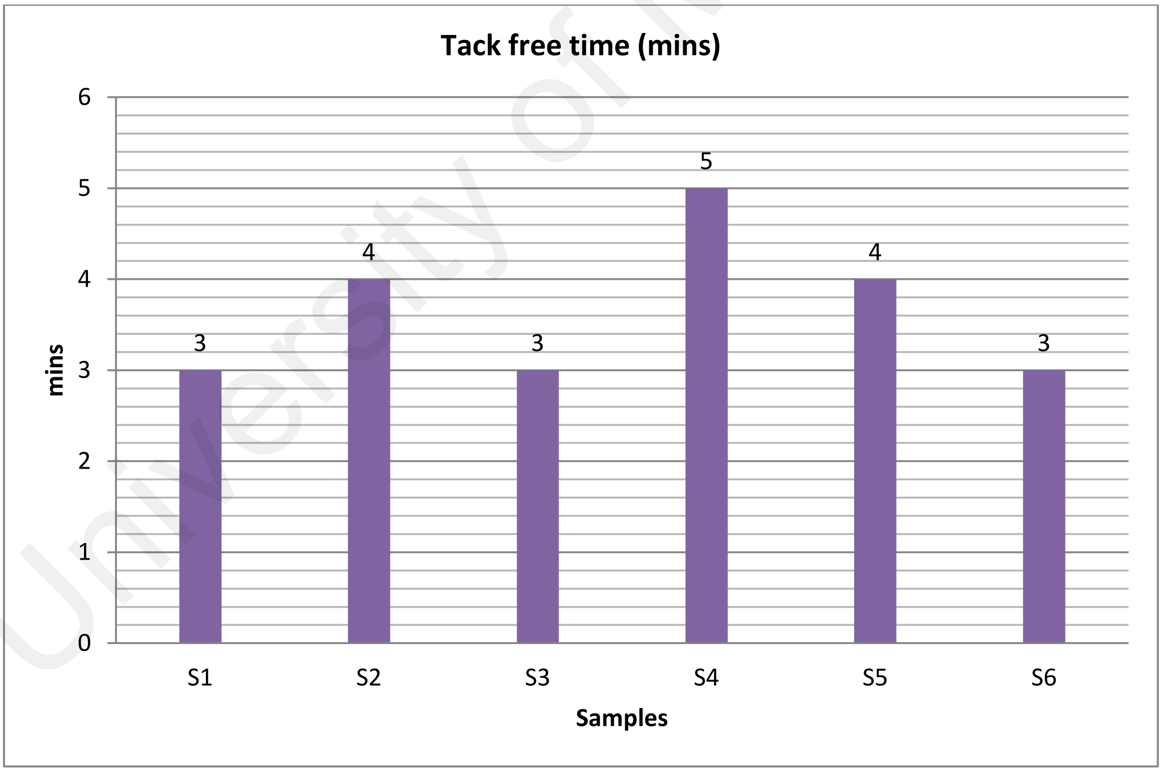


Figure 4.11 The tack free time (mins)

4.2.6 THE EFFECT OF THE AMOUNT OF BENZOPHENONE TO THE OPTICAL MEASUREMENTS OF THE SAMPLES

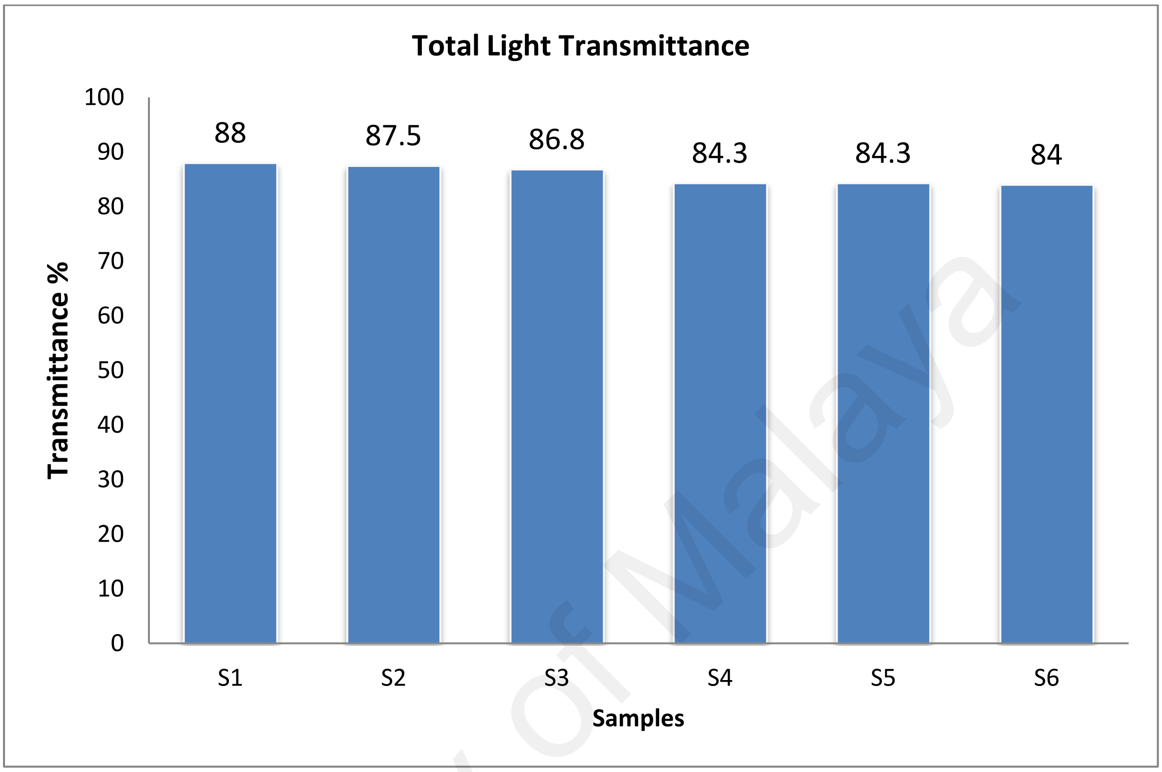


Figure 4.12: The percentage of total light transmittance

Total transmittance is the measurement of light in the visible portion of the spectrum that passes through the samples. It is affected by the small angle scattering of incident light. It is also considered as a measurement of sample transparency. As the total light transmittance increases, it allows more light to penetrate through the samples and maintain the clarity of the glass.

Figure 4.12 shows the total light transmittance for all the samples. As the amount of benzophenone increases, the total light transmittance slightly decreases. This is due to the fact that more lights has been diffused and scattered when passing through the samples with higher amount of solute, resulting of some interference at the small angle light scattering. The lowest total light transmittance was observed for samples S6 that contains the highest amount of benzophenone, which is 84%. However, this result is still considered as a high clarity sample. Based on rules and regulations, the minimum light transmittance for vehicle windscreens in most countries in the world is between 70% and 75% (RTA, 2003).

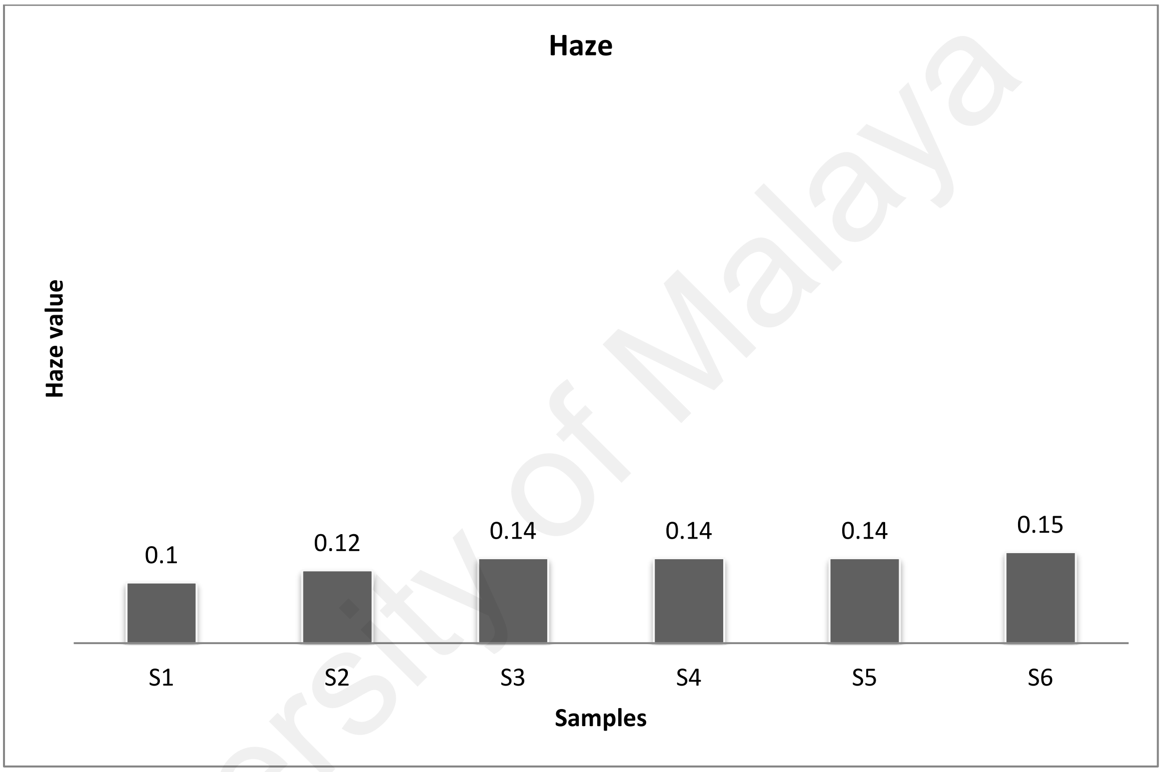


Figure 4.13: The Haze values

The amount of benzophenone as a UV absorber that was mixed into the coating formulations should provide the highest protection from the UV rays but not sacrificing the clarity and transparency of the coatings. Haze value is affected by the wide angle light scattering (more than 2.5 degree). As the benzophenone completely dissolved in the coating mixture, there was minimum interference of the wide angle scattering. Figure 4.13 shows the haze values of the samples. As the amount of benzophenone increased, the haze value slightly increased. The average haze values of the coating were 0.13. It can be concluded that the amount of benzophenone from 0.5% to 6% did not significantly affect the haze value of the samples, and the samples remained clear.

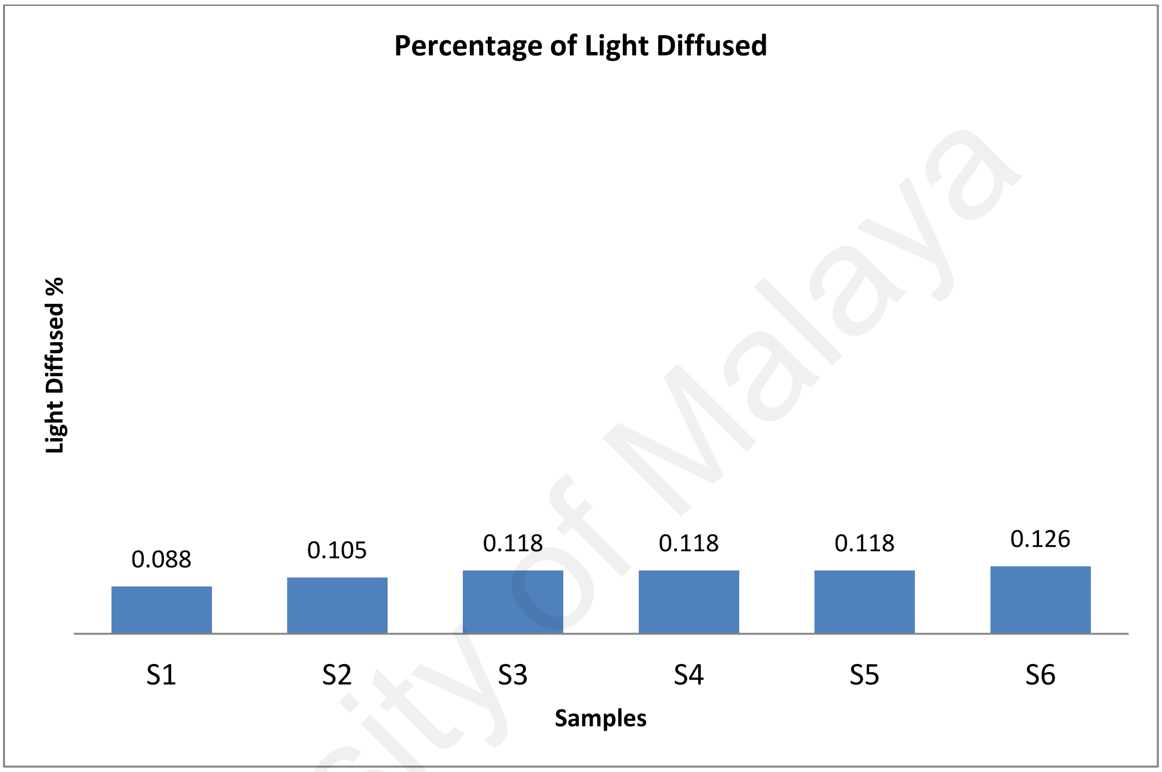


Figure 4.14: Percentage of light diffused of the dried samples

Light diffused can be thought of as the deflection of a ray from a straight path; for example, by irregularities in medium and/or particles, or in the interface between two media. The result of light diffused through the dried samples is shown in figure 4.14. As the amount of benzophenone increased, the percentage of light diffused showed a slight increment. However, it still unnoticeable with the naked eye. Therefore, it can be concluded that there were very minimal changes; thus clarity of the coating remains the same.

4.2.7 THE EFFECT OF THE AMOUNT OF BENZOPHENONE TO THE PERCENTAGE OF TRANSMITTANCE AT THE UV WAVELENGTH

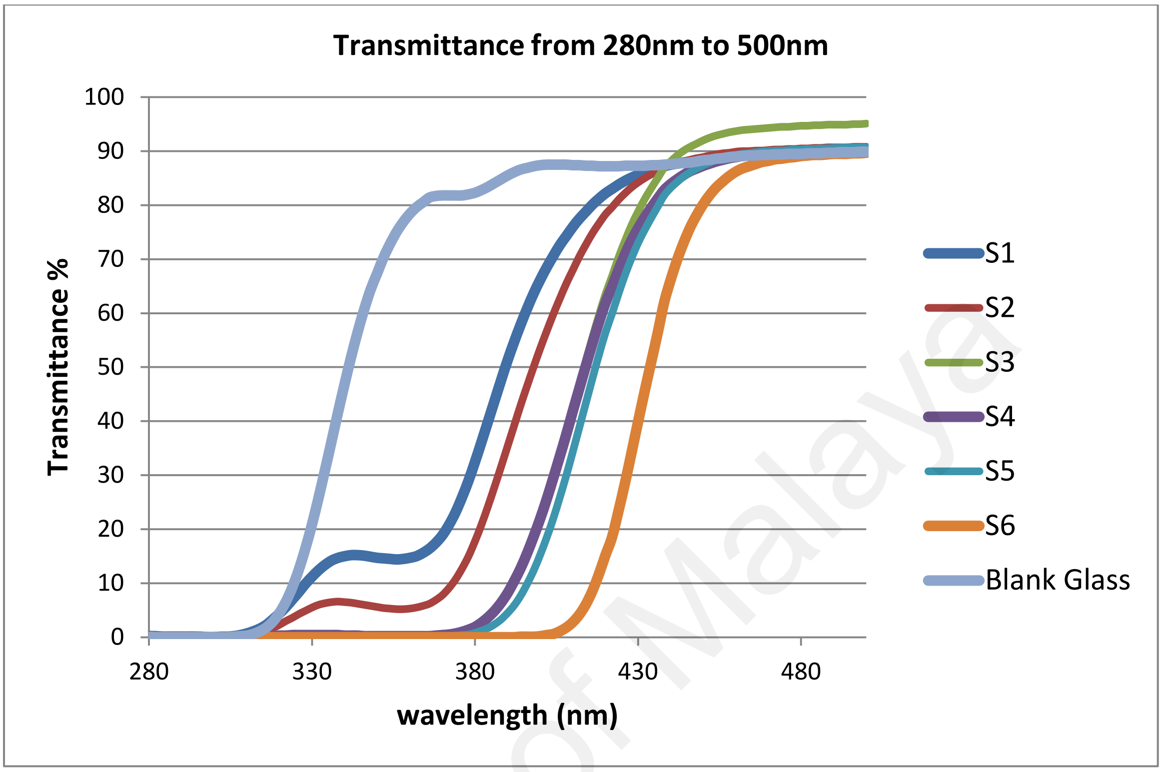


Figure 4.15: The spectrum data of UV transmittance through the samples

Percentage of UV transmittance from 280 nm to 400 nm was measured for different amounts of benzophenone are shown in figure 4.15. It is clearly seen that 5% wt of benzophenone managed to block almost all the UV A and UV B radiations. At any particular frequency, the transmittance shows a general trend of a decrease as the mount of UV absorber used is increased.

Figure 4.16 shows a plot of transmittance against the amount of UV absorber used at 350 nm. The lowest transmittance was obtained from the sample that was mixed with 5% wt of benzophenone (S6) and 67.4% of light transmittance from a 6 mm blank glass.

The transmittance of the wavelength decreased as the amount of benzophenone increased due to the absorption at the 300 nm to 400 nm. Benzophenone which absorbs the UV rays and undergoes the cleavage upon irradiation. 5% wt of benzophenone in the coating system will be chosen as the best formulation for UV protection coating.

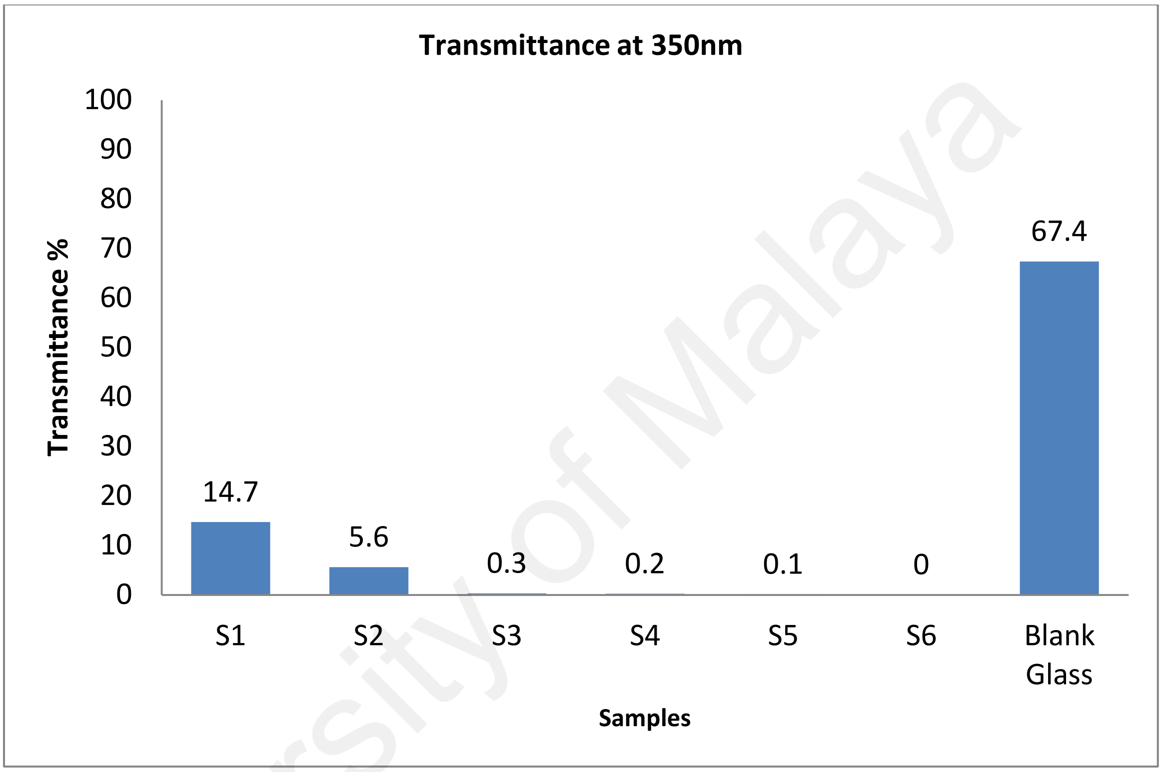


Figure 4.16: The transmittance of UV rays at 350 nm

4.2.8 APPLICATION OF UV PROTECTION SOL GEL COATING ON GLASS SUBSTRATE

The coating was applied directly on the glass. One layer of coating is sufficient to filter an average of more than 99% UVA and UVB rays from penetrating through the samples. The coating was applied on the substrate using a melamine sponge from BASF (Figure 4.17) at room temperature. The polymer foams were tested by soaking it into the liquid sol completely, and observed for swelling. Melamine sponge was chosen due to its open cell foam and fine structure that allows the liquid coating to be absorbed easily into the pores, and to be released back on the substrate during the coating application.

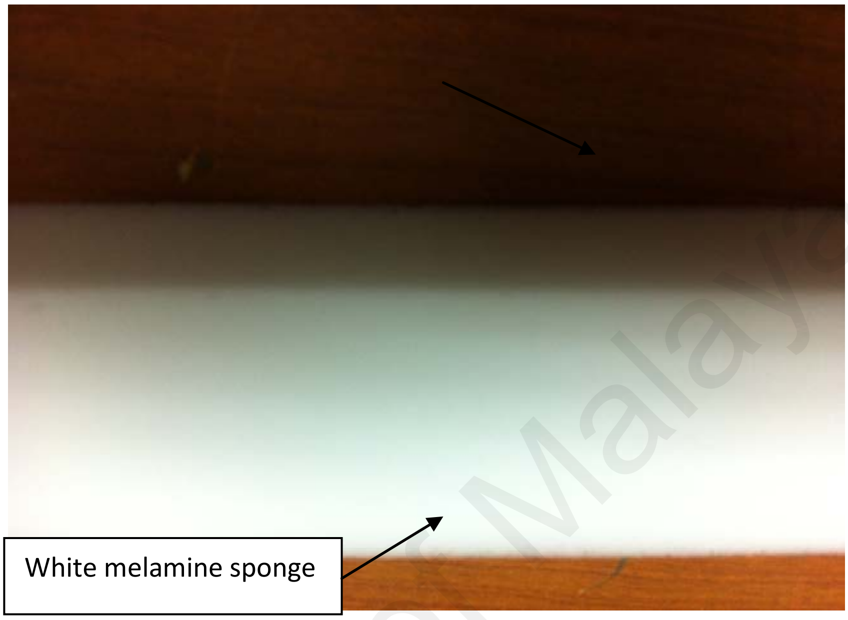


Figure 4.17: Melamine sponge used for coating application

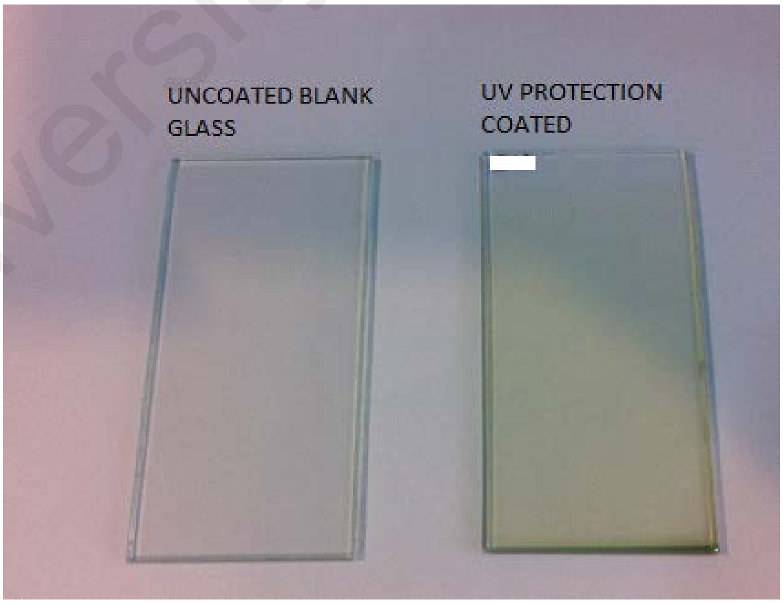


Figure 4.18: Blank Glass and coated glass

Figure 4.18 shows the comparison of appearance for coated and uncoated glass samples. A very pale yellow tint was observed for the coated glass sample due to the existing colour of benzophenone. However, the clarity of the sample remains the same.

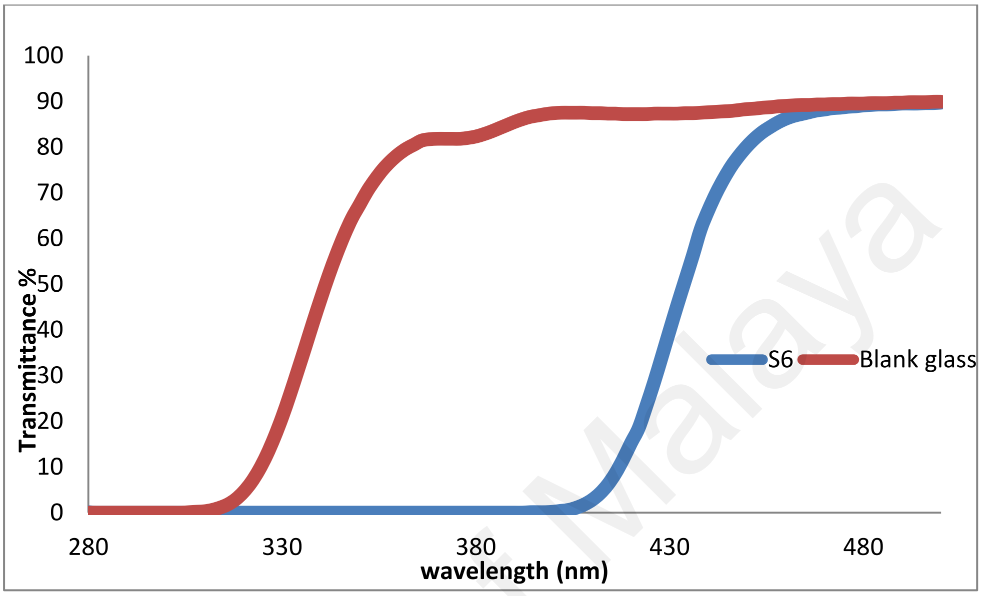


Figure 4.19: UV transmittance for sample S6 and Uncoated blank glass

Figure 4.19 shows the comparison of UV light transmittance for sample coated with 5% benzophenone and uncoated blank glass. The transmittance of the UV has been reduced significantly due to the high absorption of benzophenone at the particular wavelength. From the graph, it shows that at 460 nm onwards which is the wavelength of visible light, the transmission of both samples are similar. This indicated that the material has a very selective spectrum absorption.

Table 7: Comparison of UV transmittance through sample S6 and blank float glass

Wavelength nm.	S6	Blank glass (% transmittance)
280	0.1	0
290	0	0
300	0	0
310	0	0.3
320	0	4.5
330	0	20.9
340	0	46.9
350	0	67.4
360	0	78.4
370	0	81.8
380	0	82.3
390	0	85.5
400	0.2	87.4

The average percentage of transmittance in the range of 280 nm to 400 nm for the sample coated with sol gel added 5% benzophenone, is only 0.023%, whereas for the uncoated sample the average is 42.72%. It can be concluded that with one layer of UV protection sol-gel coating, it has managed to block an average of 99.97% of rays (280–400) nm from penetrating through the glass. This frequency range is for UV protection coatings because it covers the ranges of UV A (320-400) nm and UV B (290-320) nm that are hazardous to humans. 5% of benzophenone in a mixture of 3-aminopropyltriethoxysilane and 3-glycidoxypropyl trimethoxysilane is chosen as the optimum formulation for UV protection sol-gel coating. The durability of this coating was not tested in this research work because another layer of functional coating (antibacterial) will be applied on top of it.

CHAPTER 5

5.0 DEVELOPING THE ANTIBACTERIAL COATINGS

5.1 SYNTHESIS AND CHARACTERIZATION OF SILVER NANOPARTICLES

Silver nanocrystal in this study was prepared via the precipitation method. 20 ml of silver nitrate solution with different molarities was prepared. Table 8 shows the sample name with different molarities of silver nitrate.

Table 8: Silver nitrate with different molarities

$AgNO_3$ Concentration (M)	Sample Name
0.1	1M
0.2	2M
0.3	3M
0.4	4M
0.5	5M
0.6	6M

0.1 ml of ethylene diamine was added into the silver nitrate solution and stirred for 5 minutes. 0.05 g of cetyltrimetyl ammonium bromide (CTAB) was added to the solution as a dispersing agent and stirred vigorously for another 5 minutes before adding hydrazine hydrate. The solution was stirred for another 5 minutes and kept at room temperature for 15 minutes. The particles were separated from the solution by centrifuging the solution at 5000 rpm for 20 minutes. The particles were washed by repeating the centrifuging process with deionised water and lastly, with ethanol. The particles gathered were dried in desiccators for 24 hours. In order to break and reduce the agglomeration of the particles, a ball milling process was carried out for three and a half hours at 300 rpm, with the weight ratio of ball to sample of 120:1. XRD was used to confirm the crystal structure and estimate the crystallite size.

The chemical route for the formation of silver nanoparticles can be described as follows:

$$Ag^{+} + (CH_2NH_2)_2 \rightarrow [Ag(CH_2NH_2)_2]^{+} \quad (1)$$

$$4[Ag(CH_2NH_2)_2]^{+} + 5N_2H_4 \rightarrow 4Ag + 4N_2H_5 + N_2 + 4(CH_2NH_2)_2 \quad (2)$$

In equation (1), the first reaction of Ag^{+} with the ethylenediamine formed the $[Ag(CH_2NH_2)_2]^{+}$ complex, and the following reaction in equation (2) with the hydrazine hydrate is to form silver metal. CTAB was added as a dispersant.

FESEM and EDX were used in the next stage of the research to study the morphology and the elemental composition of the precipitate**.** XPS analysis was carried out to determine the chemical composition at the surface of the particles.

5.1.1 XRD FOR THE SILVER PRECIPITATE

The silver precipitate produced were structurally analysed by XRD from 5^0 to 90^0 2θ angle. From figure 5.1, same peaks appeared in all of the samples. The sharp peaks were observed at 38° (2θ). The XRD study confirmed that the crystal consists of silver atoms only. The crystals formed are face-centred cubic structure

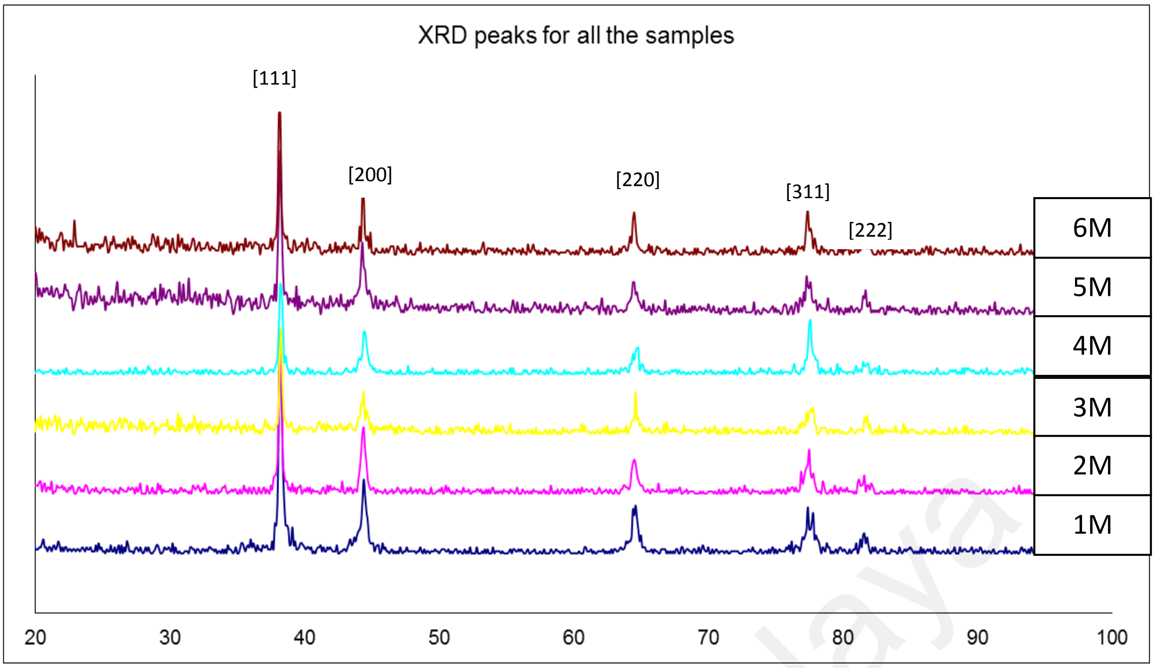


Figure 5.1: XRD of silver particles produced

5.1.2 ESTIMATION OF CRYSTALLITE SIZE OF THE NANOSILVER FOR DIFFERENT SILVER NITRATE MOLARITY

The Scherrer formula used to estimate crystallite size of the silver nanocrystals, *S*:

$$S = \frac{0.95}{\beta \cos \theta} \lambda$$

Where:

λ = wavelength of the X-rays (A^0)

β= Full width Half Maximum of the peak chosen in radian

θ = line peak position chosen

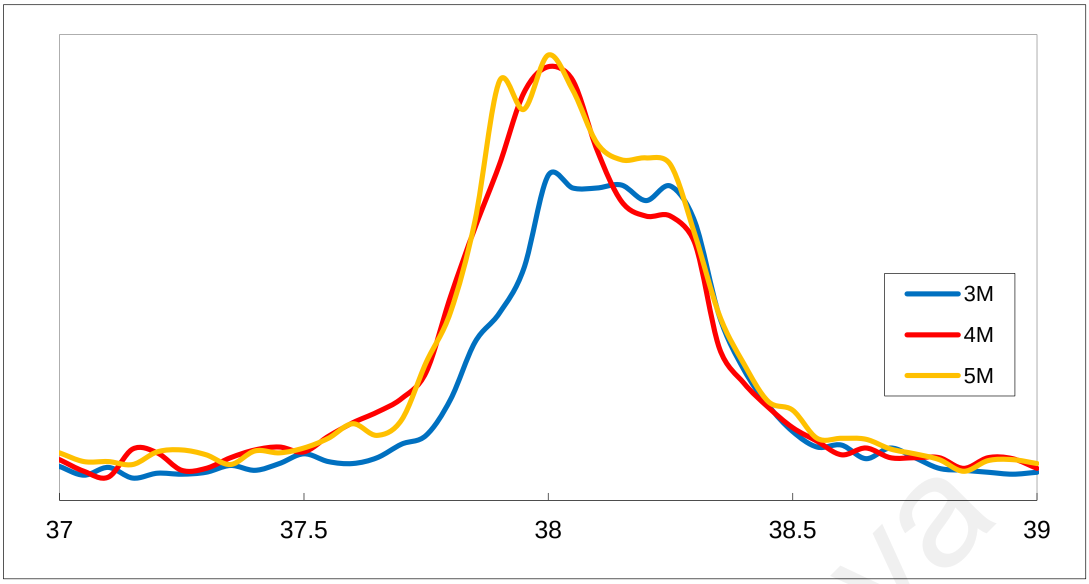


Figure 5.2: Peak [111] for sample 0.3M, 0.4M and 0.5M

Estimation of silver crystallite size was made through Lorentzian curve fit to the strongest peak in the XRD pattern Ag [111] from 2θ of 37^0 to 42^0 (Figure 5.2). The estimation of crystallite size of the samples calculated was shown in Figure 5.3.

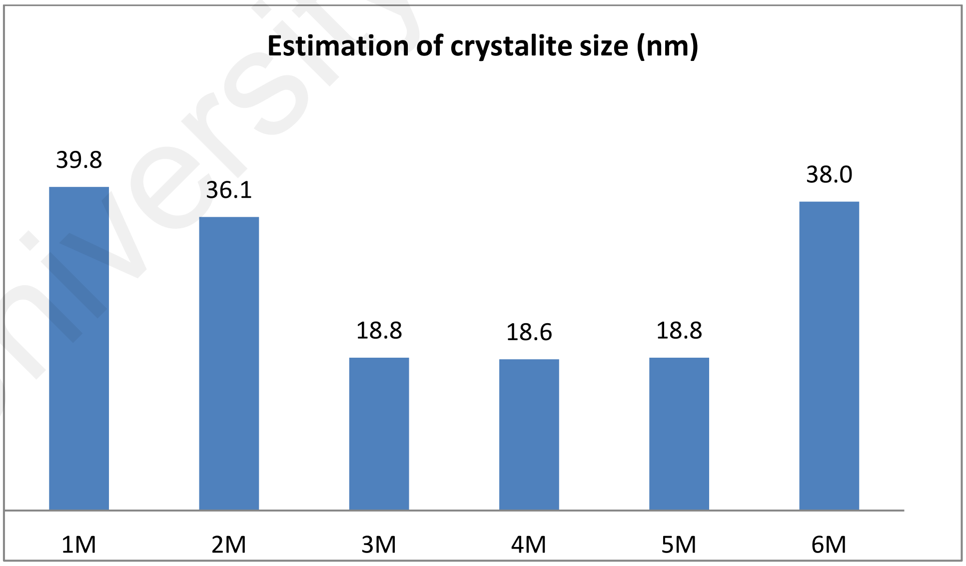


Figure 5.3: Variation of crystallite size of silver nanoparticles with silver nitrate molarity

Figure 5.3 clearly show that with molarity of 0.3M to 0.5M, the crystallite size produced was the smallest. The silver crystals were analysed by FESEM to get the image of the particles and clusters of the crystals. Crystallite size of the silver is an important factor that determines the antibacterial efficiency. This is attributable to the high ‘surface area to volume’ ratio. Silver metal particles in nanometer size have attracted considerable interest in recent years, as they have tremendous applications in the area of biomedicine, catalysis, and optoelectronics due to their unique size-dependent properties. Smaller particles have larger surface areas and hence, direct contact will be greater compared to larger particles of the same active agent. The silver nanoparticles produce a greater amount of ROS (Reactive Oxygen Species). Silver has also been reported to be toxic to bacteria (Kim et. Al 2008)

5.13 AUGER SPECTROSCOPY OF THE NANO SILVER CRYSTALLITE

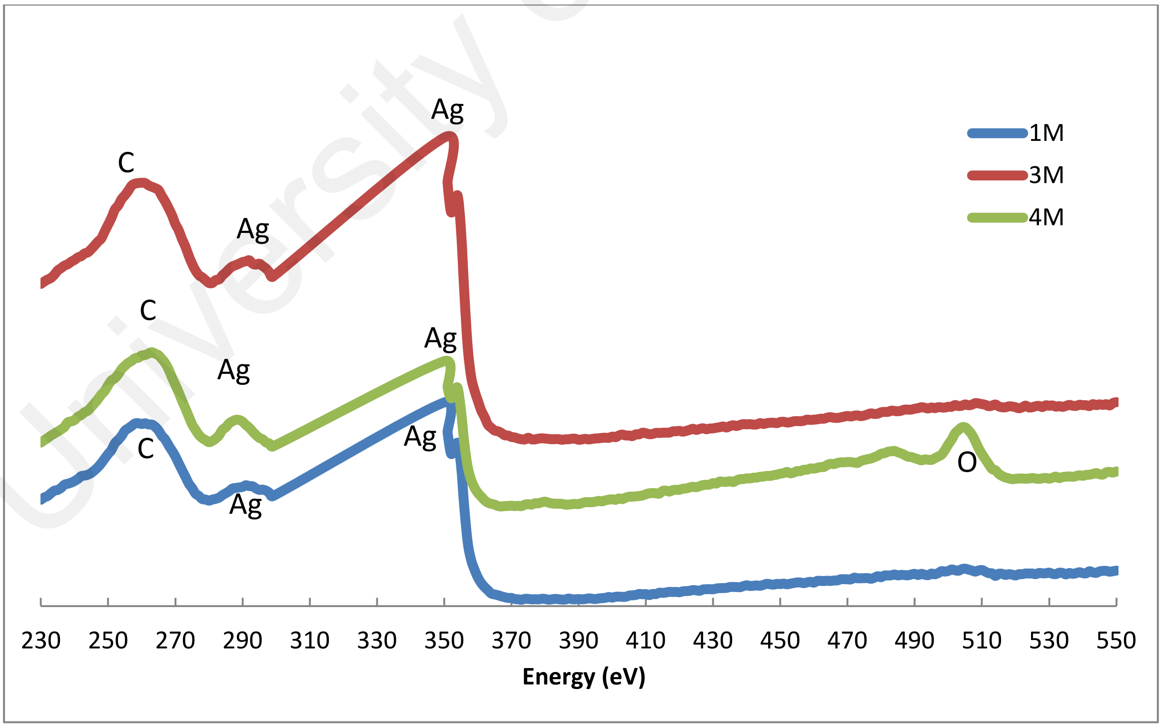


Figure 5.4: Auger spectroscopy of the silver precipitates for samples that was produced from $AgNO_3$ concentration of 0.1M (1M), 0.2M (2M) and 0.3M (3M)

Figure 5.4 clearly shows that the precipitates contain silver element. However, the presence of C was detected in all samples and O was observed from sample 4M which silver nitrate 0.4M. This may due to the residue of the reactant although the samples have been washed a few times with deionized water and ethanol. In addition to that, the samples were not prepared in an inert atmosphere.

5.14 FESEM STUDY ON NANO SILVER CRYSTALLITE

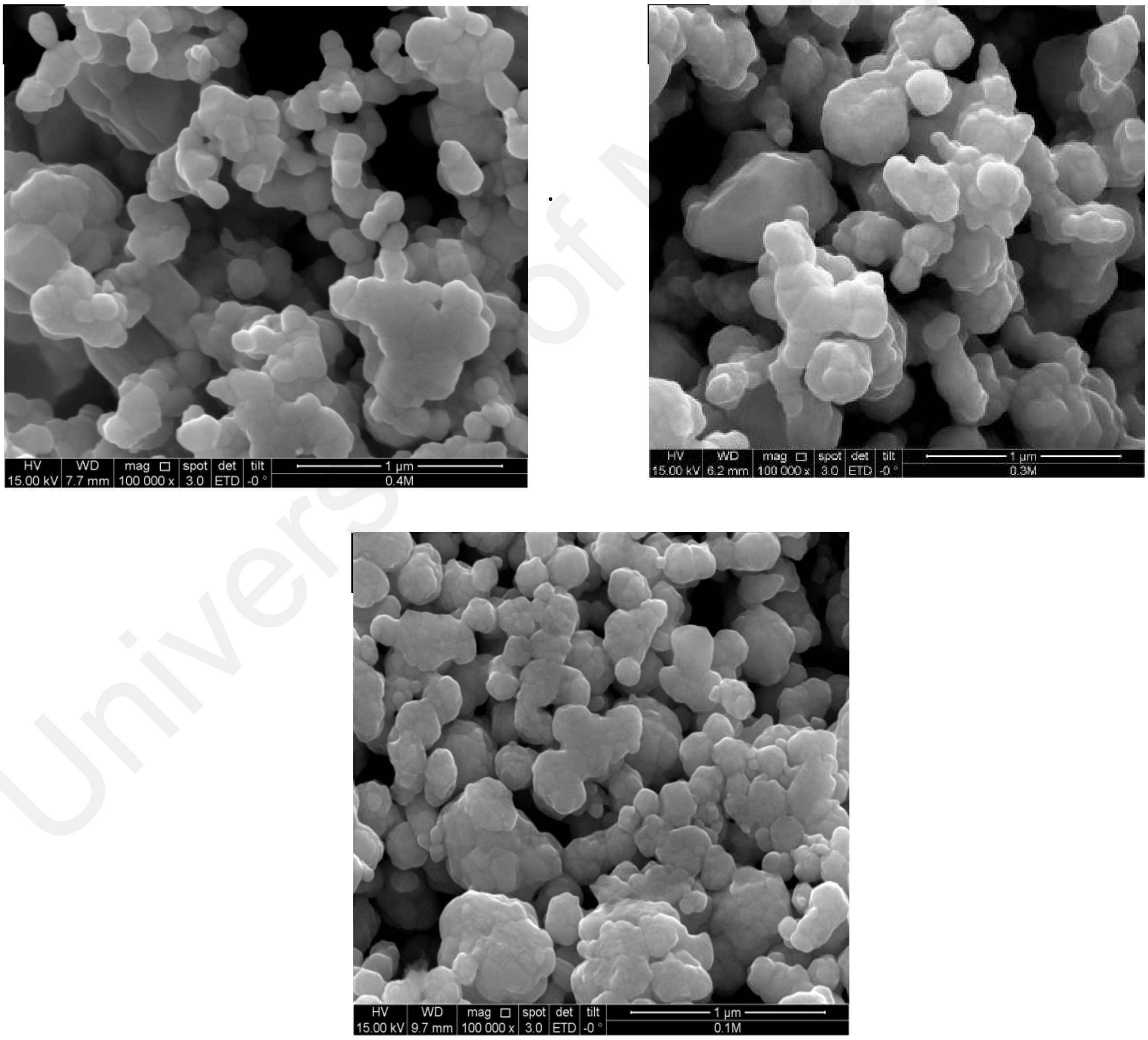


Figure 5.5: FESEM image of 100,000x magnifications for sample a) 1M, b) 3M and c) 4M

From Figure 5.5, the FESEM micrographs clearly show clustering or agglomeration of the silver crystallites even though CTAB was used as a dispersing agent. The ball milling process using silicon nitride balls was further carried out to break the agglomeration.

5.1.5 XPS AND EDX ANALYSIS ON THE NANOSILVER

The main purpose of XPS analysis is to confirm the oxidation state of silver on the surface. This is mainly important not only had to detect the element existed on the surface of the silver particles but also to identify the antibacterial agent between Ag $^{(0)}$ or Ag $^{(+)}$. The XPS analysis on the particle surface shows the presence of the elements C, W, Ti, N and Ag (Figure 5.6). The main contribution to the existence of these contaminants is the residues of chemicals during the precipitation process. Other than that, the elements can also come from the milling process which is contamination from the milling balls and bowl. Oxide layers on the other hand may form on the surface of the particles as the process was not carried out in an inert atmosphere. That could be the main reason for the existence of the Oxygen atoms on every sample.

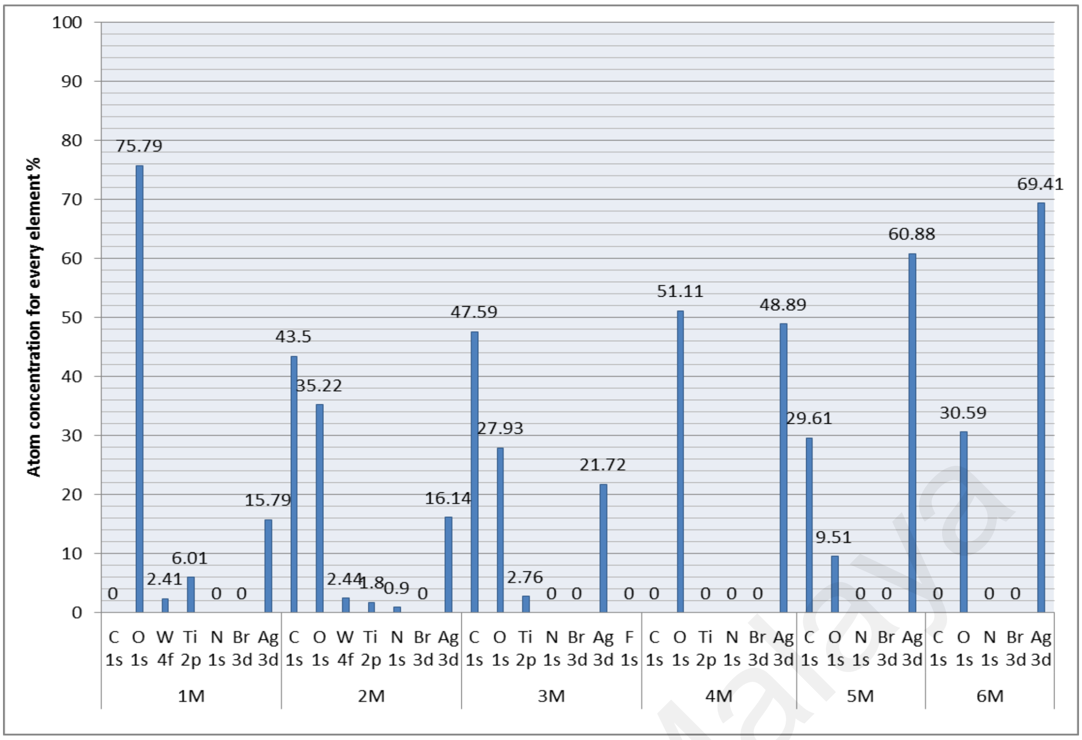


Figure 5.6: Atomic concentration % on the surface of the particle as measured by XPS

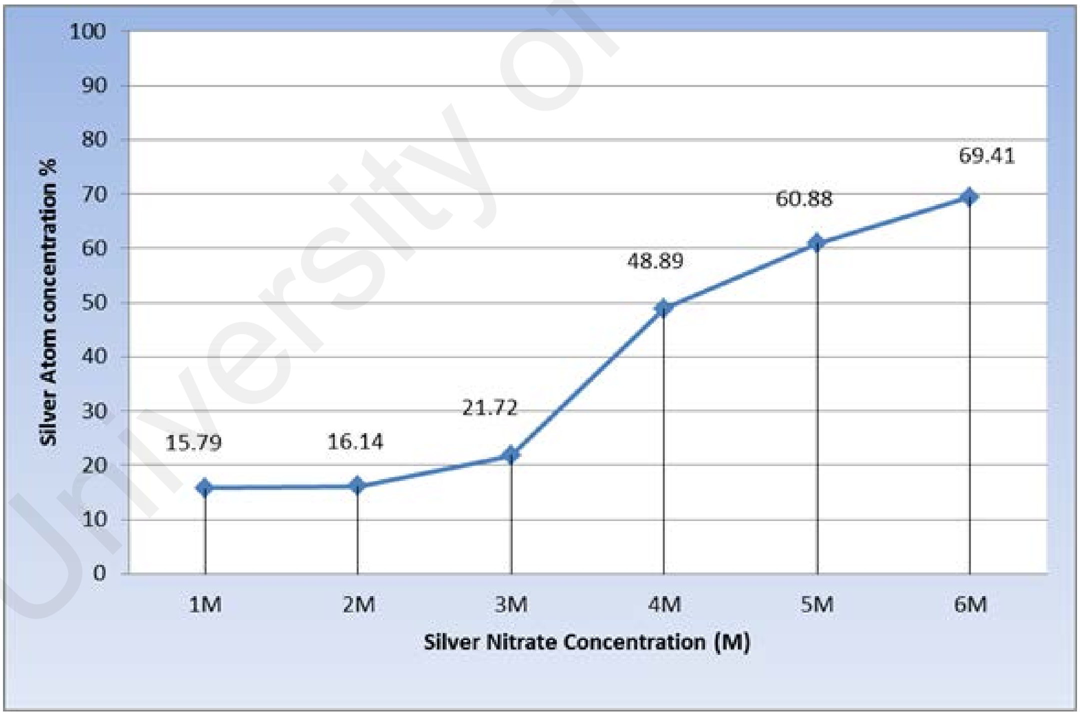


Figure 5.7: Silver atom Concentration detected by XPS

Atomic concentration of Ag accordingly increases when the silver nitrate molarities increased (Figure 5.7).

Table 9: Charging effect calculation and the corrected binding energy

Sample	C- Alpha Binding Energy (eV)	Charging Effect (eV)	Ag Binding Energy (eV)	Corrected Binding Energy (eV)
1M	285.30	0.80	368.60	367.80
2M	285.30	0.80	368.52	367.72
3M	285.33	0.82	368.54	367.72
4M	285.13	0.63	368.42	367.80
5M	285.08	0.57	368.38	367.80
6M	285.15	0.65	368.42	367.77

Table 9 shows the charging effect and the correction of binding energy based on the binding energy of carbon which is 284.5 eV. The corrected binding energy of the samples was used to identify the main compound’s presence on the surface of the samples. The data was compared with the database from NIST.

Table 10: The data of silver oxide Ag_2O from NIST database

Element:	Ag	Ag
Formula:	Ag_2O	Ag_2O
Name:	silver(I) oxide	silver(I) oxide
CAS Registry No:	20667-12-3	20667-12-3
Classes:	oxide	oxide
Author Name(s):	Gaarenstroom S.W., Winograd N.	Hammond J.S., Gaarenstroom S. W., Winograd, N.
Journal:	J. Chem. Phys. 67, 3500 (1977)	Anal. Chem. 47, 2194 (1975)
Data Type:	Photoelectron Line	Photoelectron Line
Line Designation:	3d5/2	3d5/2
Binding Energy (eV)	367.8	367.7

Figure 5.8 shows a narrow scan of Ag $3d_{7/2}$ and Ag $2d_{5/2}$ in a sample synthesised with 0.1M, 0.3M and 0.4M silver nitrate solutions. The peak difference between Ag $3d_{7/2}$ and Ag $2d_{5/2}$ is 6eV; it is confirmed that the samples contain the silver element. The same pattern of peaks was observed in all the samples. The binding energy of all the samples is 367.70 to 367.80 and according to NIST database, the samples are Ag_2O with the oxidation state of Ag+. The binding energy of Ag_2O is 367.8 eV and 367.7 eV. The binding energy for Ag(0) or pure silver is 368.3 eV. Table 10 shows the information for silver oxide, Ag_2O, from the reference of NIST database

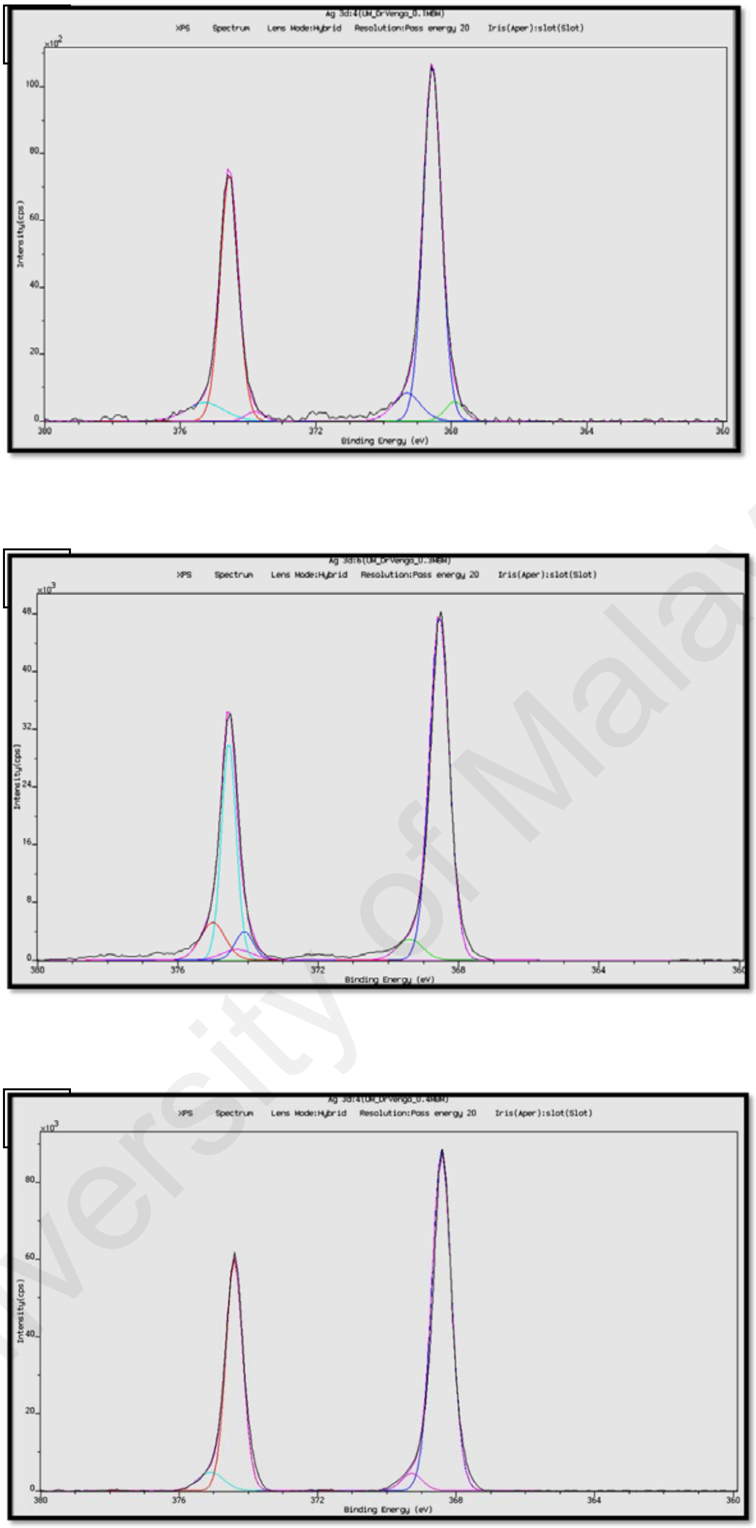


Figure 5.8: Narrow scan of Ag 3d in sample a) 1M, b) 3M and c) 4M

EDX analysis was conducted on every sample to compare the results of atomic concentration with XPS (Table 9).

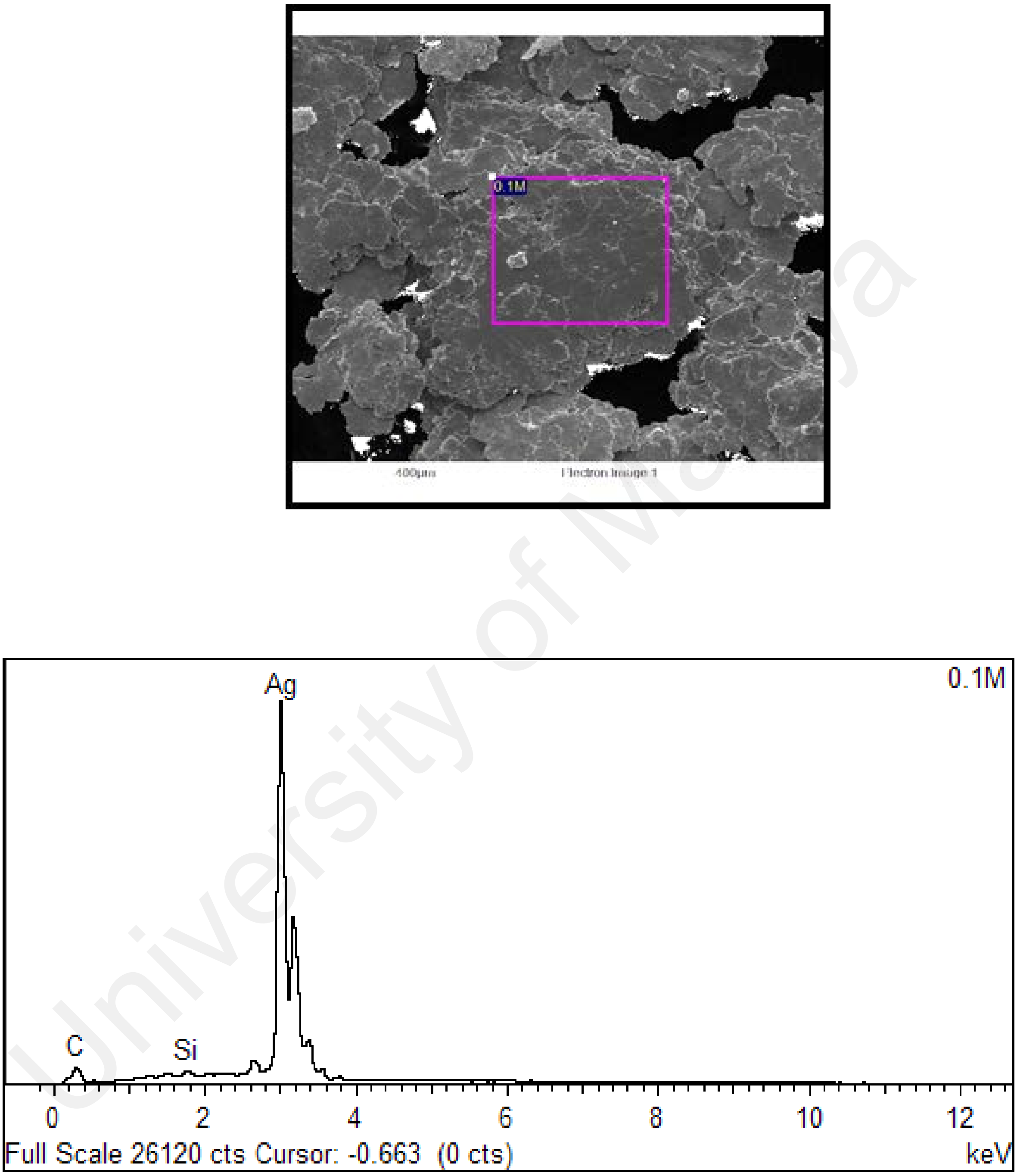
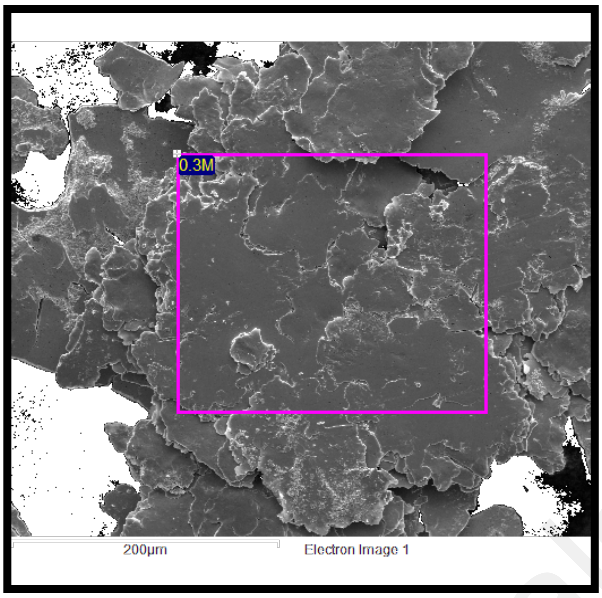


Figure 5.9: EDX analysis of sample 1M



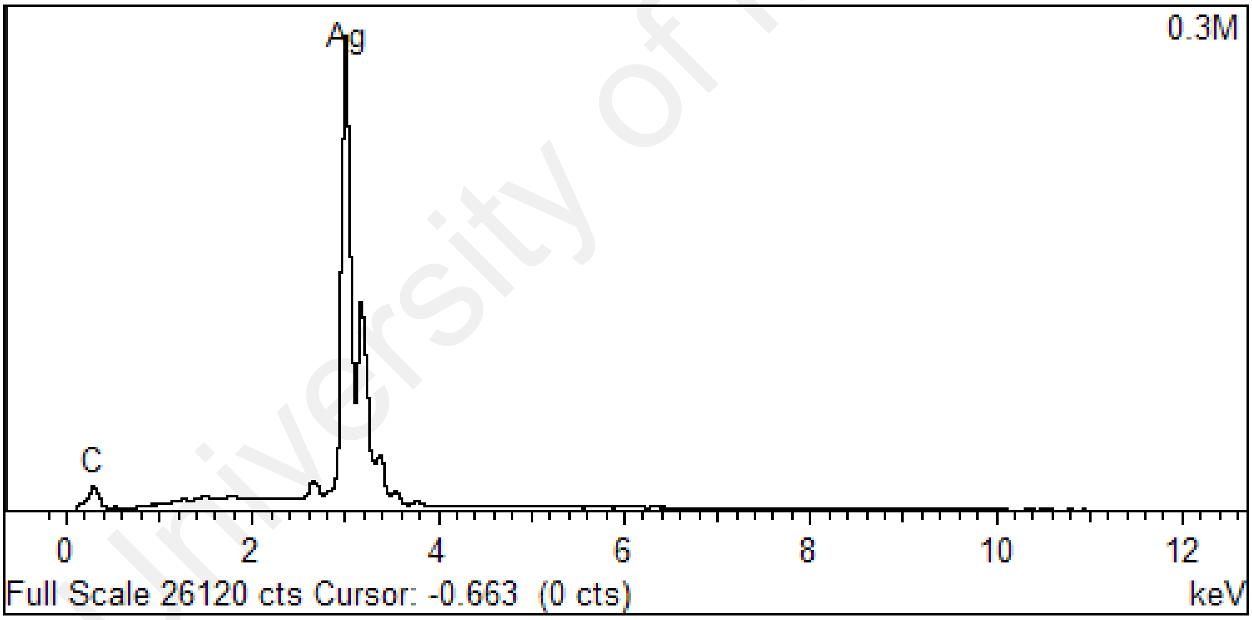
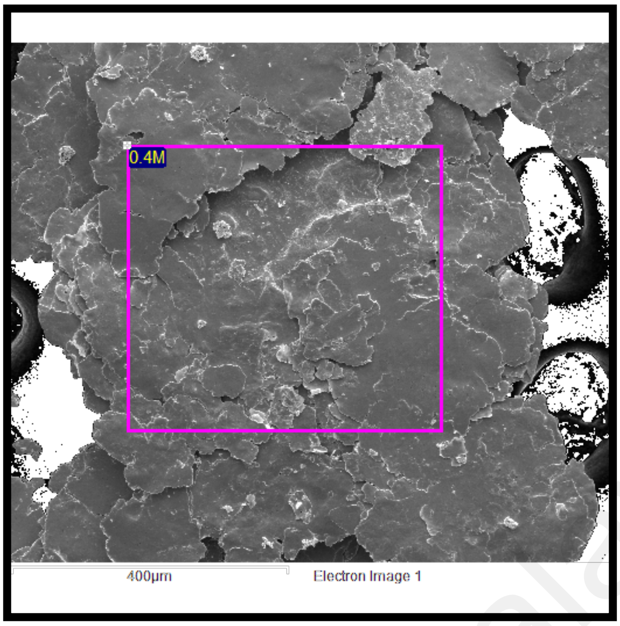


Figure 5.10: EDX analysis of sample 3M



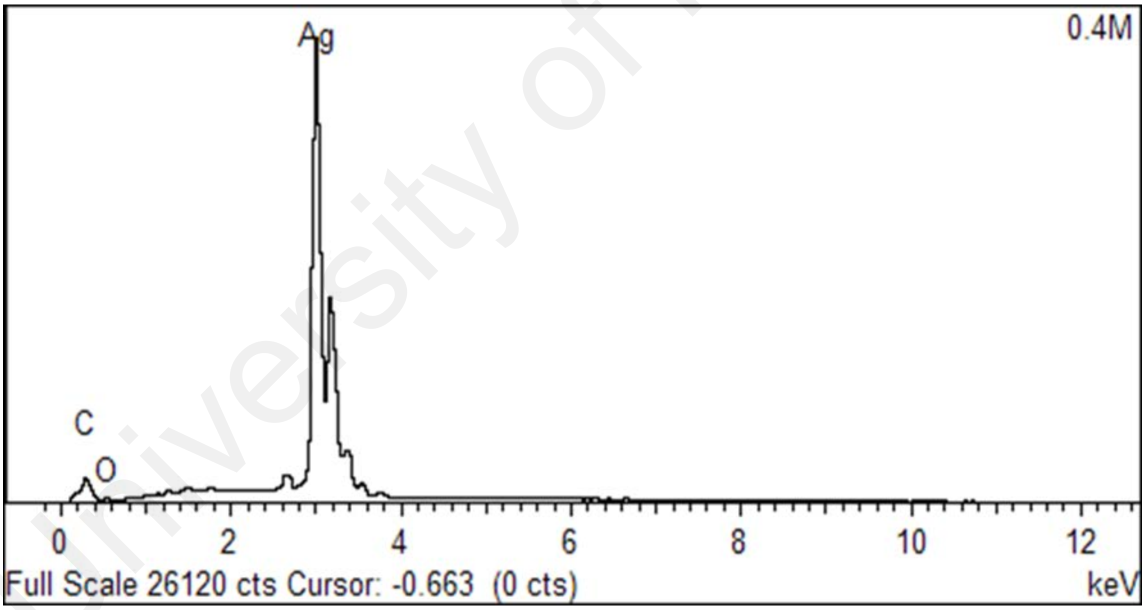


Figure 5.11: EDX analysis of sample 4M

Table 11: Comparison of element detected with EDX and XPS

Sample	Elements	Detected with EDX (%)	Detected with XPS (%)
0.1	O	-	75.79
	W	-	2.41
	Ti	-	6.01
	Ag	83.18	15.79
	Si	1.53	-
	C	15.29	-
0.3	C	15.90	47.59
	O	-	27.93
	Ti	-	2.76
	Ag	84.10	21.72
0.4	O	4.89	51.11
	Ag	80.25	48.89
	C	14.86	-

From Table 11, there are some atoms that are detected by XPS and not detected by EDX. This is mainly because XPS detects the elemental composition of the surface (normally 1– 10 nm depth) whereas EDX detects the elemental composition of the surface top of depth around 1µm. Therefore, more contaminants have been detected on the surface of the particles by XPS, and EDX relatively can be considered as the analysis of the bulk of the sample.

From table 12, it can be concluded that the precipitates are silver nano crystallites and Ag_2O existed on the surface of the crystallite. Based on the size estimation, sample 3M which was produced from 0.3M silver nitrate will be used as the antibacterial agent and will be incorporated into the antibacterial sol-gel coating.

5.2 DEVELOPMENT OF COATING BINDER SYSTEM

The silver nano crystals need to be added into a clear coating formulation to be coated over the substrates for antibacterial protection. Before the nanocrystals were incorporated into the coating system, a binder study was conducted to choose the best formulation for antibacterial coating. Once the optimum formulation was chosen, silver nano crystals were added into the coating system. This antibacterial coating was coated on top of the UV protection coating that has been dried for more than 7 days. The samples that have both coatings were kept at room temperature for at least 7 days before they were sent to SIRIM QAS Sdn Bhd for antibacterial efficacy test according to JIS 2801; antimicrobial products test for antimicrobial activity and efficacy.

5.2.1 SAMPLE PREPARATION OF THE COATING:

Glass slides of 2 mm thickness was cleaned with water and finally, with the acetone to remove the grease and contaminants on the surface. The solvents and methyl trimethoxy silane ($Si\text{-}CH_3\text{-}(OCH_3)_3$) were mixed in a beaker with the ratio of 1:1 to study the compatibility of the substances. No modification has been made to the chemicals that were purchased from the supplier. Nitric acid diluted to 5% with the pH of 0.1 was added to the mixture by 10% wt as a catalyst. The mixtures were stirred for 30 seconds and coated on the prepared glass substrates (5 cm x 10 cm x 6 mm) using a melamine sponge (1.5 cm x 1.5 cm x 4 cm). The coated samples were dried at room temperature of 25°C and absolute humidity of 30%. 0.5 ml of the coating was used for every sample, and the coating was spread with a single stroke to maintain almost the same thickness of the coating. Temperature and humidity play important roles in the curing of the sol-gel film. Therefore, these two factors need to be constant throughout the experiment. The dried samples were measured for transparency using haze meter with D65 illumination light at room temperature. Mitsubishi pencil scratch tester was used with the load of 1 kg to measure the scratch hardness of the coated films on the glass substrate.

5.2.2 ROLE OF THE BINDER IN THE COATING SYSTEM

The coating formulation consists of binder the methyl trimethoxy silane ($Si\text{-}CH_3\text{-}(OCH_3)_3$) and the acid catalyst (nitric acid diluted to 5% with the pH of 0.1) added to the mixture by 10% wt. Various types of alcohols were used in this research and each coating system was tested and evaluated for the best desired property.

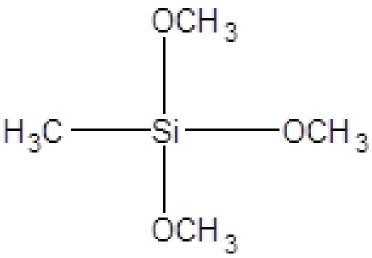


Figure 5.12: Chemical structure of methyl Trimethoxy silane

Table 12: Chemical Properties of Methyl Trimethoxy silane

Chemical Name	Metyltrimethoxysilane
CAS No.	1185-55-3
Formula	$C_4H_{12}O_3Si$
Molecular Weight	136.22
Boiling Point	101°C [760mmHg]
Flash Point	5°C
Color and Appearance	Colorless clear liquid
Density [25°C]	0.950
Refractive Index [25°C]	1.369
Purity	99.0% by GC

5.2.3 EFFECT OF DIFFERENT SOLVENTS ON THE VISCOSITY OF THE COATING

Although the viscosity of methyl trimethoxy silane is relatively low as a monomer, organic solvents are frequently used in sol-gel processing as they allow the control of the reaction of alkoxide precursors with water, hence directing with more flexibility the structure of sol-gel products. Solvents are added into the system to prevent liquid-liquid phase separation during the initial stages of the hydrolysis, and to control the concentrations of silicate and water that influence the gelation. In this study, the common alcohols were used as solvents in sol-gel processing. The availability of labile protons in protic solvents such as water and alcohols influences the extent of the reverse reactions, reesterification, or siloxane bond alcoholysis or hydrolysis.

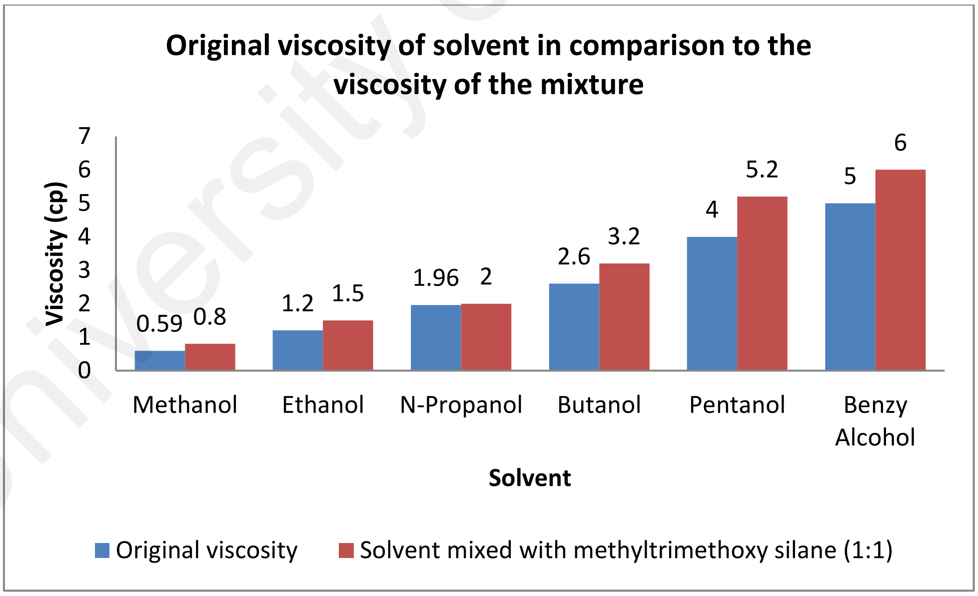


Figure 5.13: The viscosity of the original solvents and viscosity of the solvent mixed with methyl trimethoxysilane in centipoise (cp) measured at 25°C

The viscosity of the liquid determines the thickness of the coating in a single deposition method (With, 2000). Based on the mixtures above, the viscosity of the coating was slightly higher to the original viscosity of the solvents (Figure 5.13). This is mainly due to the relatively higher molecular weight of the monomer compared to the molecular weight of the solvents caused the slightly viscosity increment of the mixture. However, as shown in figure 5.13, the viscosity increment is very minimal. Therefore, viscosity of the solvents chosen determines the viscosity of the final coating mixture. The viscosity of the coatings is also determined by the form and composition of the fluid before application. All of the mixtures above have the viscosity that is suitable to be coated using a sponge.

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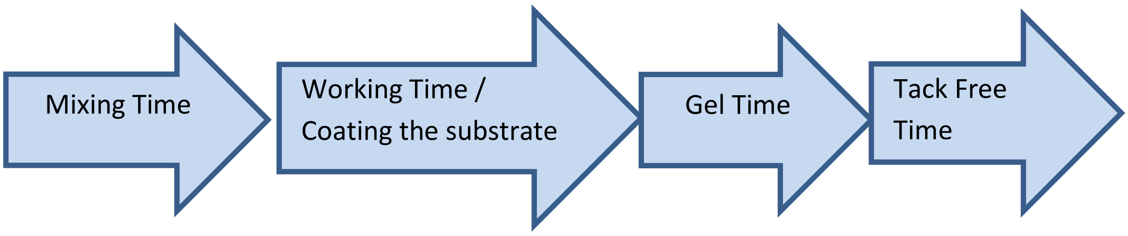
5.2.4 EFFECT OF DIFFERENT SOLVENTS ON THE TACK FREE TIME OF THE COATING

Tack-free time is just one of the diagnostics that shows the characteristics of the coating drying process. It is defined as the point when the coated surfaces no longer feel sticky. The tack free time is important in coating process because the time should be long enough to complete the procedure but not too long until it can affect the coatings properties. The work for coating process started at mixing time where all the substance being mixed together also known as ‘pot life’. Working time or coating process will take place after the mixing. The coating will form a gel and before harden or known as ‘tack free time’ (Pierre 1998).



In this study, the coating was tacked by hand, i.e., when there is no finger print mark on the surfaces which is visible to the naked eye. The time taken to achieve that condition is considered as ‘tack-free time’. For actual systems such as coatings and sealant, the tack-free time is the period at which the material is assumed sufficiently robust to resist damage by touch or other forms of weathering processes.

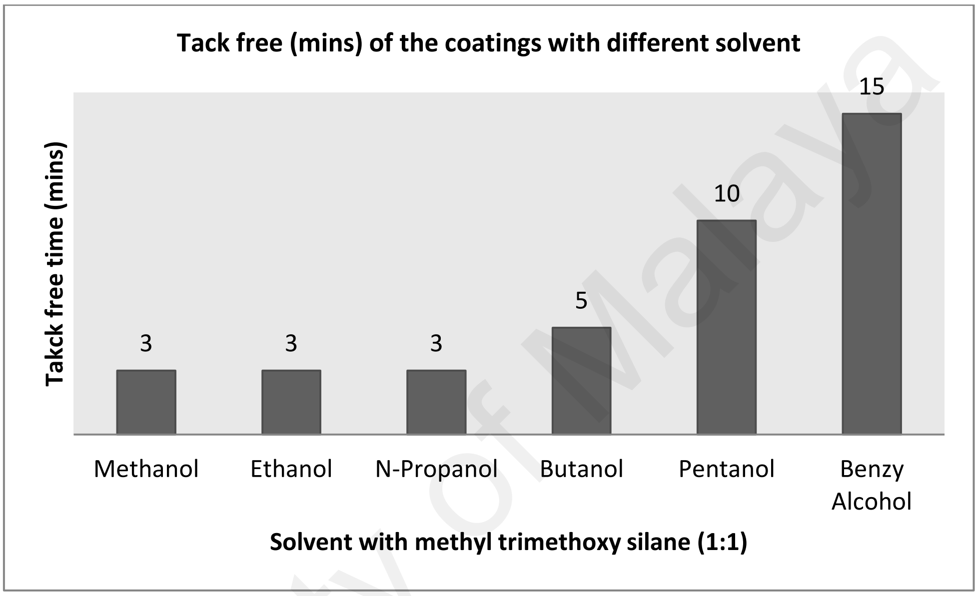


Figure 5.14: Tack Free time of the coatings with different solvent

The gelation of a solution involves the polymerization of monomers to form particles, crosslinking in the polymer structure. Figure 5.14 shows the tack-free time of the samples with different alcohols as solvents. The drying mechanism of the sol-gel was suggested (Pierre, 1998) to obey the capillary mechanism. Capillary mechanism occurs as follows:

1. Evaporation creates liquid vapor meniscus at the exit pores in the gel
2. This induces a hydrostatic tension in the liquid, which is balanced by an axial compression on the solid

3. The latter compression makes the gel shrink
4. As a result of shrinkage, more liquid is fed to the menisci at the exit of the gel pores as shown in figure 5.15.

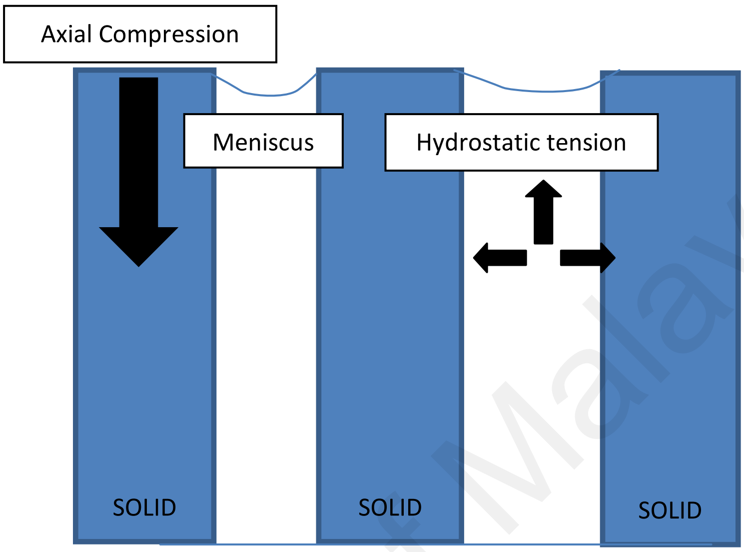


Figure 5.15: Capillary mechanism during drying process of sol gel coating (Pierre 1998)

Evaporation rate, vapor pressure and boiling point of the solvent that were chosen for the coatings' formulations play important roles in determining the drying speed of the coatings and the tack-free time. Vapor pressure or equilibrium vapor pressure is the pressure exerted by a vapor in thermodynamic equilibrium with its condensed phases (solid or liquid) at a given temperature in a closed system. It is also as an indicator of the liquid's evaporation rate by relating the tendency of the particles to escape from the liquid (or a solid). The material with a higher vapor pressure are considered to be more volatile. In general, vapor pressures of liquid at ambient temperatures increase with decreasing boiling points.

In this study, the tack-free time remained constant for the sample that was mixed with methanol, ethanol and N-propanol. However, a longer tack-free time was obtained from the samples that were mixed with butanol, pentanol and benzyl alcohol. This could be explained by the higher boiling point and lower evaporation rate for those solvents. The boling points of butanol, pentanol and benzyl alcohol is 117ºC, 137ºC and 205ºC. The boiling points for the methanol, ethanol and n propanol is below 100ºC. Higher molecular weight alcohol will cause higher boiling point and lower evaporation rate due to the intermolecular attractions.

5.2.5 EFFECT OF DIFFERENT SOLVENTS ON THE SCRATCH HARDNESS OF THE COATING

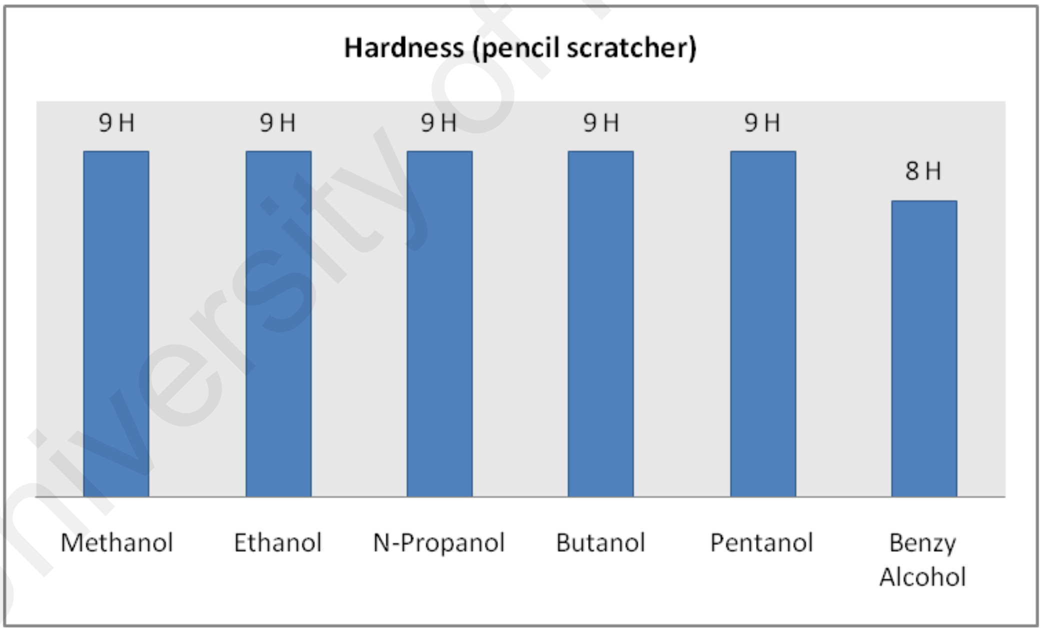


Figure 5.16: The scratch hardness values based on the Pencil scratcher

Pencil scratch hardness is widely used in measuring the hardness of the coating film. The structure of the dried coating depends on the competition between the capillary forces, which tend to compress the network, and the condensation reaction, which stiffens the network and leads to an increased hardness. Figure 5.18 shows that there were no significant changes in hardness values of the coatings when different solvents were used in this experiment. Therefore, it can be concluded that the type of solvent chosen does not pose any significant effect on the hardness of the dried coatings (Figure 5.16).

5.2.6 MEASUREMENT OF TOTAL LIGHT TRANSMITTANCE, LIGHT DIFFUSE AND PARRALEL TRANSMITTANCE

Total light transmittance is the measurement of light that penetrates through a sample which contributes to the clarity and transparency of the samples measured. The light that was scattered less than 2.5 degrees contributed to the clarity of the samples. The highest total transmittance is needed to get the highest transparency of the coating. Parallel transmittance is that portion of the light that passes through the sample without being scattered or diffused by the irregularities on the surface or the interior of the film. Light diffused is the portion of light that is scattered by the irregularities. The optimum formulation would be the sample with the highest total transmittance and parallel transmittance, and the lowest light diffused.

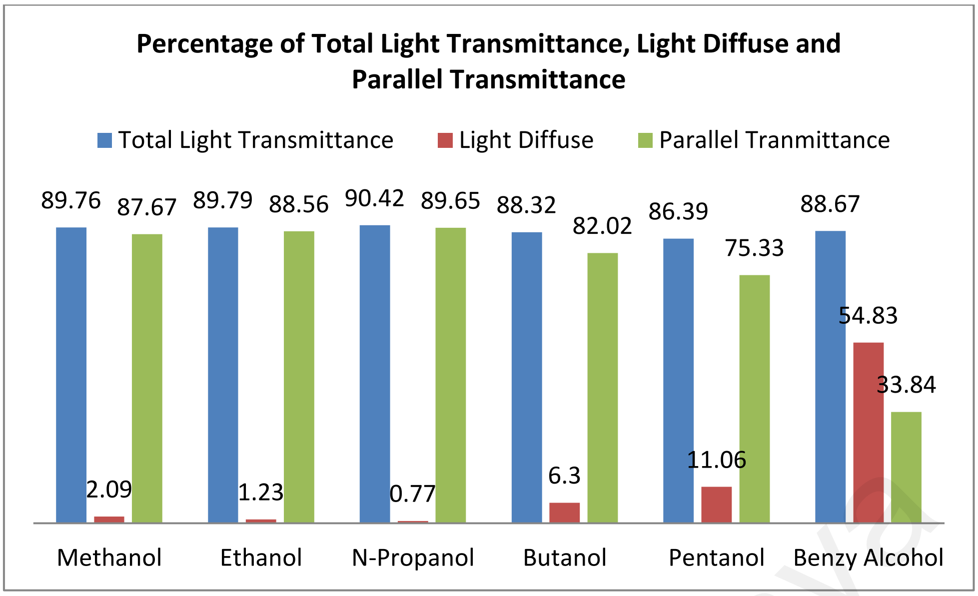


Figure 5.17: Percentage of total light transmittance, light diffuse and parallel transmittance

Figure 5.17 shows a plot of total light transmittance, light diffuse and parallel transmittance for coatings with different solvents. Values of greater than 89 percent of light transmittance through the coating were obtained when methanol, ethanol and N-propanol were used as solvent. Parallel transmittance measurement indicated value of greater than 88 percent for both ethanol and N-propanol. Measurement of percentage of light diffused through the sample in Figure 5.17 shows that the percentage of light diffused was minimal with a value of 0.77 percent for N-propanol and 1.23 percent for ethanol. Some samples exhibit the high haze values and low transmittance due to the high diffusion of light when penetrating through the sample. This can be seen from sample that was mixed with benzyl alcohol. When the drying time was too long, more dust stick on the samples and caused the coating surface to be rough. The rough surface and contamination caused interference on the angle of light that penetrating and affected the transmission of the light.

5.2.7 EFFECT OF DIFFERENT SOLVENTS TO THE HAZE VALUES OF THE COATING

Haze is a measurement of the cloudiness of an object. Normally, it is caused by the scattering of light. Light may be scattered by suspension of particles in a substance, such as pigments or contaminants, or by an imperfect surface caused by dirt, oil or surface structure. Light that was scattered more than 2.5° from the incident light is considered to contribute to haze.

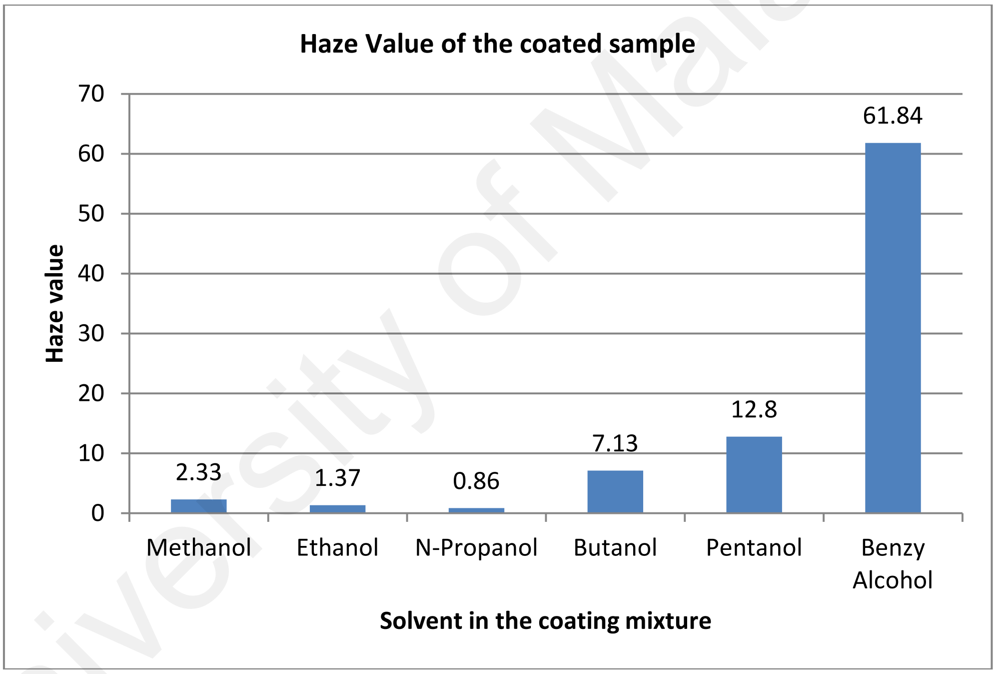


Figure 5.18: The haze values of the coated samples

Results from the haze measurement and optical comparison of the coating using various solvents were partially conclusive in eliminating methanol, butanol, pentanol and benzyl alcohol as suitable solvents. As shown in figure 5.18, the haze value indicates a value of 0.86 for N-propanol and 1.37 for ethanol. It is thus concluded that the choice of solvent to be were between N-propanol and ethanol.

5.2.8 EFFECT OF DIFFERENT SOLVENTS ON THE OPTICAL IMAGE OF THE COATING

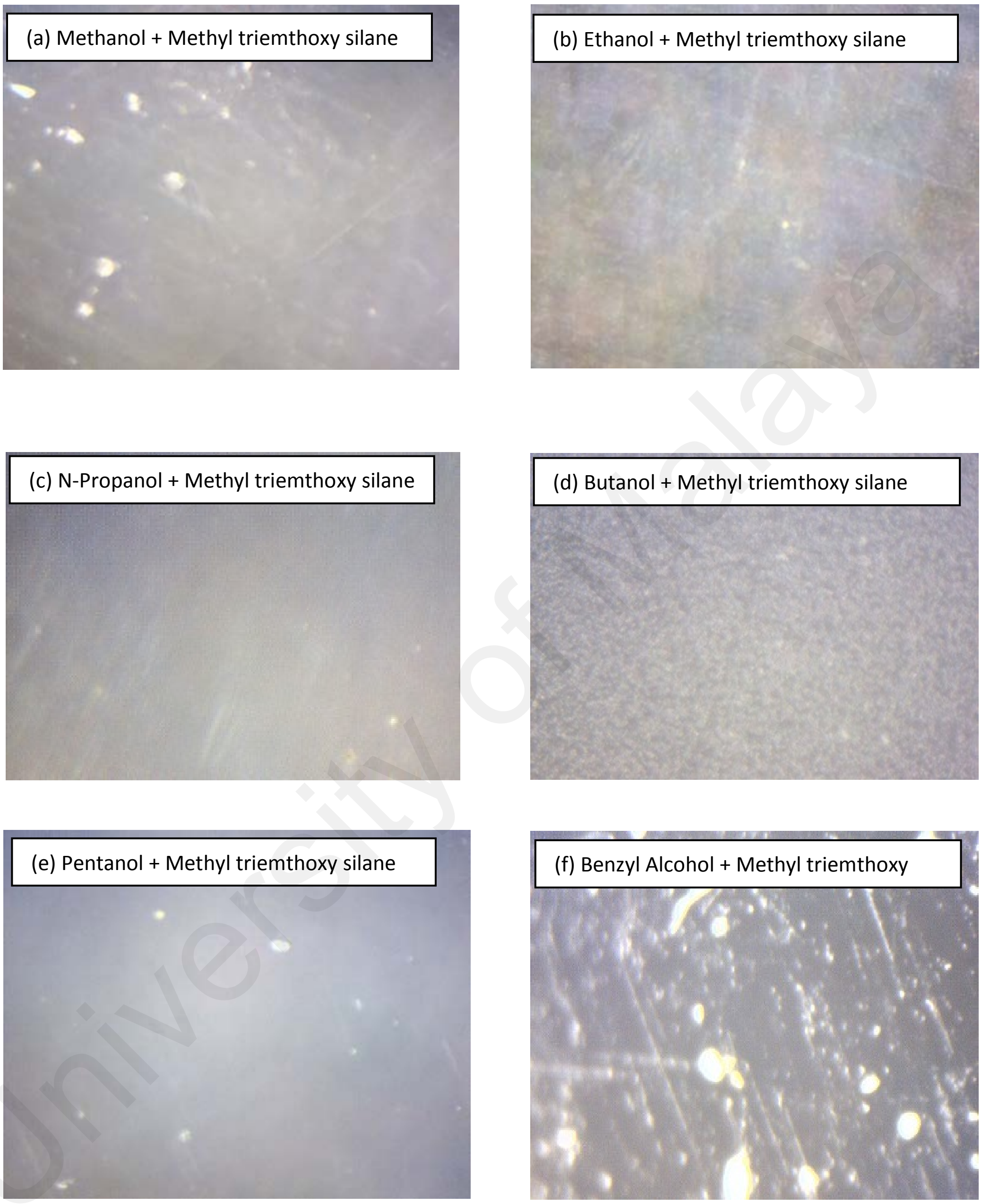


Figure 5.19: The image of dried coatings with methyl trimethoxy silane and alcohols with the ratio of 1:1

Figure 5.19 are the images of the coating surface in magnification of 500X. Figure 5.19 (a) shows the rough surface of the coating prepared with methanol. The poor leveling properties of the solvent caused the ununiformed layer of the coatings formed. The sponge marks were also observed on the coating surface. This happens because the evaporation of the solvent was too fast and affected the leveling properties of the coating. As a result, it affects the visual appearance and the clarity of the coatings. Figure 5.19 (b) and (c) show the images of smooth coating for sample prepared with Ethanol and N-propanol as a solvent. The compatibility of the solvents to binder system with good leveling properties of the solvents forms a uniform layer of coatings. Thus, maintaining the clarity of the samples. Figure 5.19 (d), (e) and (f) show the image of coatings prepared with butanol, pentanol and benzyl alcohol. The rough surfaces were observed on the samples due to the longer tack free time that caused dust contamination on the wet coatings. Based on the results above, ethanol and N-propanol have shown the most promising solvents compared to the other alcohols. The next approach was to study the comparison of N-propanol to the ethanol with different percentages of solvents into the binder system to choose the best formulation for the antibacterial coating.

5.2.9 COMPARISON OF N-PROPANOL AND ETHANOL AS A SOLVENT

The coating was mixed according to Table 13 and Table 14. N-Propanol and ethanol has shown very promising results based on the total light transmittance, parallel transmittance and light diffused. Therefore, the best ratio of binder and solvents will be studied to obtain the most optimum formulation. Ethanol is one of the most common and widely used diluents in the coating industry

Table 13: The sol gel formulation using N-propanol as solvent

Sample	0N	20N	40N	50N	60N	80N	90N
N-Propanol (%)	0	20	40	50	60	80	90
Methyl trimethoxy silane (%)	100	80	60	50	40	20	10
Appearance	Cracking	Cracking	Clear	Clear	Hazy	Hazy	Hazy

Table 14: The sol gel formulation using ethanol as solvent

Sample	0E	20E	40E	50E	60E	80E	90E
Ethanol (%)	0	20	40	50	60	80	90
Methyl trimethoxy silane (%)	100	80	60	50	40	20	10
Appearance	Cracking	Cracking	Clear	Clear	Hazy	Hazy	Hazy

5.2.10 EFFECT OF DIFFERENT AMOUNT OF SOLVENTS ON THE OPTICAL IMAGE OF THE COATING

For both solvents, visually, the coatings appeared clear and transparent when the percentage of the solvents was between 40 to 50 percent in the coating formulation. When the silane percentage became too high or exceeded 60 percent, the dried coating cracked and flaked due to the high density of the cross-linking, causing the brittleness of the coating layer that cannot undertake the compression from the capillary effect during the drying process and the internal stress of the coating (figure 5.20 and 5.21). The evaporation of the solvents in thick coatings caused the network to compress and break the bonding. This phenomenon occurs when the solvents on the top layer of the coating evaporates faster than the solvent in the bulk consequently forming the gel on the coating surface. The solvent in the bulk coating will escape from the bottom to the top, and at the same time, this solvent will attack the gel on the surface resulting in the cracking of the coating.

However, when the binder percentage is too low, the coatings will become hazy due to the rough surface formed, and the binder supplied would be insufficient to cover the whole surface of the substrate (Figure 5.23). The rough and uneven surfaces that were caused by the lack of binder will diffuse more light through the samples, resulting in higher haze values. The best image was obtained from samples that contained a percentage of the solvent in the range of 40% to 50% for both solvents (figure 5.22).

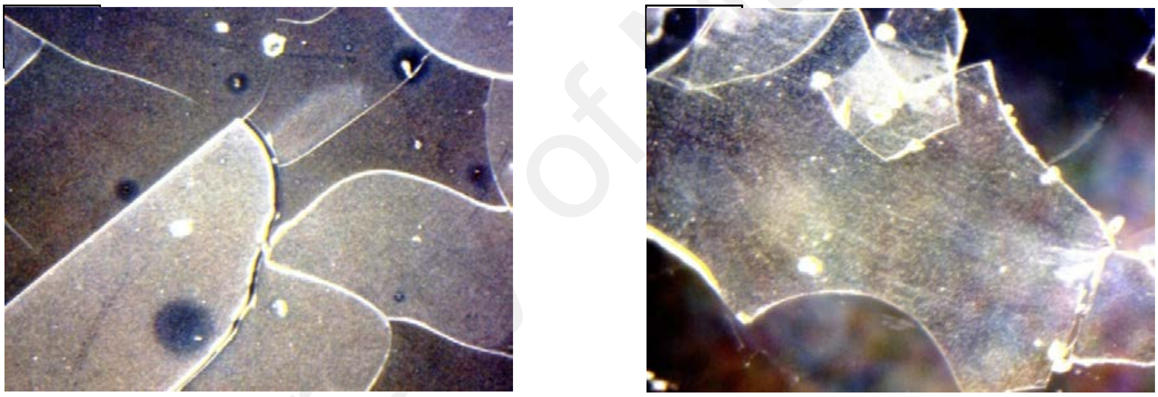


Figure 5.20: The 500x magnification of the surface of coatings from a) sample 0N and b) sample 0E

Figure 5.21: The 500x magnification of the coating surface from a) sample 20N and b) sample 20E

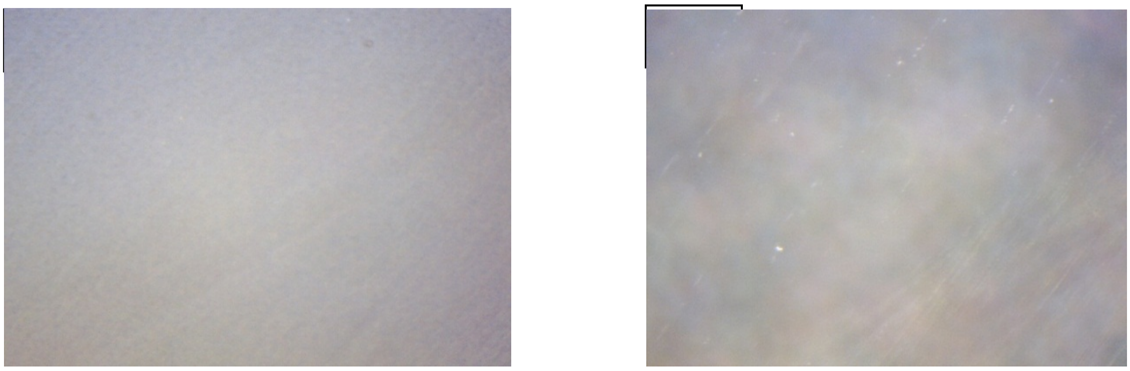


Figure 5.22: The 500x magnification of the coating surface from a) sample 50N and b) sample 50E

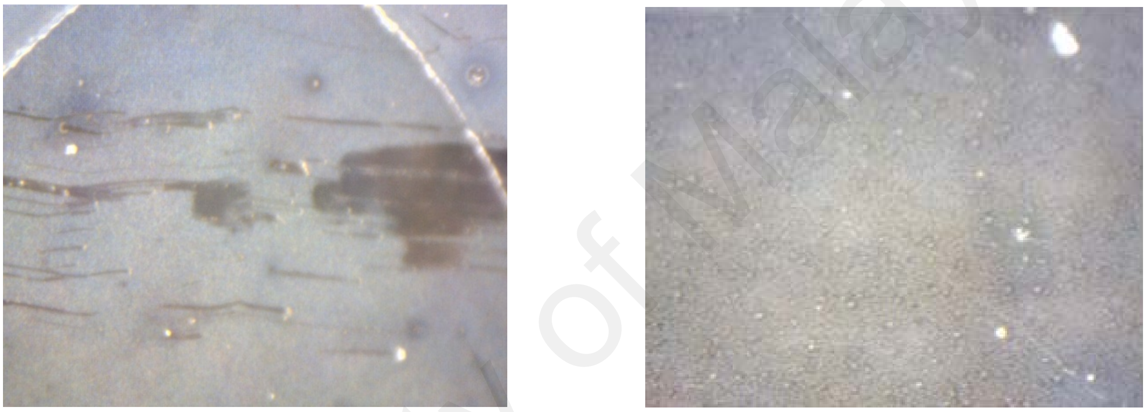


Figure 5.23: The 500x magnification of the coating surface from a) sample 90N and b) sample 90E

5.2.11 LIGHT TRANSMITTANCE RESULTS FOR THE DRIED COATINGS

Although the coating with solvents amount of 40% to 50% visually appear to be clear and smooth. Light transmittance measurement was carried out to choose the best coating formulation and to confirm the clarity of the samples by measuring the total transmittance, paralleled transmittance, and the light diffused.

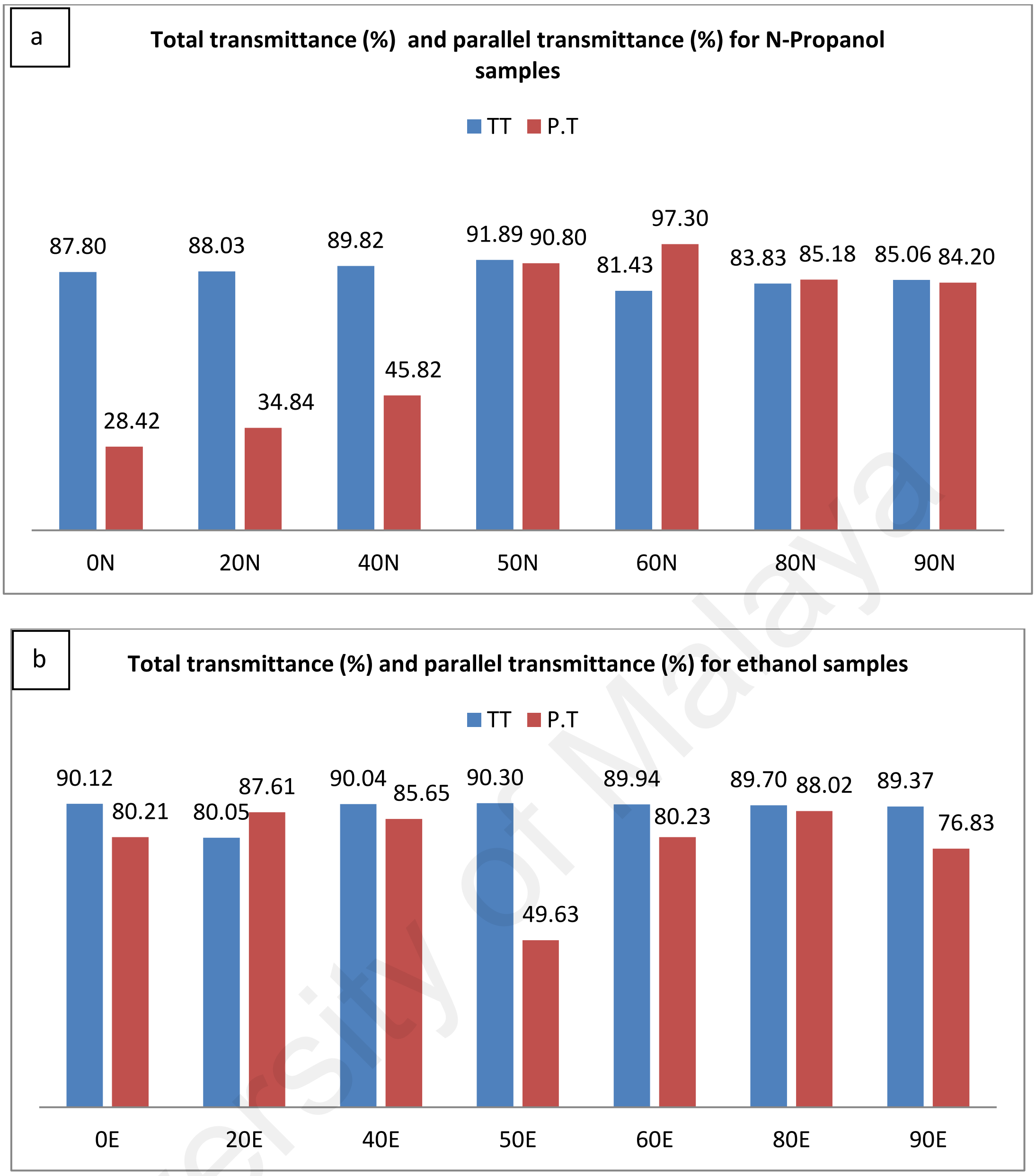


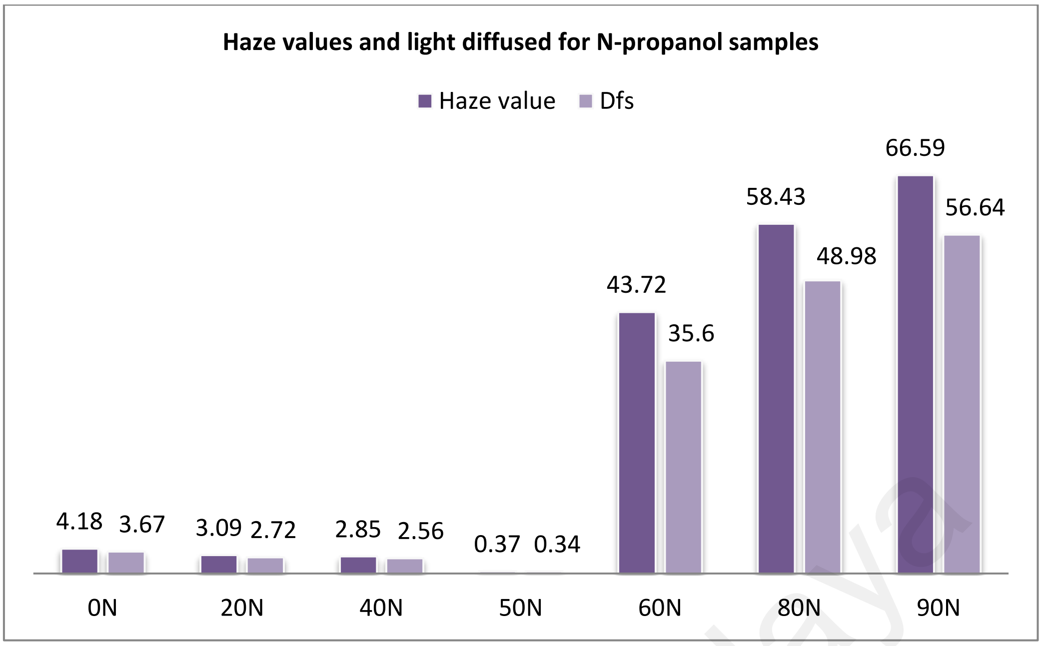
Figure 5.24: Total Transmittance and Parallel Transmittance of samples of trimethoxy silane that were mixed with a) N-Propanol and b) Ethanol as solvent

From figure 5.24, the highest total transmittance was obtained from sample 50N which has a total transmittance of 91.89% compared to 50E which has 90.30%. The next step is to conduct the haze measurement to confirm the best formulation with the highest clarity and the lowest haze values.

5.2.12 THE HAZE MEASUREMENTS OF THE DRIED SOL GEL

The haze values and light diffused measurements were carried out for all the samples in order to confirm the best solvents and formulations. The results were tabulated in Figures 5.25 (a) and 5.25 (b). The objective in this part of the research is to choose the best formulation with the lowest haze and light diffused.

Figure 5.25 clearly shows that the best result was obtained from the sample 50N that was mixed with N-propanol 50% and silane binder 50% with the haze values of 0.37% and 0.34% of light diffused. The overall haze values and the light diffused from the samples that were mixed with ethanol were slightly higher compared to the samples that were mixed with N-propanol. It can be concluded that the ratio of 1:1 of methyl trimethoxy silane to N-propanol is the best formulation and will be used as the coating formulation for the antibacterial coating system.



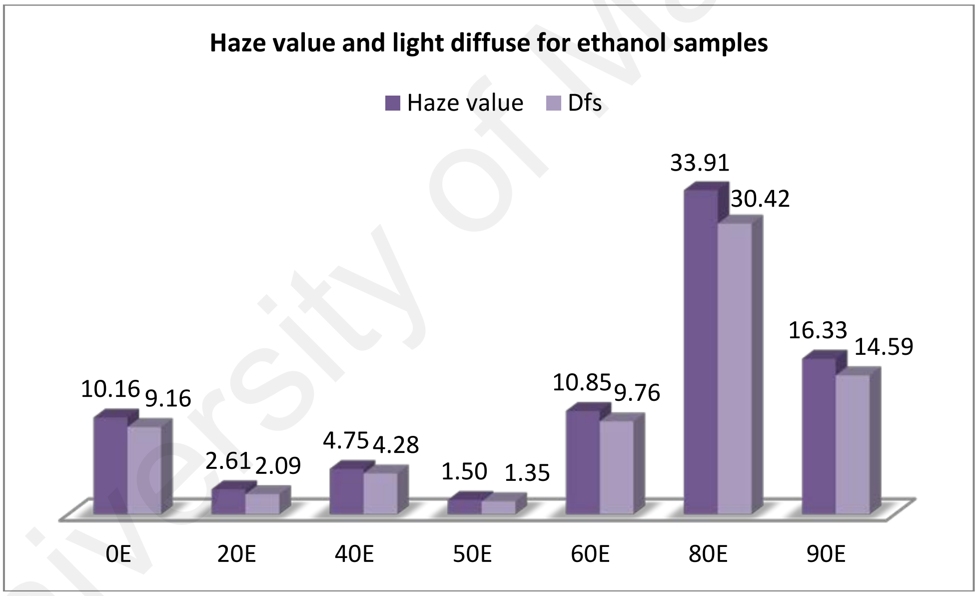


Figure 5.25: The haze values and percentage of light diffused of the dried sol gel from the mixture of silane and a) N-Propanol and b) Ethanol

5.3 COATINGS WITH SILVER NANOCRYSTAL AND ANTI-BACTERIAL TEST

5.3.1 INTRODUCTION

Antibacterial is an important branch of functional coating that plays an important role not only for general hygiene but also in saving lives as a disinfectant in places such as operation theatres in hospitals. There is an enormous interest in the research of highly efficient and low-cost antibacterial surface treatments to avoid the breeding and spreading of the harmful microorganisms.

Most of the approaches for achieving antibacterial surfaces are based on silver particles. The silver particles provide ions which are highly toxic to bacteria. The advantage of silver as an antibacterial agent is the selective toxicity to a wide range of microorganisms. Over the years, studies have shown that the miniaturization of silver particles have significantly improved the performance as an antibacterial agent. Nanoparticles with a higher specific area are more efficient in releasing silver ions.

Most of the antibacterial studies evolve around *Staphylococcus aureus*, *Escherichia Coli* and *Pseudomonas Aeruginosa*. *Staphylococcus Aureus* is frequently found in human respiratory tracts and skin. It is a common cause of skin infections, respiratory diseases and food poisoning. On the other hand, *Eschericia Coli* is commonly found in the lower intestines of warm-blooded organisms. It usually causes the food poisoning and is occasionally responsible for product recalls due to food contamination. The third bacteria, *Pseudomonas Aerugirosa* (figure 5.26), is considered as one of the toughest bacterial strain and is able to survive in harsh environments. It does not usually cause illness to healthy people but it is described as an opportunistic organism causing serious infections when our normal defence system weakens. It represents a great threat to the most vulnerable hospital patients, for example, intensive care patients, those with depleted immune system such as cancer patients, people with serious burn, and premature babies in neonatal units.

Figure 5.26: SEM image of *Pseudomonas Aeruginosa* (Photo Credit: Janice Haney Carr)

Pseudomonas aeruginosa is a common bacterium that can cause diseases in animals including humans. It is found in soil, water, skin, flora, and most man-made environments throughout the world. It thrives not only in normal atmospheres, but also in hypoxic atmospheres, and has, thus, colonized many natural and artificial environments. It uses a wide range of organic materials for food; in animals, the versatility enables the organism to infect damaged tissues or those with reduced immunity.

The symptoms of such infections are generalized inflammation and sepsis. If such colonizations occur in critical body organs, such as the lungs, the urinary tract, and kidneys, the results can be fatal. Because it thrives on most surfaces, this bacterium is also found on and in medical equipments, including catheters, causing cross-infections in hospitals and clinics. It is a Gram-negative, aerobic, coccobacillus bacterium with unipolar motility. An opportunistic human pathogen, *P. aeruginosa,* is also an opportunistic pathogen of plants. *P. aeruginosa* is a type of species of the genus *Pseudomonas*.

Other than *P. aeruginosa*, there is also *Stapphylococcus Areus*. *Staphylococcus aureus* is a bacterium that is a member of the *Firmicutes*, and is frequently found in the human respiratory tracts and on the skin. Although *S. aureus* is not always pathogenic, it is a common cause of skin infections (e.g. boils), respiratory disease (e.g. sinusitis), and food poisoning. Disease-associated strains often promote infections by producing potent protein toxins and expressing cell-surface proteins that bind and inactivate antibodies. The emergence of antibiotic-resistant forms of pathogenic *S. aureus* (e.g. MRSA) is a worldwide problem in clinical medicine.

S. aureus (figure 5.27) is a gram positive strain bacteria and is responsible for many infections but it may also occur as a commensal. The presence of *S. aureus* does not always indicate infection. *S. aureus* can survive from hours to weeks, or even months, on dry environmental surfaces, depending on strain. *S. aureus* can infect tissues when the skin or mucosal barriers have been breached. This can lead to many different types of infections including furuncles and carbuncles (a collection of furuncles). In infants, *S. aureus* infection can cause a severe disease — staphylococcal scalded skin syndrome (SSSS).

S. aureus infections can spread through contact with pus from an infected wound, skin-to-skin contact with an infected person by producing hyaluronidase that destroys tissues, and contact with objects such as towels, sheets, clothing, or athletic equipments used by an infected person. Deeply-penetrating *S. aureus* infections can be severe. Prosthetic joints put a person at particular risk of septic arthritis, and staphylococcal endocarditis (infection of the heart valves) and pneumonia. *S. aureus* can host phages, such as Panton-Valentine leukocidin, that increases its virulence.

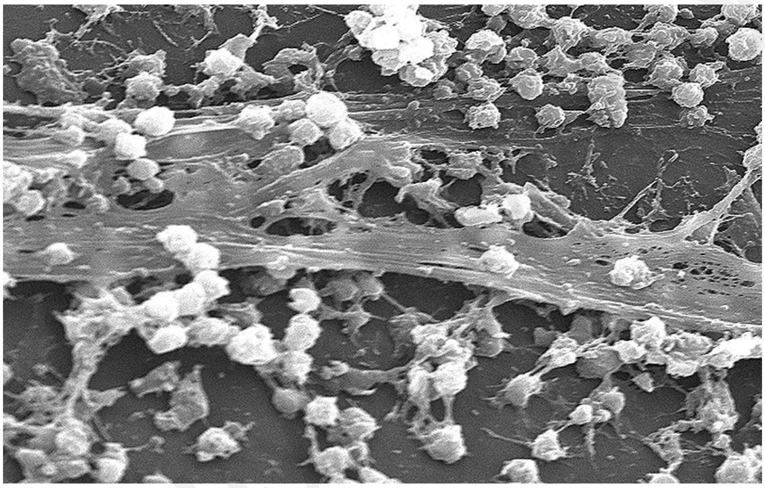


Figure 5.27: SEM image of *S. aureus* (Photo credit: CDC/ Rodney M. Donlan, Ph.D.; Janice Carr)

Escherichia coli (figure 5.28), commonly abbreviated *E. coli,* is a Gram-negative, facultative anaerobic, rod-shaped bacterium that is commonly found in the lower intestine of warm-blooded organisms (endotherms). Most *E. coli* strains are harmless, but some serotypes can cause serious food poisoning in humans, and are occasionally responsible for product recalls due to food contamination. The harmless strains are part of the normal flora of the gut, and can benefit their hosts by producing vitamin K2, and by preventing the establishment of pathogenic bacteria within the intestine.

E. coli cells are typically rod-shaped, and are about 2.0 microns (µm) long and 0.5 µm in diameter, with a cell volume of 0.6–0.7 (µm). It can live on a wide variety of substrates. *E. coli* uses mixed-acid fermentation in anaerobic conditions, producing lactate, succinate, ethanol, acetate and carbon dioxide.

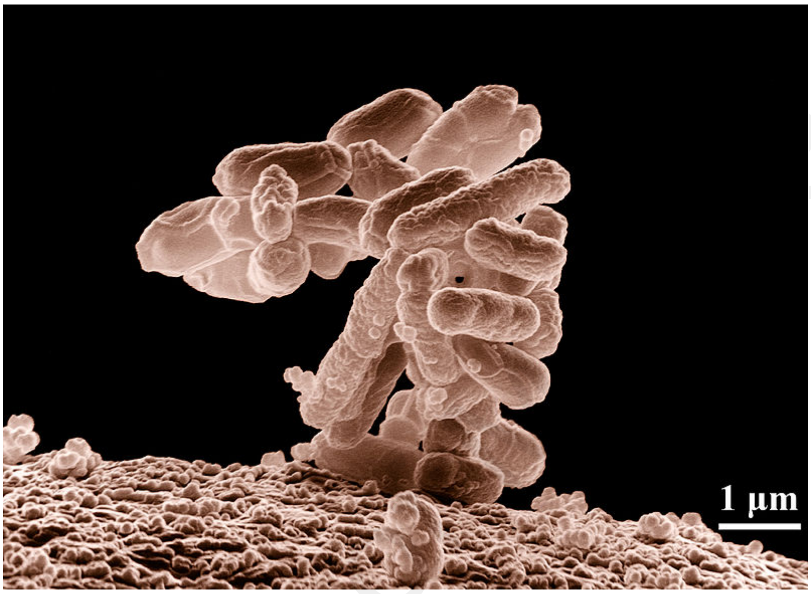


Figure 5.28: SEM image of E-Coli (Photo credit: Eric Erbe)

For antibacterial activity measurement, it is a common procedure to carry out the test according to the Japanese Industrial Standard, JIS Z 2801. This method was developed to measure the antibacterial activity in hydrophobic materials, originally resulting from the incorporation of silver ions into rigid polymers. Developed by a consortium of workers comprised of manufacturers of silver-based antimicrobial agents, government-based research organisations and universities under the organisation of the Society of Industrial technology for Antimicrobial Articles (SIAA), the method has then been validated by ring tests within Japan and now forms the basis of a draft ISO standard which is being validated by the SIAA in collaboration with the International Biodeterioration Research Group (IBRG). In JIS Z 2801, the antibacterial activity is measured by quantifying the survival of bacterial cells which have been held in intimate contact for 24 hours at 35°C with a surface that contains an antibacterial agent. The antibacterial effect is measured by comparing the survival of bacteria on a treated material with that achieved on an untreated material.

5.3.2 SAMPLE PREPARATION

N-Propanol and methyltrimethoxy silane ($Si\text{-}CH_3\text{-}(OCH_3)_3$) were mixed in a beaker with the ratio of 1:1. 2.5% wt of silver nanocrystal was added into the system and was grinded in the ball mill for 1 hr. Nitric acid was diluted to obtain the pH of 0.1 and was used as a catalyst (10% wt). The coating was coated using melamine sponge, and coated on a glass substrate with a UV protection coating that has been kept for more than 7 days. The coating process was carried out at room temperature of 26 °C and absolute humidity of 30%. The dried sample was kept at room temperature for 7 days and tested against *Staphylococcus Aureus, Eschericia Coli* and *Pseudomonas Aerugirosa* according to JIS Z 2801:200 (Antimicrobial Product – Test for antimicrobial activity and efficacy) by an accredited testing lab (SIRIM QAS International Sdn Bhd).

5.3.3 ANTIBACTERIAL TEST RESULT

Figure 5.29 shows three glass surfaces that have been applied with the antibacterial coating. Slide-A was the uncoated glass whereas Slide-B and Slide-C were both coated with 2.5% and 3.5% of Ag. The coating was transparent. The presence of Ag nanoparticles powder is visible on the surface when the slides were tilted to a certain angle.

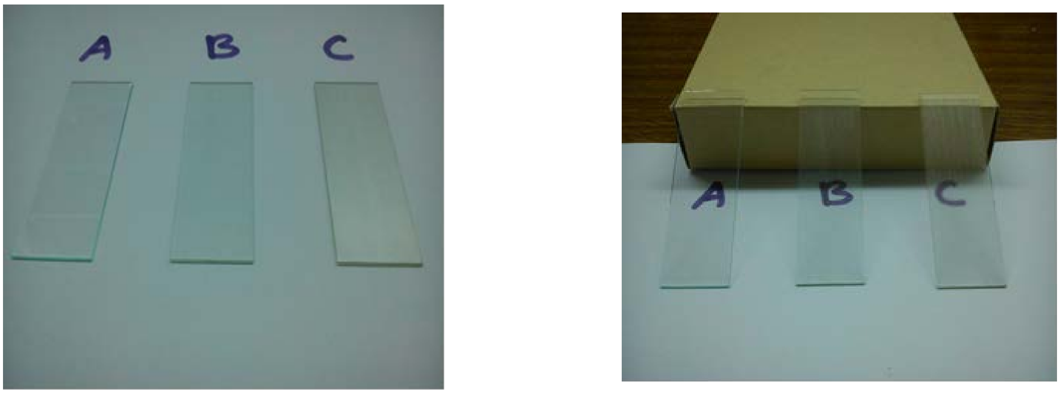


Figure 5.29: A transparent antibacterial coating applied onto a glass surface; (a), and (b) slide-A -uncoated surface, slide -B -Ag 2.5 % -coated surface and Slide-C-Ag 3.5 % - coated surface.

Table 15: The total transmittance and haze values of antibacterial coating

Sample	% of Ag in the sample	Total transmittance (%)	Haze
A	0% Ag	80.74	0.35
B	2.5% Ag	78.94	1.75
C	3.5% Ag	69.70	3.14

Table 15 shows that total haze level increases as the amount of Ag higher. Total light transmittance also decreases. This is due to the fact that the nano silver in the coatings affected the transmittance of light and transparency by causing the light diffusion in the samples.More particles will cause the light being scattered and diffused throughout the samples. Visible light transmittance reduced with higher amount of nano silver.

(a) (b)

(c)

Figure 5.30: Optical comparison of transparency level by placing the slides approximately 2-cm in front of the lense of digital camera; a) slide A-non-coated, b) slide B-2.5 % Ag and c) slide C-3.5 % Ag

Figure 5.30 show the optical properties of coating samples that were added with silver nanocrystals. Based on the observation, the sample with 2.5% Ag is better in terms of clarity compared to the one with 3.5% Ag. This shows that 2.5% is the maximum amount of silver nanocrystals that can be added into the coating mixture to maintain the clarity of the coatings. Sample with 2.5% silver nanocrystals were sent to SIRIM QAS International Sdn. Bhd. for antibacterial test according to JIS Z 2801: (Antimicrobial product-test for antimicrobial activity and efficacy). The results for the antibacterial test against *Staphylococcus Aureus*, *Eschericia Coli* and *Pseudomonas Aerugirosa* according to JIS Z 2801: (Antimicrobial product-test for antimicrobial activity and efficacy) of the coating are shown in Table 16.

Table 16: The antibacterial efficacy against *Pseudomonas Aerugirosa, Eschericia Coli* and *Staphylococcus Aureus*

Bacteria species	Sample	Number of viable cells of bacteria at 0hr	Number of viable cells of bacteria after 24hrs	Value of antimicrobial activity
Pseudomonas Aerugirosa	2.5% silver coating	1.8×10^5	2.0×10^2	4.6
	Control	1.9×10^5	9.5×10^6	-
Eschericia Coli	2.5% silver coating	4.0×10^5	<10	7.2
	Control	4.4×10^5	1.7×10^8	-
Staphylococcus Aureus	2.5% silver coating	2.0×10^5	8.9×10^2	4.2
	Control	2.0×10^5	1.5×10^7	-

* 2.5% silver coating – coating consists of silver and sol-gel formulation

**control - Glass slides with no coating applied

Coating with antimicrobial activity greater than 2 is classified as antibacterial. The antibacterial test result clearly shows that the value of antimicrobial activity of 4.6 for *Pseudomonas Aerugirosa,* 7.2 for *Eschericia Coli,* and 4.2 for *Staphylococcus Aureus.* All the values exceeded the value of 2 which confirmed the antibacterial coating and therefore, complies with the standard of JIS Z 2801.

In order to verify that the antibacterial properties come only from the Ag nanoparticles and not from the sol-gel formulation, we carried out antibacterial tests to slides coated with only sol-gel (no Ag nanoparticles were used). The non-coated slides were used as controls. The results in Table 18 show that the number of bacteria has increased after a 24-hour period for all types of bacteria for the sol-gel coated slides. This verifies and proves that the sol-gel does not have antibacterial properties.

Table 17: The antibacterial tests against *Pseudomonas Aerugirosa*, *Eschericia Coli* and *Staphylococcus Aureus* on glass slides that were coated only with sol gel; without any Ag nanoparticles

Bacteria species	Sample	Number of viable cells of bacteria at 0hr	Number of viable cells of bacteria after 24hrs	Value of antimicrobial activity
Pseudomonas Aerugirosa	Sol-gel coated slide	2.0×10^5	3.6×10^7	-
	Control	1.9×10^5	9.5×10^6	-
Eschericia Coli	Sol-gel coated slide	4.6×10^5	1.1×10^8	-
	Control	4.0×10^5	1.7×10^8	-
Staphylococcus Aureus	Sol-gel coated slide	2.0×10^5	1.5×10^7	-
	Control	2.0×10^5	1.5×10^7	-

* Sol-gel coated slide – coating consists only sol gel; no Ag silver

** Control - Glass slides with no coating applied

As shown in table 17, no antimicrobial activity was observed when Ag nanoparticle was not incorporated into the coating system. Antibacterial nanocrystallite silver may work in two ways; firstly, it breaks through the permeability of the outer membrane, resulting in the leakage of cellular materials. It is well known that bacteria possess an outer membrane to serve as a selective permeability barrier which protects bacteria from harmful agents such as detergents, drugs, toxins, and degradative enzymes; and to penetrate nutrients to sustain bacterial growth. Kim et al. (2011) reported studies based on *S. aureus* and *E. coli* that the free radicals could induce bacterial cell membrane damage by enhancing the permeability of the membrane. The bacteria will then undergo a protein-leakage as a result of the increasing membrane permeability.

Secondly, as a result of the increasing permeability, nanocrystallite silver can enter the inner membrane and inactivate respiratory chain dehydrogenases, thus inhibiting respiration and growth of cells. Holt and Bard (2005) proved this by showing that Ag^+ can inhibit the respiration of *E. coli* by determining change of oxygen dissolved in culture resolution. A report on *Pseudomonas aeruginosa* also suggested that silver nanoparticles not only inhibited the growth but also the ability of the organism to synthesize the exopolysachharide. The exopolysachharide functions not only to protect the bacteria from the host defence mechanism but also mediates the adhesion of the organism to the surface. At the same time, the silver could as well affect some proteins and phosphate lipids, and induce collapse of membrane, resulting in cell decomposition and death eventually. This is supported by Kim et al (2011). who found that Ag+ interacted with thiol (–SH) group of cysteine by replacing the hydrogen atom to form –S–Ag, thus hindering the enzymatic function of the affected protein to inhibit the growth of *E. coli*.

CHAPTER 6

6.0 CONCLUSION

The most significant conclusion that can be drawn from this research work is, we managed to present a prototype coating system with two different functionalities which are UV protection and antibacterial coatings. A high transparency of UV protection coating that has the ability to block about 99.99% of the average UV A and UV B in the range of 300 nm to 400 nm. One layer of the coating was enough to block almost all of the harmful UV rays from penetrating through the samples. The clear sol-gel coating with 5% wt of 2, 4 dihydroxyl benzophenone managed to block the harmful UV rays, yet the clarity of the sample remains. Open-celled melamine sponge was used as the coating applicator.

For antibacterial coatings, 2.5% wt of the synthesized silver nano crystals was incorporated into the clear sol-gel coatings managed to kill the three species of bacteria *Pseudomonas Aerugirosa, Eschericia Coli* and *Staphylococcus Aureus* according to JIS Z 2801: 2000 Antimicrobial products-Test for antimicrobial activity and efficacy. A patent has been filed for this research work and the IP number is PI 2014701054. The significant of this patent is that, the coating has been proven that to eliminate *Pseudomonas Aerugirosa.* This particular pathogen is known as an opportunistic bacterium that causes fatal nosocomial infection to patients with low immunity. It can penetrate through cuts and wounds. This will cause serious problems especially for patients with low immune systems and post-trauma. Since it has the ability to survive in extreme conditions, temperature and humidity control in the operation theatre will not kill these bacteria. Thus, the great significant of this antibacterial coating is the application in those particular surroundings.

The requirement of the best formulation to satisfy the demand for the functional coating has been developed. Sol-gel technology in the coating binder that has been implemented for both functional coatings managed to achieve the high-clarity and low-haze value. Highest parallel light transmittance and total light transmittance with lowest haze values were obtained from the formulation of N-propanol and methyl trimethoxy silane. The pencil scratch hardness of 9H has proven that the adhesion of the coating is acceptable. Tack free time of 3 mins indicates that the curing and drying time of the developed coating is acceptable. The coatings would be good alternatives to end who require these functionalities yet maintain the original appearance of the substrate e.g. glass windows, painted walls, clear packaging, etc.

The most attractive aspects of this research work are the simplicity that has been introduced in the coating method, and the high performance of the functionality that it offers. The potential application for this coating would be wider due to the hybrid structure of the organic and inorganic chain in the binders that will make the coatings strongly adhere to both the organic and inorganic substrate. Therefore, the coatings can be coated on raw glass, ceramics, tiles, and concrete; at the same time, it can also be coated on the organic paints as the top coat that will protect the paints underneath, hence extending the lifetime of the paints and substrate.

The coatings can be applied as suggested by Figure 6.1 or individually according to the needs. Both functional coatings work separately yet do not interfere with each other when combined together. When combined together, it is important for the antibacterial coating to be the top coat because of the maximum direct contact between the silver nanocrystals and the bacteria.

The ideal application of the coating in this research is as follows:

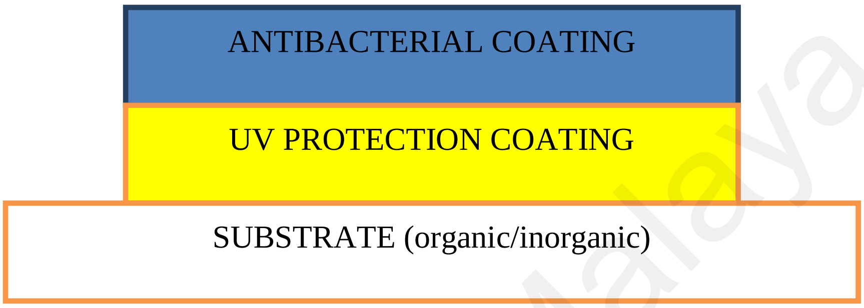


Figure 6.1: The ideal applications of the coatings

6.1 FURTHER RESEARCH:

The developed coating has been proven to eliminate 3 types of bacterial tested according to JIS Z 2801: 2000 Antimicrobial products-Tests for antimicrobial activity and efficacy which are *Pseudomonas Aerugirosa. Eschericia Coli* and *Staphylococcus Aureus. Pseudomonas Aerugirosa* is a major threat since it is known as one of the toughest strain bacteria. The main problem of *Pseudomonas Aerugirosa* in operation theatres, intensive care units and in hospital in general is the problem of no known solution to date in all hospital all over the world. It is known for causing the nosocomial infections to the patients. In the United States, it has been estimated that 9.2 out of every 100 patients acquire a nosocomial infection. Nosocomial infections are infections that have been acquired in hospitals and other healthcare facilities. To be classified as a nosocomial infection, the patient must have been admitted for reasons other than the infection. He or she must have also shown no signs of active or incubating infection. A survey has been done by WHO in 55 hospitals and involved 14 countries around the regions of Europe, South East Asia, Eastern Mediterranean and Western Pacific. An average of 8.7% of hospital patients contract nosocomial infections. Nosocomial infections cause many illnesses such as urinary tract infection, pneumonia, surgical site infection, etc.

These infections occur:

- up to 48 hours after hospital admission
- up to 3 days after discharge
- up to 30 days after an operation
- in a healthcare facility when a patient was admitted for reasons other than the infection

The most significant application of the developed antibacterial coating is to fight the antibacterial that causes nosocomial infections. However, further clinical validation in real time need to be obtained before the utilization of the product can be materialised. Research work also needs to be done on the effect of this coating on the fungi and virus that also cause nosocomial infections.

On another fact, the usage of silver as antibacterial agent is well established due to the fact that silver had been known for century as an antibacterial agent. However, the actual mechanism for the elimination of the bacterial by silver has not been properly established. In the role of ROS (reactive oxygen species) as the cause for elimination of bacteria need a very detail analysis for optimization of the coating.

The silver production via inorganic route can be improvised, since the applications are in medical area. Precipitation method is known as a ‘dirty’ method due to the fact that contaminants are still detectable on the end product although the precipitates had been thoroughly washed. The emergence of ‘green synthesis’ will perhaps overcome this problem. Preliminary studies in reduction of silver nitrate using material extract such as tea leaves have shown promising results. Further research using green synthesis to extract silver from silver nitrate should be pursued so that the end product of silver would be less hazardous to human environment.

The other major problem of precipitation method is the agglomeration of silver nanocrystal. The agglomeration to a certain extend reduce the effectiveness of the reagent due to the decrease of surface contact area. Through green synthesis it is perhaps possible to find organic extract agent not only to reduce silver nitrate to silver but also leave behind an end product that encapsulate the silver nanoparticle produced so as to reduce agglomeration. The natural dispersing agent plays an important role in dispersing the nanocrystallite silver.

REFERENCES

Akhavan, O. (2009) Lasting antibacterial activities of Ag–TiO2/Ag/TiO2 nanocomposite thin film photocatalysts under solar light irradiation. *Journal of Colloid and Interface Science* 117-124.

Allen C. (2004) http://www2.lbl.gov/Science-Articles/Archive/sb/Aug-2004/3_coolroofs-

A.Fujishimaa, X. Zhang and D. A. Tryk, (2008) TiO_2 photocatalysis and related surface phenomena. *Surface Science Reports* 63 (12), 515-582

A. Ranga Rao and V. Dutta (2007) Low-temperature synthesis of TiO_2 nanoparticles and preparation of TiO_2 thin films by spray deposition. *Solar Energy Materials and Solar Cells* 91(12) 1075-1080

Annamalai Prathee Kumara, D. D. (2009) Nanoscale particles for polymer degradation and stabilization—Trends and future perspectives. *Progress in Polymer Science* 479-515.

Annalisa C., Gabriella L., Marinella S., Gaetano D. M and M. L. Curri (2008) Effect of shape and surface chemistry of TiO_2 colloidal nanocrystals on the organic vapor absorption capacity of TiO_2/PMMA composite. *Polymer* 49 (25) 859-870.

www.bccresearch.com/market-research/chemicals/paints-coatings-markets-technology retrieved on february 2013

B. Mahltig, H. Böttcher, K. Rauch, U. Dieckmann, R. Nitsche and T. Fritz (2005), Optimized UV protection coating by combination of organic and inorganic UV absorbers *Thin solid film* 485, 108-114

Bernd Nowack and Thomas D. Bucheli (2007) Occurrence, behavior and effects of nanoparticles in the environment, *Environmental Pollution* 150 (1) 5-22

Birla S, Tiwari V, Gade A, Ingle A, Yadav A, Rai M., (2009) Fabrication of silver nanoparticles by Phoma glomerata and its combined effect against Escherichia coli, Pseudomonas aeruginosa and Staphylococcus aureus, *Letters in Applied Microbiology* 48(2) 173-179.

Bräuer, G., February (1999) Large area glass coating. *Surface and Coatings Technology* 358-365.

Brookfield engineering (2009) http://www.brookfieldengineering.com

Bucheli, B. N. (2007) Occurrence, behavior and effects of nanoparticles in the environment. *Environmental Pollution* 5-22

Charlotte Young, (2009) Solar ultraviolet radiation and skin cancer, *Occupational Medicine* 59, 82-88

Clive H. Hare (1992) The Degradation of Coatings by Ultraviolet Light and Electromagnetic Radiation, *Journal of protective coatings and linings*

C. Euvananonta, C. Junina, K. Inpora, P. Limthongkula and C. Thanachayanont (2008) TiO_2 optical coating layers for self-cleaning applications. *Ceramics International* 34(4), 1067-1071

C. Gil, M. A. (2004) Superficial colouring of lead crystal glassn by sol–gel coatings. *Journal of the European Ceramic Society* 25(5) 711-718

C. N. R. Rao, A. M. (2004) *The Chemistry of Nanomaterials.* Weinheim: Wiley VCH.

C.M. Liao, Y. H. Chiang and C.P. Chioa (2008) Model-based assessment for human inhalation exposure risk to airborne nano/fine titanium dioxide particles *Science of The Total Environment* 407(1), 165-177

www.cs.cornell.edu/ retrieved on july 2013

David S. Goodsell, (2001), The Molecular Perspective: Ultraviolet Light and Pyrimidine Dimers, *The oncologist* 298-299

D.K. Chattopadhyay, and K.V.S.N. Raju (2007) Structural engineering of polyurethane coatings for high performance applications *Progress in Polymer Science* 32 (3), 352–418

D. Katsamberis, K. Browall, C. Iacovangelo, M. Neumann and H. Morgner (1997) Highly durable coatings for automotive polycarbonate glazing *Progress in Organic Coatings* 34(1), 130-134

D. P. Dowling, E, A. J. Betts, C. Pope, M. L. McConnell, R. Eloy and M. N. Arnaud (2003) Anti-bacterial silver coatings exhibiting enhanced activity through the addition of platinum. *Surface and Coatings Technology* 163-164, 637-640.

Danqing Zhu, Wim J van Ooij (2002) Corrosion protection of AA 2024-T3 by bis-[3-(triethoxysilyl)propyl]tetrasulfide in sodium chloride solution.: Part 2: mechanism for corrosion protection *Corrosion Science* 45(10), 2177-2197

Donald R. Baer, P. E.-A. (2003) Enhancing coating functionality using nanoscience and nanotechnology *Progress in Organic Coatings* 342-356

D. R. Monteiro, L. F. Gorup, A. S. Takamiya, A. C. R. Filho, E.R. Camargo and D. B. Barbosa (2009) The growing importance of materials that prevent microbial adhesion: antimicrobial effect of medical devices containing silver *International Journal of Antimicrobial Agents* 34, 103-110.

D.P.Dowling, K.Donelly, M.L.McConel, R.Eloy and M.N.Arnaud (2001) Deposition of antibacterial silver coatings on polymeric substrate *Thin Solid Film* 398-399, 602-606.

Duangkamon Jiraroj, Sukkaneste Tungasmita, Duangamol N. Tungasmita (2014) Silver ions and silver nanoparticles in zeolite A composites for antibacterial activity *Powder Technology* 264, 418-422

Emi Ukaji, T. F. (2007) The effect of surface modification with silane coupling agent on suppressing the photo-catalytic activity of fine TiO_2 particles as inorganic UV filter *Applied Surface Science* 563-569 .

Elcometer Pencil Hardness: http://www.bamr.co.za retrieved on 10 January, 2010

Filiz Kara, Eda Ayse Aksoy, Zehranur Yuksekdag, Hasirci, Serpil Aksoy (2014) Synthesis and surface modification of polyurethanes with chitosan for antibacterial properties, *Carbohydrate Polymers* 112, 39-47

G. F. Tjandraatmadja, L. S. Burna and M. C. Jollands (2002) Evaluation of commercial polycarbonate optical properties after QUV-A radiation—the role of humidity in photodegradation *Polymer Degradation and Stability* 76(3), 435-448

G. J. Chia, S. W. (2002) Antibacterial activity of anodized aluminum with deposited silver. *Surface and Coatings Technology* 157 (2-3), 162-165

Gary T. Howard (2002) Biodegradation of polyurethane: *a review International Biodeterioration & Biodegradation* 49 (4), 245-252

Gladitz M, Reinemann S, Radusch HJ. (2009) Preparation of Silver Nanoparticle Dispersions via a Dendritic-Polymer Template Approach and their Use for Antibacterial Surface Treatment. *Macromolecular Materials and Engineering* 294 (3) 178-89

Grazyna Bystrzejewska-Piotrowskaa, J. G. (2009). Nanoparticles: Their potential toxicity, waste and environmental management. *Waste Management* 29 (9) 2587-2595

Guan, K. (2005) Relationship between photocatalytic activity, hydrophilicity and self-cleaning effect of TiO_2/SiO_2 films. *Surface and Coatings Technology* 191(2-3) 150-160.

Guodong Jin, Hui Qin, Huiliang Cao, Shi Qian, Yaochao Zhao, Xiaochun Peng, Xianlong Zhang, Xuanyong Liu, Paul K. Chu (2014) Synergistic effects of dual Zn/Ag ion implantation in osteogenic activity and antibacterial ability of titanium, *Biomaterials* 35 (27), 7699-7713

Guy Applerot, N. P. (2009) Coating of glass with ZnO via ultrasonic irradiation and a study of its antibacterial properties. *Applied Surface Science* 256(3) s3-s4

H. Yamashita, H. Nakao, M. Takeuchi, Y. Nakatani and M. Anpo (2003) Coating of TiO_2 photocatalysts on super-hydrophobic porous teflon membrane by an ion assisted deposition method and their self-cleaning performance, *Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms* 206, 898-901

H.M. Yates, L. B. (2008) Photo-induced self-cleaning and biocidal behaviour of titania and copper oxide multilayers. *Journal of Photochemistry and Photobiology A: Chemistry*, 197 (2-3) 197-205

H. M. Hawthorne, A. Neville, T. Troczynski, X. Hub, M. Thammachart, Y. Xie, J. Fu and Q. Yang (2004) Characterization of chemically bonded composite sol–gel based alumina coatings on steel substrates, *Surface and Coatings Technology* 176(2), 243-252,

Hariharan, C. (2006) Photocatalytic degradation of organic contaminants in water by ZnO nanoparticles, *Applied Catalysis A: General* 304, 55-61

Holt KB, Bard AJ. (2005) Interaction of silver (I) ions with the respiratory chain of Escherichia coli: an electrochemical and scanning electrochemical microscopy study of the antimicrobial mechanism of micromolar Ag^+. *Biochemistry* 44(39):13214-23.

Hossam E. Emam, Salwa Mowafi, Hamada M. Mashaly, Mohamed Rehan, (2014) Production of antibacterial colored viscose fibers using in situ prepared spherical Ag nanoparticles, *Carbohydrate Polymers* 110, 148-155

Imai S (2005) The Development of an ISO Standard for Measuring the Antibacterial Activity, *Hygienic coating and surfaces* Paris, France

Ismail WA, Ali ZA, Puteh R. (2012) Optical and Physical Properties of Methyltrimethoxysilane Transparent Film Incorporated with Nanoparticles. *Advances in Materials Science and Engineering*. 2012

J.H. Lia, R.Y. Hong, M.Y. Li, H.Z. Li, Y. Zheng and J. Ding, (2009) Effects of ZnO nanoparticles on the mechanical and antibacterial properties of polyurethane coatings *Progress in Organic Coatings* 64, 504-509

J.O. Carneiroa, V. Teixeiraa, A. Portinhaa, A. Magalhãesa, P. Coutinhob, C.J. Tavaresa and R. Newton (2007) Iron-doped photocatalytic TiO_2 sputtered coatings on plastics for self-cleaning applications *Materials Science and Engineering: B* 138 (2), 144-150

J. Malzbender, G. De With (2000) The effects of drying, aging and curing on an organic - inorganic coating, *Journals of Material Science* 35, 4809-4814

J. Malzbender, G. de With (2000) Cracking and residual stress in hybrid coatings on float glass, *Thin Solid Films* 359 210–214

James E. Pickett, Jonathan R. Sargent, Holly A. Blaydes and Nicole Babbie (2009) Effects of temperature on the weathering lifetime of coated polycarbonate *Polymer Degradation and Stability* 94(7), 1085-1091

J.R. Villalobos-Hernándeza and C.C. Müller-Goymann (2006) Sun protection enhancement of titanium dioxide crystals by the use of carnauba wax nanoparticles: The synergistic interaction between organic and inorganic sunscreens at *nanoscale International Journal of Pharmaceutics* 322, (1-2), 161-170

Jayesh P. Ruparelia, A. K. Chatterjee, S. P. Duttagupta and S. Mukherji (2008) Strain specificity in antimicrobial activity of silver and copper nanoparticles, *Acta Biomaterialia* 4, 707-716.

J.K Liuar, X.H Yang and X.G Tian (2008) Preparation of silver/hydroxyapatite nanocomposite spheres *Powder Technology* 184 (1). 21-24

Jianwen Hu, Xiaogang Li, Jin Gao and Quanlin Zhao (2009) Ageing behavior of acrylic polyurethane varnish coating in artificial weathering environment *Progress in Organic Coatings* 65 (4), 504-509

Jun Chena and Chi-sun Poon (2009) Photocatalytic construction and building materials: From fundamentals to applications *Building and Environment* 44(9), 1899-1906

K.H. Tam, A. D. (2007). Antibacterial activity of ZnOnext term nanorods prepared by a hydrothermal method. *Thin Solid Films* 6167-6174

Kalishwaralal K, BarathManiKanth S, Pandian SRK, Deepak V, Gurunathan S. (2010) Silver nanoparticles impede the biofilm formation by Pseudomonas aeruginosa and Staphylococcus epidermidis. *Colloids and Surfaces B: Biointerfaces* 79(2):340-344.

Kelly J. Higgins, Heejung Jung, David B. Kittelson, Jeffrey T. Roberts and Michael R. Zachariah (2002) *The Journal of Physical Chemistry A*106 (1) 96-103

Kim JY, Lee C, Cho M, Yoon J (2008) Enhanced inactivation of E. coli and MS-2 phage by silver ions combined with UV-A and visible light irradiation. *Water Research* 42 (1-2) 356–362

Kim S-H, Lee H-S, Ryu D-S, Choi S-J, Lee D-S. (2011) Antibacterial activity of silver-nanoparticles against Staphylococcus aureus and Escherichia coli. *Korean Journal of Microbiology and Biotechnology* 39(1):77-85

Laura Raibeck, John Reap and Bert Bras (2009) Investigating environmental burdens and benefits of biologically inspired self-cleaning surfaces *CIRP Journal of Manufacturing Science and Technology* 1 (4), 230-236

L. Peruchona, E. P.-E. (2008) Characterization of self-cleaning glasses using Langmuir–Blodgett technique to control thickness of stearic acid multilayers: Importance of spectral emission to define standard test *Journal of Photochemistry and photobiology A: Chemistry* 197 (2-3) 170-176

Lead, Y. J.-N. (2008) Manufactured nanoparticles: An overview of their chemistry, interactions and potential environmental implications. *Science of The Total Environment* 400 (1-3) 396-414.

Linda Y.L. Wua, Edmund Chwa, Z. Chen and X.T. Zeng (2008) A study towards improving mechanical properties of sol–gel coatings for polycarbonate *Thin Solid Films* 516 (6), 1056-1062

Li Q, Mahendra S, Lyon DY, Brunet L, Liga MV, Li D, et al. (2008) Antimicrobial nanomaterials for water disinfection and microbial control: Potential applications and implications. *Water Research*. 42(18): 4591- 4602

Weng Zhang, Zhiguo Zhang and Wei Li (2013) Antibacterial Coating Incorporating Silver Nanoparticles by Microarc Oxidation and Ion Implantation. *Journal of Nanomaterials 2013*

Li W-R, Xie X-B, Shi Q-S, Zeng H-Y, OU-Yang Y-S, Chen Y-B. (2010) Antibacterial activity and mechanism of silver nanoparticles on Escherichia coli. Applied microbiology and biotechnology 85(4):1115-1122

Li W-R, Xie X-B, Shi Q-S, Duan S-S, Ouyang Y-S, Chen Y-B. (2011) Antibacterial effect of silver nanoparticles on Staphylococcus aureus. *Biometals* 24(1):135-141

Malvern Nanotechnology: http://malvern.com retrieved on 8 January, 2010,

M. Kawashita, S. Tsuneyama, F. Miyaji, T. Kokubo, H. Kozuka and K. Yamamoto (2000) Antibacterial silver -containing silica glass prepared by sol–gel method *Biomaterials* 21 (4), 393-398

M. Sabzia, S.M. Mirabedini, J. Zohuriaan-Mehra and M. Atai (2009) Surface modification of TiO_2 nano-particles with silane coupling agent and investigation of its effect on the properties of polyurethane composite coating *Progress in Organic Coating* 65(2), 222-228

M. E. Nichols and C. A. Peters (2002) The effect of weathering on the fracture energy of hardcoats over polycarbonate *Polymer Degradation and Stability* 75(2), 439-446

M.C. Hidalgo, S. Sakthivel and D. Bahnemann (2004) Highly photoactive and stable TiO_2 coatings on sintered glass, *Applied Catalysis A: General* 277(1-2), 183-189.

Marambio-Jones C, Hoek EM. (2010) A review of the antibacterial effects of silver nanomaterials and potential implications for human health and the environment. *Journal of Nanoparticle Research* 12(5):1531-51

Masayuki Nogami, Shohei Hotta , Kazumasa Kugimiya, Hideaki Matsubara, (2010) Synthesis and characterization of transparent silica-based aerogels using methyltrimethoxysilane precursor, *J Sol-Gel Sci Technol* 56 107–113

M. Parhizkar, N. K. (2005) Nanocrystalline ZnO films prepared by pyrolysis of Zn-arachidate LB multilayers. *Colloids and Surfaces A: Physicochemical and Engineering Aspects* 445-449.

Martin Melchiors C, M. S. (2000) Recent developments in aqueous two-component polyurethanen (2K-PUR) coatings. *Progress in Organic Coatings* 40 (1-2), 99-109.

Masayuki Yamane (2006) Unique commercial applications of the sol-gel process in Japan, J *Sol-Gel Sci Techn* 40, 273–279

Matthew J. Hayat, Nadia Howlader, Marsha E. Reichman and Brenda K. Edwards (2006) Cancer Statistics, Trends, and Multiple Primary Cancer Analyses from the Surveillance, Epidemiology, and End Results (SEER) Program, *The Oncologist* 19 (9), 20-37

Minglin Ma and Randal M. Hill (2006) Superhydrophobic surfaces *Current Opinion in Colloid & Interface Science*

Müller-Goymann, J. V.-H. (2006) Sun protection enhancement of titanium dioxide crystals by the use of carnauba wax nanoparticles: The synergistic interaction between organic and inorganic sunscreens at nanoscale. *International Journal of Pharmaceutics* 322 (1-2) 161-170.

Mukherjee, R. B. (2008) Biological properties of “naked” metal nanoparticles. *Advanced Drug Delivery Reviews*, 60 (11) 1289-1306.

Niall Stobie, Brendan Duffy, Steven J.Hinder, Patrick McHale and Declan E. McCormack (2009) Silver doped perflouropolyether-urtethane coatings: Antibacterial activity and surface analysis 1 *Colloids and Surface B: Biointerfaces* 72, 62-67.

http://webbook.nist.gov/chemistry/form-ser.html retrieved on june 2010

Okkyoung Choi, Kathy Kanjun Deng, Nam-Jung kim, Louis Ross jr., Rao Y. Surampali and Zhiqiang Hu (2008) The inhibitory effects of silver nanoparticles, silver ions, and silver chloride colloids on microbial growth: *Water Research* 42 (12), 3066-3074

http://www.onclive.com retrieved on july 2013

Oveisi H, Rahighi S, Jiang X, Nemoto Y, Beitollahi A, Wakatsuki S, et al. (2010) Unusual antibacterial property of mesoporous titania films: drastic improvement by controlling surface area and crystallinity. *Chemistry–An Asian Journal* 5(9):1978-1983

P. Madgwick, J. Houdmont and R. Randall (2011) Sun safety measures among construction workers in Britain, *Occupational Medicine* 61, 430-433

Pallavicini P, Taglietti A, Dacarro G, Antonio Diaz-Fernandez Y, Galli M, Grisoli P, et al. (2010) Self-assembled monolayers of silver nanoparticles firmly grafted on glass surfaces: Low Ag release for an efficient antibacterial activity. *Journal of colloid and interface science* 350(1):110-116

Paul, S. (1997) *Surface Coatings Science and Technology second edition.* West Sussex: John Wiley & Sons Ltd.

Pierre.C.A. (1998) Introduction to Sol Gel Processing, Kluwer Academic Publishers

Philippe Belleville (2010) Functional coatings: The sol-gel approach, *Académie des sciences* 13 (1-2), 97 -105,

Ploux L, Mateescu M, Anselme K, Vasilev K. (2012) Antibacterial properties of silver-loaded plasma polymer coatings. *Journal of Nanomaterials 2012*

Poon, J. C.-s. (2009) Photocatalytic construction and building materials: From fundamentals to applications. *Building and Environment* 44 (9) 1899-1906 .

Qilin Li, shaily Mahendra, Deliva Y. Lyon, Lena Brunet, Michael V. Liga, Dong Li and Pedro J.J Alvarez (2008) Antimicrobial nanomaterial for water disinfection and microbial control: Potential applications and implication, *Water Research* 42, 4591-4602

R. P. Singh, Namrata S. Tomer and S. Veera Bhadraiah (2001) Photo-oxidation studies on polyurethane coating: effect of additives on yellowing of polyurethane *Polymer Degradation and Stability* 73 (3), 443-446

R. Cai, G.M. Vana, P.K. Awa and K. Itoh (2006) Solar-driven self-cleaning coating for a painted surface *Comptes Rendus Chimie* 9 (5-6), 829-835

Rajeev Jain and Meenakshi Shrivastava (2008) Photocatalytic removal of hazardous dye cyanosine from industrial waste using titanium dioxide *Journal of Hazardous Materials* 152(1), 216-220

Resham Bhattacharyaa and Priyabrata Mukherjee (2008) Biological properties of “naked” metal nanoparticles *Advanced Drug Delivery Reviews* 60 (11), 1289-1306

Rosa Taurino, Elena Fabbri, Massimo Messori, Francesco Pilati, Doris Pospiech and Alla Synytska (2008) Facile preparation of superhydrophobic coatings by sol–gel processes, *Journal of Colloid and Interface Science* 325 (1), 149-156

R. Zhang, P. E. Mallon, H. Chen, C. M. Huang, J. Zhang, Y. Li, Y. Wu, T. C. Sandreczki and Y. C. Jean (2001) Characterization of photodegradation of a polyurethane coating by positron annihilation spectroscopy: correlation with cross-link density *Progress in Organic Coatings*, 42 (3-4), 244-252

S. Cavallu, V. Simon, C. Albon and C. Hozan (2007) Bioactivity evaluation of silver doped bone cement for prosthetic surgery, Journal of optoelectronic and advanced material 9(3), 690-693

Sha Jin and Fumihide Shiraishi (2004) Photocatalytic activities enhanced for decompositions of organic compounds over metal-photodepositing titanium dioxide *Chemical Engineering Journal* 97 (2-3), 203-211

Surface Machine System: http://www.surfacemachines.com 8 January, 2010

S.S. Madaeni and N. Ghaemi (2007) Characterization of self-cleaning RO membranes coated with TiO2 particles under UV *irradiation Journal of Membrane Science* 303(1-2), 221-233

S. Sakthivel, B. N. (2003) Solar photocatalytic degradation of azo dye: comparison of photocatalytic efficiency of ZnO and TiO_2. *Solar Energy Materials and Solar Cells* 77 (1) 65-82.

Samuel Brunner, P. R. (2005) Accelerated weathering device for service life prediction for organic coatings. *Polymer Testing* 24 (1), 25-31 .

Schluesner, X. Chen and H.J. (2008) Nanosilver: A nanoproduct in medical application. *Toxicology Letters* 176, 1-12.

Shackelford, J. F. (2000) Material Science for Engineers, Fifth Edition. New Jersey, United States of America: Prentice-Hall Inc.

Shrivastava, R. J. (2008) Photocatalytic removal of hazardous dye cyanosine from industrial waste using titanium dioxide. *Journal of Hazardous Materials* 152 (1) 216-220.

Shinetsu Chemical. (n.d.). Retrieved 13 January, 2010, from http://www.silicone.jp/e/products/type/silane/detail/index.shtml

Skoog, H. a. (1997). Principle of Instrumental Analysis, Fifth Edition. United States of America: Brooks/Cole, Thomson Learning.

Sofiane Sedira, Ahmed Abdelhakim Ayachi, Sihem Lakehal, , Merouane Fateh, Slimane Achour (2014) Silver nanoparticles in combination with acetic acid and zinc oxide quantum dots for antibacterial activities improvement—A comparative study, *Applied Surface Science* 311, 659-665

Sukalyan Dash, Soumyashri Mishra, Sabita Patel, Bijay K. Mishra (2008) Organically modified silica: Synthesis and applications due to its surface interaction with organic molecules, *Advances in Colloid and Interface Science* 140, 77-94

Sumin Kim, Hyung-Joong Kim (2006) Antibacterial performance of colloidal silver treated laminated wood flooring: *International Biodeterioration & Biodegradation* 57, 155-162.

www.trc-canada.com retrieved on june 2010

Xiao Song, Zhangwei Guo, Yaohua Dong, Na Guo, Xueting Chang (2014) Prolonged antibacterial effect of silver nanocomposites with different structures, *Colloids and Surfaces B: Biointerfaces* 116, 793-796

T. Yuranova, V. Sarria, W. Jardim, J. Rengifo, C. Pulgarina, G. Trabesingerd and J. Kiwi (2007) Photocatalytic discoloration of organic compounds on outdoor building cement panels modified by photoactive coatings *Journal of Photochemistry and Photobiology A: Chemistry* 188, (2-3), 334-341

Takeshi Morimoto, Hiroyuki Tomonaga and Akemi Mitani (1999) Ultraviolet ray absorbing coatings on glass for automobiles, *Thin Solid Films* 351, 61-65

Thabet M. Tolaymat, amro M. ElBadawy, Ash Genaidy, kirk G. Scheckel, Todd P.Luxton, Makram Suidan (2009) An evidence-based environmental perspective of manufactured silver nanoparticle in syntheses and application. *Science of the total environment* 408 (5), 999-1006

T. Kemmitt, N. I.-S. (2004). Photocatalytic titania coatings. *Current Applied Physics* 4 (2-4), 189-192

V.I. Kondratiev, I. Kink, A.E. Romanov (2013), Low temperature sol gel techniques for processing Al-doped zinc oxide films, *Materials Physics and Mechanics* 17, 38-46

W. Boentoro, A. Pflug and B. Szyszka (2009) Scratch resistance analysis of coatings on glass and polycarbonate, *Thin Solid Films* 517 (10), 3121-3125

Walid A. Daoud and John H. Xin (2004), Low temperature sol gel processed photo catalytic titania coating, *Journal of sol gel science and technology* 29, 25-29

Wing Sze Tunga and Walid A. Daoud (2009) Photocatalytic self-cleaning keratins: A feasibility study *Acta Biomaterialia* 5(1) 50-56

With, J. M. (2000) Cracking and residual stress in hybrid coatings on float glass. *Thin Solid Films* 359 (2), 210-214.

Won Hyuk Suha, K. S.-H. (2009) Nanotechnology, nanotoxicology, and neuroscience. *Progress in Neurobiology* 87 (3), 133-170.

X. Chen and H.J. Schluesener (2008) Nanosilver: A nanoproduct in medical application *Toxicology Letter* 176 (1), 1-12

Xiujian Zhao, Q. Z. (2008) Development of multifunctional photoactive self-cleaning glasses *Journal of Non-Crystalline Solids* 354 (12-13) 1424-1430

Xu Kang, Wei-Wei Zi, Zhu-Guo Xuand Hao-Li Zhang (2007) Controlling the micro/nanostructure of self-cleaning polymer coating *Applied Surface Science* 253 (22), 8830-8834

Y. Li, P. Leung, L. Yao, Q.W. Song, E. Newton (2006) Antimicrobial effect of surgical masks coated with nanoparticles, *J Hosp Infect* 62 (1), 58-63

Yon Ju-Nam and Jamie R. (2008) Lead Manufactured nanoparticles: An overview of their chemistry, interactions and potential environmental implications *Science of The Total Environment* 400 (1-3), 396-414

Zheng Huang, P.-C. M. (2000) Bactericidal mode of titanium dioxide photocatalysis. *J. Photochem. Photobiol. A. Chem.* 130 (2-3) 163-170.

Zeno W. Wicks Jr, F. N. (1999) *Organic Coatings Science and Technology Second Edition.* United States Of America: Wiley-Interscience.

Zhaoyue Liua, Xintong Zhanga, Taketoshi Murakamia and Akira Fujishima (2008) Sol–gel SiO2/TiO2 bilayer films with self-cleaning and antireflection properties *Solar Energy Materials and Solar Cells* 92(11), 1434-1438