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Functional Coatings: Superhydrophopbic And Conductive Coatings

Seyed Amirhossein Seyedmehdi
The University of Western Ontario

Supervisor
Dr Jesse Zhu
The University of Western Ontario

Graduate Program in Chemical and Biochemical Engineering
A thesis submitted in partial fulfillment of the requirements for the degree in Doctor of Philosophy

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FUNCTIONAL COATINGS: SUPERHYDROPHOPBIC AND CONDUCTIVE COATINGS

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by

Seyed Amirhossein Seyedmehdi

Graduate Program in Engineering Science
Department of Chemical and Biochemical Engineering

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The University of Western Ontario
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THE UNIVERSITY OF WESTERN ONTARIO
School of Graduate and Postdoctoral Studies

CERTIFICATE OF EXAMINATION

Supervisors	Examiners
Dr Jesse Zhu	Dr Ajay Ray
Dr Hui Zhang	Dr Hassan Gomaa
	Dr Jun Yang
	Dr David Potter

The thesis by

Seyed Amirhossein Seyedmehdi

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Abstract

There are many superhydrophobic and self-cleaning surfaces in the nature such as wings of butterfly and the leaves of the lotus plant as well known example of self-cleaning surfaces. Water droplets on these surfaces can pick up dirt particles and remove contaminations. The significant ability of these surfaces has inspired many researchers to fabricate superhydrophobic coatings, mimicking self-cleaning property, by using different methods. Most of the superhydrophobic coatings in the literatures need to be cured in ovens and thus hard to be applied or be maintened on the work place. Therefore, there is the need to develop room temperature curing superhydrophobic coatings that can be made by simple and cheap processes. This study demonstrates the fabrication of room temperature superhydrophobic coatings by using RTV (Room Temperature Vulcanzing) silicone rubber and fluoropolyurethane polymers. Also the effect of various parameters such as resin and solvent type, additives, coatings thickness and production methods, on the properties of superhydrophobic coatings, was evaluated. The final coatings showed contact angles higher than 145° and good UV and water durability. In addition, the superhydrophobic RTV silicone rubber coatings passed the erosion and track resistance test, a major test for high voltage insulator coatings in the industry.

Conductive coatings are used in a variety of applications such as antistatic surfaces, electromagnetic interference shielding (EMI) and sensors. Despite enormous researches, most of conductive coatings in the market that have high conductivity are made from metallic conductive fillers that are expensive and need to be compounded with polymers in high concentrations. Also, conductive mesh coatings used in the market require a complex process and should be prepared with some different processing steps. This project focuses on conductive coatings and mesh coatings that show good conductivity and have low cost. The results indicated that nano clay could improve the electrical and mechanical properties of conductive coatings. Also, conductive mesh coatings prepared by emulsion method could be a good candidate to make simple and cheap mesh coatings for electromagnetic shielding.

Keywords: Superhydrophobic coatings, RTV silicone rubber, fluoropolyurethane, nano silica, ultrafine fluoric particle, nano calcium carbonate, glass bead, alumina tri-hydroxide, contact and sliding angle, UV durability, track and erosion resistant, conductive coatings, nano clay, emulsion coatings, surface resistivity

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CHAPTER 1

Introduction

Coatings are mainly used for decorative, protective and functional properties. Functional coatings include coatings that have special functions besides classical properties of a coating like decoration and protection. Functional coatings can be divided by their special actions like physical, mechanical, thermal and chemical properties. Chemically active functional coatings show their activities either at film–substrate interface (e.g., anticorrosive coatings), in the bulk of the film (e.g., fire-retardant or intumescent coatings), or at air–film interfaces (e.g., antibacterial, self-cleaning). This project works in superhydrophobic and conductive coatings (Stoye et al, 1998).

Many surfaces such as wings of butterfly and the leaves of Nelumbo Nucifera Gaertn (Indian cress) in nature are highly hydrophobic and self-cleaning. The best known examples in the nature are the leaves of the lotus plant. The surface of lotus leaves shows jutting nubs about 20-40µm apart each that are covered by a smaller scale rough surface of epicuticular wax. The combination of micrometer and nanometer-scale roughness, along with a low surface energy material leads to contact angle higher than 150º and low sliding angle. This effect causes self cleaning property. Water droplets on these surfaces can pick up dirt particles and remove contaminations. Also superhydrophobic surfaces can reduce ice adhesion. These surfaces can be used in many applications such as promotion of self-cleaning processes generated by rain water on outdoor surfaces like automobile and traffic lights, the inhibition of clotting in artificial blood vessels, the production of waterproof clothes, the preservation of monuments, and high voltage insulators (Manoudis et al, 2009). Environmental contaminations such as coastal salt water and cement dust found in industrial settings in combination with moisture make a continuous water film that have caused power losses and reduced the reliability of electric power transmission systems since their inception. These contaminations on insulators result in current leakage and flashover and finally end up with power waste on the distribution system. In order to reduce the contaminations, different technologies with varying degrees of success have been applied to the industry and Room Temperature

Vulcanized (RTV) Silicone Rubber coating has shown better performance than other methods. Good dielectric properties, ultraviolet durability, excellent chemical and thermal degradation resistance come from silicone rubber coatings. However, the most obvious advantage of silicone rubber is the ability to retain water repellency. On contaminated surfaces, these coatings can release low molecular weight silicone fluid that comes from the bulk of coating, surrounds contaminants and recover hydrophobicity (Cherney et al, 1999). Researchers have been working on improving silicone rubber coatings for insulators, but despite some good properties of these coatings, they cannot fully prevent the accumulation of dust on surfaces due to unsatisfactory water repellency. The water contact angles of current RTV coatings are smaller than 120 degrees. Also these coatings do not show satisfactory performance during cladding ice season, so they cannot reduce the ice adhesion considerably (Li et al, 2010). Super- hydrophobic coating, mimicking the natural property of lotus leaves, with water contact angles higher than 140 degrees can remove contaminations much more effectively and reduce ice adhesion to the insulator surfaces because of its self cleaning properties. The significant ability of these surfaces has inspired many researchers to fabricate superhydrophobic coatings, mimicking self-cleaning property, by using different methods like sol-gel, lithography, plasma treatment and etc (Hill et al, 2006). Most of the superhydrophobic coatings described in literatures are cured in ovens and hard to be used for maintenance or be applied on the work place like bridges, tanks and pipes. Furthermore, some of the techniques needed some complicated and expensive processes. Therefore, it is required to make room temperature curing superhydrophobic coatings that are made by simple and in-expensive process. This study indicated the fabrication of room temperature superhydrophobic coatings by combining RTV silicone rubber or fluoropolyurethane coatings with hydrophobic additives, fillers or the combinations of them.

Paints are inherently non-conductive. To produce a conductive paint, it is necessary to incorporate conductive fillers into the system or to employ self-conductive polymers. Electrically conductive coatings are required for a variety of applications such as static charge dissipation and electromagnetic/radio frequency interference (EMI/RFI) shielding. Electrostatic discharge causes fires and explosion in explosive industries (Lee et al, 2002). Oil tanks are the main part in petrochemical industries that can accumulate static charge, so antistatic coatings are applied on the inner wall of oil tanks to prevent the accumulation of static electricity in them. Electromagnetic shielding is the process of limiting the flow of electromagnetic fields between two locations, by separating them with a barrier made of conductive material. Generally two methods are used for electromagnetic shieldings that are sheet metals and conductive coatings. The holes in the sheet or mesh should be considerably smaller than the wavelength of the radiation. Also conductive coatings make a continuous conductive layer that can be electrically connected to ground, so they can make effective shielding (Zhong et al, 2008). Many conductive filler (pigments) such as carbon black, graphite, carbon fiber, carbon nanotube, pure metal particles, and metal coated particles have been used to make conductive coatings. Despite enormous researches about using nano fillers like carbon nanotube and nano silver, most of conductive coatings in the market that have high conductivity are made from metallic conductive fillers that are expensive and should be compounded with polymers in high concentrations, so further researches needs to make conductive coatings with high conductivity and low cost. Also, mesh coatings that are used in the markets need a complex process and should undergo some different processing steps. This work focuses on producing conductive coatings and mesh coatings that have high conductivity and low cost. Nanocaly has an unusual aspect ratio and is used in nanocomposites to improve mechanical and gas barrier properties. It can enhance the conductivity of polymers because of existing ionic moieties in the layered structure. The effect of nano clay on electrical and mechanical property of conductive coatings including nickel coated carbon fiber was examined. Also conductive mesh coatings were prepared from the mixing of polypropylene, hammer finishes additives or water (emulsion) with conductive inks.

1-1 Objectives

The overall objectives of this doctoral research are outlined below:

Development of superhydrophobic and icephobic coatings

-To fabricate room temperature superhydrophobic coatings by the combining RTV silicone rubber or fluoropolyurethane coatings with hydrophobic additives (nano silica or ultrafine fluoric particle), hydrophobic fillers (nano calcium carbonate or glass bead treated with FAS) or the combination of hydrophobic fillers and hydrophobic additives. Also, the effect of superhydrophobic coatings in ice adhesion will be examined.

- To evaluate the effect of various factors that could influence in the hydrophobicity or the mechanical properties of superhydrophobic coatings. They include: the effect of PDMS fraction in RTV silicone rubber coatings; the role of coupling agents in adhesion of superhydrophobic coatings; the effect of production method, solvent type, resin type and thickness on hydrophobicity of coatings; the role of dispersing additives in coating dispersion; and the effect of hydrophobic additive concentrations in silicone fluid that can be released in the RTV silicone rubber coatings.

Development of conductive coatings

- To produce highly conductive and low cost coatings by blending the nanoclay and conductive coatings. The effect of mixing time and resin to hardener ratio in nano clay polyurethane conductive coatings will be examined too.

- To make conductive mesh coatings from the mixing of some materials like plastics, additives and water (emulsion coatings) that have simple process and are not expensive. Also, the effect of surfactant concentration, retarder concentration, solvent type and the effect of curing process in emulsion conductive mesh coatings will be evaluated.

1-2 Thesis structure

This thesis includes 7 chapters and pursues the “Monograph” format as outlined in the Thesis Regulation Guide by the School of Graduate and Postdoctoral Studies (SGPS) of the University of Western Ontario. The brief description of the following chapters included in this thesis is discussed below:

Chapter 1 gives a brief introduction about the functional coatings (superhydrophobic and conductive coatings) that are discussed in this study. Also research objectives, thesis structure and the major contribution are declared.

Chapter 2 reviews the coatings systems, coatings components, production methods, application methods and the film formation of coatings.

Chapter 3 reports on materials and methods of productions for superhydrophobic, icephobic and condutive coatings. Also, the formulations that were used will be discussed.

Chapter 4 reports about the superhydrophobic surfaces and different methods of their productions. Also, the results of superhydrophobic RTV silicone rubber coatings will be discussed and the effect of some parameters like thickness and productine methods will be indicated.

Chapter 5 illustrates the results of superhydrophobic fluoropolyurethane coatings. Moreover, gives a brief description about the icephobic coatings. The results of icephobic coatings and superhydrophobic coatings will be analyzed too.

Chapter 6 describes conductive coatings. Also, the results of conductive coatings and mesh coatings will be reviewed and the effect of nanoclay on conductive coatings and the role of some materials like surfactant in mesh coatings are evaluated.

Chapter 7 summarize the conclusion of superhydrophobic and icephobic coatings in addition to conductive coatings. It also gives some recommendations for future studies.

1-3 Major contributions

This doctoral research has aimed to work in two functional coatings leading to the following major contributions:

- Room temperature superhydrophobic coatings have been developed that show the micro and/or nano structure on surfaces. Through incorporation of hydrophobic additives or combinations of hydrophobic additives and fillers, superhydrophobic coatings have been prepared. Superhydrophobic RTV silicone rubber coatings have passed the track and erosion resistance test that is the major test for RTV silicone rubber coatings in the industries and they can be presented to the market as a new type of RTV silicone rubber coatings for high voltage insulators. Also, superhydrophobic fluoropolyurethane coatings have indicated good hardness and have the potential to be used for applications that this property is important. The superhydrophobic RTV silicone rubber and fluoropolymer coatings have demonstrated less ice adhesion to the surface too.

- Conductive coatings with high conductivity and low price have been produced. The nano clay can influence in the electrical and the mechanical properties of coatings. Conductive mesh coatings that have been produced by emulsion method can be a good candidate for electromagnetic shielding because they have easy process and low price.

CHAPTER 2

Coating review

Paints or coatings are in liquid, paste or powder forms that are applied on the surfaces to have a decorative function, provide information like traffic signs, protect surface against corrosion, weathering, and mechanical damages; or to have other functions. The earliest evidence of well-preserved prehistoric paintings that are related to 10th millennium B.C can be seen in caves in southern France (Lascaux), Spain (Altamira), and South Africa. The used colors were pure oil paints that were prepared from the mixing of animal fat with mineral pigments such as ocher, manganese ore (manganese dioxide), iron oxide, and chalk. The oldest rock paintings in the North Africa (Sahara) were dated between the 5th and the 7th millennium B.C. Also many paintings from Babylon, Egypt, Greece, and Italy that were dated from the 1st and 2nd millennium B.C. are famous. The first painted objects were found in China. A layer of paint in an artistic design had covered furniture and utensils. The oldest tradition work was related to around 200 B.C. The lacquer that was used in this work came from the milky juice from the bark of the lacquer tree. The oldest recipe for a lacquer was made from linseed oil and the natural resin sandarac in 1100 A.D. The most important raw materials for paint production until early 1900s were natural products such as vegetable oils and wood resins. The introduction of faster production equipment such as belt conveyors made necessary the development of new paints. The first rapid-drying resin was nitrocellulose that was manufactured on a large scale in existing guncotton plants after World War I. The phenolic resin was made as first synthetic resin in 1920. Then alkyd resin came in 1930 (Stoye et al, 1998).

Paints are made of different components that the kind of components depends on the method of application, the requested properties, the surface to be covered, and environmental concerns. Paint materials can be divided to volatile or nonvolatile. Volatile coating materials include organic solvent and water. Nonvolatile materials include resins, plasticizers, additives, pigments and fillers. Solvent and pigments do not always present in coatings. The powder coatings do not have solvents and varnishes do not have pigments. The main part of paint formulation is the resin or binder. Resins usually determine the method of coating application, drying, adhesion to surface, mechanical and chemical properties. This chapter is going to review the paint systems, the component of coatings, production technology, application methods and film formation of coatings (Paul, 1985).

2-1 Coating systems

Paints and coating materials usually consist of a mixture of resins, pigments, additives and solvents, but powder coatings do not have solvents and are more environmentally friendly than other coatings. Generally coatings depending on the solvent type or presenting solvent on them can be divided to three different systems that are solvent base (borne), water base (borne) and powder coatings that will be explained below:

Solvent borne: The coatings of this group include organic solvents. Organic solvents are used to dissolve resins and additives to disperse pigments or filler on them. Also, solvents can adjust the viscosity of final coatings and affect drying of paints. The dissolution behavior and solvent release during and after application are two important factors for choosing solvents. Moreover, the evaporation of the solvents can affect surface smoothness and mechanical properties of the film. Small amount of solvents may remain in these coatings after curing that can reduce internal tension and linear shrinkage behavior of final films. Since the beginning of the 1980s environmental requirements have become considerably important, the use of solvent born paints has been decreased. Solvent-free and low-solvent are also made to comply with increasingly strict environmental requirements. Water borne and powder coatings (solvent free) are two examples of new paint systems. The selection of solvents is also restricted based on the combustion and flammability of the paint when they are stored or transported. However, the use of solvent borne coating has been recently restricted because of environmental concerns, but they have not been replaced with other coating systems in special applications like silicone rubber coatings. This project is about liquid coatings, so liquid coatings (solvent or water base systems) will also be discussed in other sections (Stoye et al, 1998).

Waterborne: Water borne (water-thinnable) coatings were presented in the 1950s to replace the common solvent base paints. Water is used as solvent in the production and applications of these coatings. Waterborne paints are different from solvent borne because of the nature of their stabilization in water; the polymer molecules should be in the form of polymer dispersion or emulsion to be dissolved or dispersed in water, but this property may decrease the applications of water base coatings and these coatings cannot be used for specific applications like some plastics that the wetting of their surfaces are difficult. The polymer particles in emulsion systems consist of high molecular mass polymers and they are produced by emulsion polymerization. The main properties of waterborne paints are relatively high solid contents, rapid dilution with water and a low content of organic solvents. Emulsions are made from the mixture of two immiscible liquids. A liquid (dispersed phase) is dispersed in a continuous phase. Surfactants or emulsifier are used to lower the surface tension of two liquids. They are amphiphilic because they contain both hydrophobic group (their tails) and hydrophilic group (their heads). The hydrophobic part can be a hydrocarbon chain, an alkyl ether chain, a fluorocarbon or siloxane chain. The surfactants are usually divided by presence of charged groups in its head. If the charge is negative, the surfactant is anionic. However, the cationic surfactants have a positive charge. The amphoteric surfactants have two oppositely charged groups. If there is not any charge in surfactant, it is named nonionic. One important factor in nonionic surfactant is HLB value. It is defined as the ratio of water loving part (hydrophile) to oil loving part (lipophile). This value is between 0.5 and 19.5. The surfactant with low HLB is more oil soluble while the surfactant with high HLB is more water soluble. For example, for making oil in water emulsion the HLB of surfactants should be between 8 and 16 (Stoye et al, 1998; Leal-Calderon, 2007).

Powder coatings: They are composed of resins, pigments or fillers and additives without any solvents (organic solvents or water). Powder coatings are produced by a process including mixing, extruding and pulverizing. All of raw materials in powder coatings are in powder/pellet forms and final coating is in the powder form. The final properties of powder coatings such as hardness, corrosion resistance are better than other paint system, but these coatings have some limitations compared to other paint systems that reduce their applications; these coatings should applied on the conductive surface and should be cured at high temperatures. For instance, they cannot be applied on the plastics surfaces because the plastics are not conductive and are usually sensitive to temperature above 80°c (Stoye et al, 1998).

2-2 Coating components

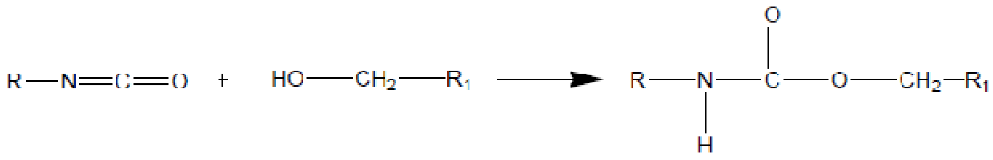
The liquid coatings are composed from Resins, Pigment or Filler, Additive and Solvents that are discussed in the following:

2-2-1 Resins

Resins or binders are the main component of a coating formulation. The application method, drying behavior, adhesion to the substrate and mechanical or chemical properties are related to resins. Resins are macromolecular products with a molecular weight between 500 and 30000. Cellulose nitrate and polyacrylate and vinyl chloride copolymers, which are suitable for physical film formation, have high molecular mass. The low molecular mass products may include alkyd resins, phenolic resins, polyisocyanates and epoxy resins. These low molecular resins must be chemically hardened after application to the substrate to make high molecular mass cross-linked polymers. The increasing relative molecular mass of the binder leads to higher solution viscosity of the binder and also improves properties such as elasticity, hardness, and impact deformation. While the effectiveness of a coating is improved by good mechanical film properties, low viscosity and low solvent content are also advantageous for ease of application and for environmental reasons. Therefore a combination of both is important. The low molecular mass resins have low viscosity and make low-emission paints that have high solids contents or even do not have solvent. The resin in these coatings consists of a mixture of several reactive components, and film formation take place by chemical drying. If the final paint will be cured even at room temperature, the binder components must be mixed together shortly before application. Resins can be natural like rosin or synthetic like epoxy, polyester and acrylate, but most resins in the market are synthetic. Moreover, some synthetic hard resin mainly based on cyclohexanone, acetophenone, or aldehydes, are used in the paint industries to increase the solid content, accelerate drying and improve surface hardness and adhesion. However, most synthetic binders are softer than hard resins and they can impart good elasticity, impact resistance, and improved adhesion. Also they can offer good resistance to weathering and chemicals (Paul, 1985). The resins related to this project (Polyurethane resins, fluoropolymer resins, epoxy resins and silicone resins) are described in details below. For other unrelated resins, please refer to Appendix I.

Polyurethane resins

The term urethane originally comes from the reaction of isocyanate groups with hydroxyl groups. However, this term now contain a large variety of resins. Paint films made of polyurethane have a polymer structure with urethane, urea or biuret coupling groups. During paint curing coupling can occur because of polyaddition of relatively low molecular mass starting products. Otherwise the paints may include high molecular polymers that are synthesized by coupling of suitable monomers. Also, adducts in which curing occurs via oxidation of conjugated double bonds or high molecular mass adducts with excess isocyanate groups are used as polyurethane paints. Figure 1-1 shows the reaction of polyester (hydroxyl group) with isocyanate.



$$R-N=C=O \ + \ HO-CH_2-R_1 \longrightarrow R-\underset{\displaystyle H}{\underset{|}{N}}-\overset{\displaystyle O}{\overset{|}{C}}-O-CH_2-R_1$$

Figure 2-1. The reaction of hydroxyl-polyester with isocyanate (Paul, 1985)

Other type of polyurethane resins include blocked reactive groups that can be activated by heat or atmospheric moisture. Another deactivation method is micro capsulation of polyisocyanates. The polyurethane paints are formulated as two-component (two-pack) or one-component (one-pack) mixtures depending on their chemical composition. They may be applied from the liquid phase that can be solvent-containing, aqueous or solvent free. They may be cured under a broad range from 0º to 200º C (Paul, 1985).

Two pack systems

Polyisocyanates can be made from different diisocyanates. However, only toluene diisocyanate (TDI), hexamethylene diisocyanate (HDI), isophorone diisocyanate (IPDI), methylenediphenyl diisocyanate (MDI), and 1,1-methylenebis (4-isocyanato) cyclohexane (HMDI) are used as commercial products. The basis of most polyurethane paint formulations are from high molecular mass polyisocyanates or prepolymer derived from such products. Polyisocyanates include very small amounts of monomers (less than 5%) that evaporate in room temperature and thus allow easy application without any concern about industrial hygiene. Polyisocyanates may differ according to their reactivity, chemical structure, functionality and isocyanate content. They are main curing component of two-pack polyurethane paints. Solvent free, liquid curing agents may contain up to 30 wt% isocyanate while curing agent solution have an isocyanate content of 5-16 wt%. Lightfast, weather-resistant coatings for enormously harsh condition are made by aliphatic and cycloaliphatic polyisocyanates. However, aromatic polyisocyanates react more quickly than aliphatic polyisocyanates and can not be used for exterior application because they are not resistant against UV radiation. The difference reactivities of aromatic and aliphatic polyisocyanates affect their use because they influence drying and curing. Polyols are used in two-pack polyurethane paints to cross-link and harden with polyisocyanates. The most important polyols include polyester polyols, hydroxyl-containing acrylic copolymers, and polyether polyols. They may contain hydroxyl group between 0.5 to 12% and may be linear or branched (Paul, 1985).

The property of the polyurethane coating is related to structure and content of reactive groups. The polyols with higher hydroxyl groups can improve the hardness, solvent and chemical resistance of the paint films. Two-pack polyurethane systems are the most important type of polyurethane coatings. The main resin systems (polyisocyanates and polyhydroxyl resins) must be mixed before application and during storage they must be kept separate. In addition to polyols, some other resins including hydroxyl groups such as alkyd resins, acrylic resin and epoxy resin can be used in the coatings. The resin (hydroxyl component) to hardener (polyisocyanates) ratio can change between 1:1 and 10:1. The two components are homogeneously mixed before applying the paint. Two-pack polyurethane paints can be applied by different methods apart from dipping because the shelf life of two component resins is usually between 4 to 6 hours and after this time they will be cured. Curing is done at room temperature, but it can be accelerated by heat. If two components are mixed in stoichiometric ratio, the reaction causes 100% cross-linking. If aliphatic polyisocynate is used as hardener, a small amount of catalyst or accelerator is used. Tertiary amines or metal-containing compounds in 0.05-0.5% are normally added to the hardener. Ester, ketones and aromatic solvents can be used in two-component polyurethane coatings, but alcohol solvents can not be used because they will react with polyisocyanates in competition with polyhydroxyl binders (Paul, 1985).

One pack system

One-pack polyurethane coatings are cured in different ways. They may be cured with atmospheric oxygen and are formed from the reaction of diisocyanates with polyols-modified drying oils. One example of this group is urethane oil that is cured oxidatively and do not contain free isocyanate groups. Another type is cured with atmospheric moisture. They contain high molecular polyols with excess diisocyanate including reactive isocyanates groups. They are used to make paints with excellent resistance to chemical and mechanical attack that cross-link with the formation of urea group under the effect of atmospheric moisture. Blocked polyisocyanates systems are another type of one-pack polyurethane resins. They are formed by chemical addition of some compounds including acidic or potentially acidic hydrogen atom like alcohols. These polyisocyanates do not contain free isocyanate groups, so they are not reactive at room temperature. However, these types of polyisocyanates can be regenerated by heating to remove the blocking agent. The curing temperature varies from 120 to 220º C that this range is related to blocking agent. The blocked polyurethane coatings have a good mechanical resistance and can be used for coil coating, high quality industrial goods and electrical insulation (Paul, 1985).

Finally polyurethane coatings have three main properties that include high mechanical resistance, outstanding chemical resistance and good weathering resistance. Practical applications change from paper coating to the equipment protection in industrial plants. They can be used in transportation (large motor vehicles, rail vehicles, aircraft and automobile finishes), the building sector (parquet floor coatings, outdoor and floor coatings), and the industrial paint (equipment, machinery and furniture). Also they are important in surface treatment of plastics and in the protecting of structural engineering and hydraulic steel structures.

Fluoropolymer resins

These resins have special properties like antistick, good weathering and chemical resistance, so they have been used in many fields. Some of the conventional fluoropolymers such as polytetrafluoroethylene (PTFE) or ethylene-tetrafluoroethylene copolymer (ETFE) has been used as antistick or anticorrosive coatings. The major problem in using thermoplastic fluoropolymers in paints is their poor solubility in organic solvents and also the necessity to cure them at temperatures higher than 200ºC. Polyvinylidene fluoride (PVDF) is the only conventional thermoplastic that is used for commercial weather-resistant paints. This crystalline polymer is composed of $–CH_2CF_2$- repeating units and is usually blended with 20-30 wt% of an acrylic resin such as poly (methyl methacrylate) to improve melt flow behavior at the curing temperature and to increase substrate adhesion. Another fluoropolymer coating is made from polytetrafluoroethylene and is used in hot cooking ware because of being nonstick and easily lubricated. This type of aqueous dispersion PTFE is produced by emulsion polymerization followed by thermal concentration of the latex (Scheirs, 1997).

Fluoropolyurethane

Fluorinated polyurethanes (fluoropolyurethane) are another group of fluoropolymers that have been used recently. Introducing fluorine into polyurethane resins makes changes in properties similar to those seen when other polymers are fluorinated. Polymer becomes more permeable to oxygen, and chemical, thermal, hydrolytic, and oxidative stability are enhanced. Fluorourethane are used in products ranging from hard, heat-resistant electrical components to biologically compatible surgical adhesives. Perhaps, surface coatings for industrial and residential structures, automobiles, ships and aircraft are the largest use of fluorourethanes. They are also used in medical products and as surface-enhancing treatments for textiles, leather and carpets. Fluorourethanes have surfaces energy smaller than 25mJ/m^2, so they can be used in low friction or hydrophobic coatings. The surface energy of a polymer is changed by the functional groups which collect at its surface. Substitution of fluorine in hydrocarbons leads to the surface energy to reduce in the order $–CH_2- > -CH_3 > -CF_2- > -CF_3$. If a polymer is fluorinated completely, it produces a low surface energy resin while it can affect other properties of polymer such as glass transition temperature, processability, the absence of porosity and low cost. It is preferable to make low surface energy polymer by deploying a small number of perfluoroalkyl groups on the surface, where they will be most effective. It is easy to produce polymers with an effective number of fluorinated groups while it is too difficult to cause them to form ordered aggregates with the fluorinated groups aligned on the surface. A wide variety of polyols are commercially available that some of them are listed in table 2-1 (Scheirs, 1997).

Table 02-1: Fluorinated alcohols for preparing polyurethane resins (Scheirs, 1997)

Alcohol	**Application**
CF_3CH_2OH	Hard Contact Lenses
$CF_3CH_2CH_2OH$	Anti-fogging coating for glass
$F(CF_2)_nOH$ [n=6-12]	Oil, water and soil resistant textile finishes
$F(CF_2CF_2)_nCH_2CH_2OH$ [n=3-7]	Emulsion polymers
$C_7F_{15}CH_2OH$	Rigid insulating foams
$H(CF_2CF_2)_5CH_2OH$	Coating for magnetic recording tape

The addition reaction of polyisocyanates with polyols is the most versatile employed method of fluorourethane production. The oxygen of the alcohol forms a new bond with the isocyanate carbon in the fist stage and then the hydrogen of the alcohol bonds to isocyanate nitrogen to form a urethane linkage. When all isocyanates groups are consumed or when steric barrier prevents further reaction, or when the polymer gels and functional groups lack the mobility to react the reaction ends. Fluorine is most frequently added to the polyols component. Although it is possible to make fluorinated polyisocyanates, but they are more difficult to synthesize and are more expensive than fluorinated polyols.

Epoxy resins

This resin is generally produced from the condensation of bisphenol A and epichlorohydrin (Figure 2-2).


Bisphenol A

Epichlorohydrin

Figure 02-2: The monomers of epoxy resins (Paul,1985)

These resins are generally not used alone and they require a hardener to be cured. A large different group of hardener may be used for curing at elevated or at room temperature. The epoxy coatings have high adhesion, flexibility, hardness, abrasion resistance, resistance to chemicals, and corrosion protection. Most epoxy resins are synthesized from the condensation reaction of bisphenol A and epichlorohydrine and are named bisphenol A resins. The ratio of bisphenol A to epichlorohydrine can affect molecular mass, meilting point, viscosity, solubility and content of epoxy and hydroxyl group. The epoxy resins with low molecular mass (360- 500) are liquid and resins with medium molecular mass (500- 7000) are in solid form in room temperature. High molecular mass resins contain very few epoxy group while have many hydroxyl groups and they can be reacted at room temperature with polyisocyanates or at elevated temperature (180-300° C) with amino resins and phenolic resins. Bisphenol F resins are another group of epoxy resins. Bisphenol F is syntehsyzed by the condensation reaction of phenol with formaldehyde in an acid medium. This compound includes a mixture of isomeric and oligomeric products. The epoxy resins that are produced by reaction of Bisphenol F and epychlorohydrin have lower viscosity and higher functionality than Bisphenol A resins, so coatings based on this type of epoxy resin have a higher solvent resistance than coatings formulated with Bisphenol A. Epoxy novolacs are made by condensation reaction of formaldehyde with phenolic substances in an acid medium that is followed by epoxidation. This type of epoxy resin also has higher functionality than Bisphenol A resins and can make coatings that have higher solvent and chemical resistance than aforementioned resins. However novolacs epoxy resins have lower adhesion to metallic substrate compared with Bisphenol A resins (Flick, 1989).

Epoxy resin hardeners

The epoxy resins can be cured by polyaddition via their epoxy or hydroxyl groups and it is related to epoxy molecular mass. Aliphatic polyamines are reacted by epoxy resins via epoxy groups at ambient temperature. Polyamine adduct is formed by the prereaction of epoxy resin with excess amines. Also polyamidoamines are made from the reaction of amines with monomeric or dimeric fatty acids. Polyamine-adduct-cured epoxy resins have a high chemical resistance and polyamidoamine-cured epoxy resins show good adhesion and flexibility. Cycloaliphatic polyamines need an accelerator for curing at room temperature (like salicylic acid) because they are less reactive than aliphatic amines.

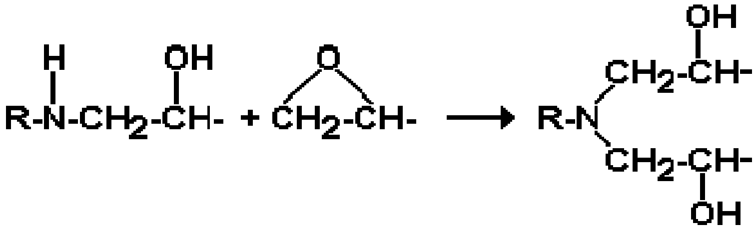


Figure 2-3: The reaction of a secondary amine with an epoxy group (Paul, 1985)

Also aromatic polyamines are even less reactive than cycloalyphatic amines and need more accelerators. Figure 2-3 demonstrates the reaction of primary amine with epoxy group.

Thiols are only used for adhesives and joint grouting because they have an extremely unpleasant smell. They can make flexible epoxy adhesives. Another hardener for epoxy resins are isocyanates that are cured with epoxy resins via hydroxyl groups to form polyurethanes. The reaction takes place in room temperature and is faster than reaction of epoxy resins with polyamines. The most important hardeners for epoxy resins are summarized in table 2-2.

Table 02-2: The most important epoxy resin hardeners and their uses (Scheirs, 1997)

Curing agent	**Curing mechanism**	**Typical use**
Amines and polyamidoamines	Room temperature curing	Two-component systems for corrosion resistant coatings
Polyamidoamines and amine adducts	Room temperature or hot curing	Industrial maintenance coatings
Polyesters	Hot curing	Powder coatings
Phenolic hardeners	Hot curing	Powder coatings
Amino resins	Hot curing	Can coatings and finishes
Polyanhydrides	Hot curing	Coil coating
Isocyanates	Room temperature curing	Two-pack polyurethane coatings
Phenolic resins	Hot curing	Can and coil coatings

Anhydrides are used to cure epoxy resins in surface coatings. These coatings are cured at oven and are used in can coatings because they have a good acid resistance and do not impart an undesirable taste to foods. Polyesters are also used as hardener for epoxy resins. They are reacted with epoxy resin by heat and usually these systems are important in the formulation of powder coatings. Polyphenols are another type of hardeners and are reacted with epoxy resin on heating and require an accelerator. They are used in powder coatings for pipes. Amino resins like urea, melamine, and benzoguanamine resins are cured in oven by epoxy resins with high molecular mass. The ether bonds are formed from the reaction of hydroxymethyl group with hydroxyl groups of the epoxy resins. This system is used for coating domestic appliances and packaging. Phenolic resins are also used as curing agent and reacted with high molecular epoxy resins at oven. They are used as "gold lacquer" to line food containers because they are colorless and have good chemical resistance, less odor during cure and the taste of food alter less in contact with them.

Epoxy resin uses

Epoxy resins can be cured at room or elevated temperature. Room temperature curing coatings include solvent-free coatings, solvent-containing coatings, Air-Drying epoxy esters coatings and waterborne coatings. Solvent-free coatings are not only used for coatings. They can be formulated as flooring coating by the addition of quartz sand. Also they can be used as adhesive and joint filler for concrete applications. Polyamines, modified polyamines and aliphatic polyamines can be used as hardener. Solvent-containing epoxy coatings are made from semisolid to solid Bisphenol A epoxy resins. Aromatic hydrocarbon and alcohols are used as solvents. These coatings are cross-linked with modified aliphatic polyamines that are in the form of amine adducts or as isolated amine adducts dissolved in xylene and butanol. The coatings from these hardeners have an extremely good hardness and good resistance to aqueous alkaline solutions and organic solvents. Polyamidoamines are the most important hardener for these types of epoxy resins and they can improve the flexibility and adhesion of coatings. Epoxy paints can not be used for outdoor applications due to they tend to yellow, become matt, and display chalking because of light and weather. Air-Drying epoxy ester coatings are also cured in room temperature. They are made from the chemical reaction of solid epoxy resin with air-drying fatty acids like linseed oil (Scheirs, 1997).

Silicone resins

Silicone resins are usually produced from hydrolysis and condensation mixture of di- and trifunctional organosilane monomers like phenyl-and methyltrichlorosilane, methylphenyldichlorosilane, and dimethyldichlorosilane). The nature of the substituent, the degree of substitution, the extent of the condensation reaction and the content of residual reactive groups can affect final properties of silicone coatings. The silicone resin may be hard, brittle monomethyl flake resins or soft, flexible phenyl-containing resins dissolved in a solvent. When the phenyl content in the resin increases, it becomes more thermoplastic, has greater heat and oxidation resistance, longer shelf-lif, and tends to be more compatible while high methyl content in resin causes faster cure rate, flexibility, hardness, and better retention of properties at low temperature. The most of pure silicone resins are too soft and for general coating applications they should be blended with other resins like alkyd, acrylic, epoxy and phenolic resins. The silicone adds gloss and color retention at elevated temperature while the organic component can improve the hardness and drying properties of the silicone (Stoye et al, 1998).

The silicone intermediates usually have the high amount of reactive or alkoxy groups and are copolymerized with polyester, alkyd, and acrylic resins containing excess hydroxyl groups in the presence of titanium catalysts. The final composition and performance of the copolymer depends on the choice of solvent and catalyst, concentration of reactants, and extent of reaction. The curing time for 100% silicone resin is 30 min at 260º C while copolymers containing 50-80% silicones are cured in 15 min at 220º C. Silicone coatings are used in extreme environments where organic paints are ineffective like boiler stacks, exhausts, ovens, furnaces, heat exchangers and hot plates. Also silicone polyester paints are used in coil coatings, exterior cookware coatings and appliance finishes (Stoye et al, 1998).

Polydimethylsiloxane (PDMS)

It is the most widely used silicone-based polymer and has a unique combination of properties resulting from the presence of an inorganic siloxane backbone and organic methyl groups attached to silicon. This chemical structure makes polymers which have low glass transition temperatures, so they are fluids over a wide range of temperatures, have good thermal stability, good oxidative resistance and good chemical stability. It is used in contact lenses, medical devices, in shampoos (makes hair shiny and slippery), caulking, lubricating oils, and heat-resistant tiles. The chemical formula for PDMS is $CH_3[Si(CH_3)_2O]_nSi(CH_3)_3$ that n shows the number of repeating monomer $[SiO(CH_3)_2]$ units. PDMS is synthesizes in industries from dimethylchlorosilane and water by the following net reaction (Clarson et al, 1993):

$$n\ Si(CH_3)2Cl_2 + n\ H2O \rightarrow [Si(CH_3)_2O]_n + 2n\ HCl$$

Hydrogen chloride gas during polymerization is potentially hazardous, so a process was developed in which the chlorine atoms in the silane precursor were replaced with acetate groups for medical uses. The reaction product of this process is nontoxic acetic acid (vinegar). Branches or cross-links in the polymer chain can be made by using silane precursors with more acid-forming groups and fewer methyl groups, such as methyltrichlorosilane. Under ideal conditions, each molecule of such a compound becomes a branch point. This can be used to produce hard silicone resins. Also, in a similar manner, precursors with three methyl groups can be used to limit molecular weight, since each such molecule has only one reactive site and so terminate the siloxane chain. The viscosity of polymers is varied from a thin pourable liquid (when n is very low), to a thick rubbery semi-solid (when n is very high). PDMS acts like a viscous liquid, similar to honey at long flow times (or high temperatures), because it is viscoelastic. Meanwhile, it acts like an elastic solid, similar to rubber at short flow times (or low temperatures). After polymerization and cross-linking, solid PDMS samples will show an external hydrophobic surface. This surface chemistry may lead to adsorption of hydrophobic contaminants because it is difficult for polar solvents (such as water) to wet the PDMS surface. It is an important component in Silly Putty because PDMS imparts its characteristic viscoelastic properties; so many people are indirectly familiar with this polymer. It has been used in the rubbery, vinegary-smelling silicone caulks, adhesives, and aquarium sealants as well as is employed as a component in silicone grease, other silicone based lubricants, defoaming agents, mold release agents, damping fluids, heat transfer fluids, polishes, cosmetics, hair conditioners and other applications. Another important application of PDMS is in making RTV silicone rubbers that have been used for electronic and power industries (Clarson et al, 1993).

Cross-linking of polydimethylsiloxane

The PDMS is an amorphous polymer and it is converted to commercially useful materials such as rubbers, resins or cured coatings by cross-linking reactions. The cross-linking reactions should not change the siloxane properties and they must produce materials like rubber and coatings which retain the desirable properties of the PDMS, especially its thermal and chemical stability and its ability to remain flexible at low temperature. The cross-linking reactions of PDMS are divided to four classes that are:

1) Peroxide-induced free radical reactions
2) Condensation reactions
3) Hydrosilylation addition reaction
4) Hydridosilane/silanol reaction

It should be noticed that the cross-linked Polydimethylsiloxane matrix produced from the using any of the above reactions is an intrinsically weak material because there is not any strong intermolecular forces in the PDMS polymer. It is necessary to reinforce the cross-linked matrix with inorganic fillers to produce acceptable commercial materials, so the choice of these fillers can also affect physical properties of cross-linked polymers (Clarson et al, 1993)

Peroxide-induced free radical reactions: Large classes of cross-linking catalysts whose molecular structure include a relatively thermally unstable oxygen-oxygen bond are named peroxides. When this bond is heated, it breaks generating free radicals which are often forceful enough to take out a hydrogen atom from a saturated hydrocarbon polymer. The discovery of this fact that peroxides could interact with polydimethylsiloxane to produce a cross-linked material with rubbery properties formed the basis of silicone rubber industry development. Two categories of peroxide are used to achieve peroxide-induced cross linking that they are vinyl specific catalysts which only work in the presence of vinyl groups and nonspecific catalysts, typically aryloxy peroxides which do not need the vinyl group to effect cross-linking. Vinyl specific peroxides do not need very great level of vinyl functionality to achieve the required level of cross-linking and it is usually in the range 0.1-0.15% w/w on the polymer. The cure mechanism for polydimethylsiloxane and diaryloxyperoxides continues by hydrogen abstraction from the Si–CH_3, by the peroxy radical, followed by combination of the resulting $SiCH_2$ radicals formed to give a $\equiv SiCH_2CH_2Si\equiv$ cross-link (Clarson et al, 1993).

$$ArOOAr \rightarrow 2ArO^{\circ}$$

$$ArO^{\circ} + CH_3Si\equiv \rightarrow ArOH + {}^{\circ}CH_2Si\equiv$$

$$\equiv SiC^{\circ}H_2 + {}^{\circ}CH_2Si\equiv \rightarrow \equiv SiCH_2CH_2Si\equiv$$

Figure 2-4: The reaction mechanism of aryloxy peroxide and PDMS

Cross-linking using condensation reactions*:* An important reaction in industrial silicone chemistry is the condensation of silanol groups to form siloxane bonds. Many groups such as alkoxy, acyloxy and oxime (–OR) that are attached to silicone are hydrolyzed to produce silanol group. However, in the absence of moisture, these groups do not react even when there is more than one –OR group connected to a single silicone atom. Therefore, in room temperature curing systems, molecules which contain $=Si(OR)_2$ or $-Si(OR)_3$ groups are synthesized as part of the siloxane chain and these groups, in the presence of atmospheric moisture, spontaneously hydrolyze and condense to make a three-dimensional cross-linked network. The acetoxy-functional condensation system is presented below:

$$=Si(OAc)_2 + H_2O \rightarrow =Si(OAc)OH + HOAc$$

Hydrosilylation addition reaction*:* It is a well-known reaction in organosilicone chemistry and involves the addition of a silicon hydrogen (SiH) bond to an unsaturated carbon carbon bond, catalyzed by a noble metal (usually Pt). As it has been shown below, the hydrosilylation reaction that in practice is used include the reaction between a hydridosilane group (SiH) and a silicone vinyl group ($SiCH{=}CH_2$)

$$\equiv SiH + \equiv SiCH{=}CH_2 \rightarrow \equiv SiCH_2CH_2Si\equiv$$

A wide range of product properties can be produced by this method of cross-linking. This method can be used to formulate heat-cured systems which can be extruded or injection molded that have application in the automotive and medical industries. Another advantage of this method is that it can be easily emulsified and used as water-based coatings for coated papers used for food release.

Hydrosilane/silanol cross-linking reaction*:* This reaction can be categorized either as a condensation or as a hydrosilylation reaction. It may be presented in the following:

$$\equiv SiH + \equiv SiOH \rightarrow \equiv SiOSi\equiv + H_2$$

This system is used as the original technology in the pressure sensitive adhesive label market because they can be cured (in the presence of tin carboxylates catalyst) to a coherent thin film when is applied to a paper substrate. Also they can be used to make silicone foams that have applications in the soundproofing of automobiles and as fire stop to seal around pipes (Clarson et al, 1993).

Silicone rubber

Silicone rubbers are usually made from polydimethylsiloxane, silane crosslinkers and mineral fillers. The curing happens at room temperature by hydrolysis of organosilicone bonds that proceeds by the condensation reaction of silanol and organosilicon under the action of tin or titanium organometallic compounds. Silica fillers reinforce the elstomers because the silanol groups on the silica surface and the polysiloxane chains can form hydrogen bonding. Present silicone rubbers are using condensation mechanisms that include one part systems which are cured by the diffusion of atmospheric moisture or two-component systems that involve the condensation of silanols with hydrosilans which generate hydrogen. The free volume of silicone rubber is high because it has high motion freedom of polysiloxane chains. Silicone elastomer has high elasticity even at low temperature and it has one of the lowest glass transition temperatures among polymers at -120º C. The intermolecular forces of silicone rubbers are rather week that this issue leads to the low viscosity of long chains which are still liquid even in high molecular weights. Furthermore, large intermolecular distance causes high gas permeability especially to water vapor and this property can be employed as a way to introduce a reactive species in a silicone material for initiating in situ chemical reactions. Silicone rubbers show high thermal stability because of high stability of Si–O bond and high depolymerization temperature. The orientation of methyl groups toward non polar surfaces are attributed to unique flexibility of the polydimethylsiloxane and this effect makes low surface tension and release properties. Silicone rubbers are hydrophobic and water repellent due to their low surface energy. Also, they show high resistance to weathering and outstanding ability because they do not absorb UV light (Marciniec et al, 1995; Ojima, 1985).

Commercial Room Temperature Vulcanizing (RTV) silicone elastomers are presented as uncured liquid or paste. RTV silicone rubbers can be used as sealant, adhesives and coatings. Silicone RTV coatings include good dielectric properties and flexibility over a wide temperature range, combined with excellent resistance to ultraviolet radiation, chemicals, thermal degradation and corona discharge. However, the most important property of silicone rubbers for insulator application is their retention of water repellency under outdoor weathering. It has been demonstrated that silicone rubbers give water repellency to the surface. On clean surfaces, its low surface energy does not allow wetting of the surface, and on polluted surfaces, low molecular weight silicone fluid that diffuses from the bulk of the coating surrounds contaminants with a monolayer of fluid that imparts a non-wetting property, or hydrophobicity, to the contaminant layer. Room temperature vulcanizing silicones were synthesized in 1958 by L. Ceyzeriat (Marciniec et al, 1995). He used methyltriacetoxysilane to cross-link silanol terminated polydimethylsiloxane chains by hydrolysis of acetoxy-silicon bonds and release of acetic acid. Alkaline and neutral systems based on various types of silane cross-linking agents were developed a few years later. The RTV commercial systems are made from encapped polysiloxanes obtained from silanol terminated polydimethylsiloxane with an excess of crosslinker and various type of fillers that are used to reinforce the silicone elastomer. One of the main filler that is widely used in this field to improve ultimate mechanical properties is silica. The silica surface is covered by silanol groups that can make strong interactions with the polysiloxanes chains by hydrogen bonding as illustrated in figure 2-5.

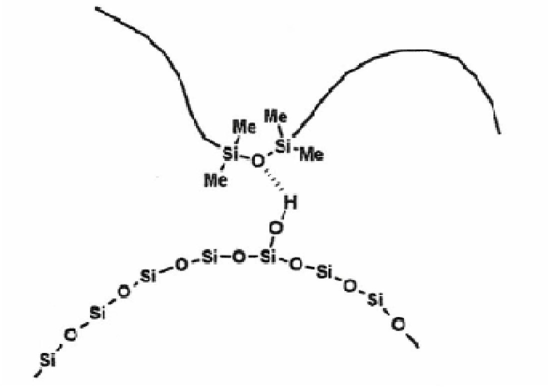


Figure 2-5: Silica-polysiloxane interactions (Marciniec et al, 1995)

The RTV silicones are cured through chemical cross-linking of the endcapped polymer and excess of cross-linker that causes a three-dimensional structure with polyfunctional cross-links. Two different methods of cross linking are used in RTV silicone coatings:

1) **One-part system (RTV-1)**: catalyst that usually is noble metal and cross linker is added to base polymer. In this mechanism, a condensation reaction of silanol groups by removing of water is used to form siloxane bands (Figure 2-6).

$$\equiv SiOH + \equiv SiOH \rightarrow \equiv SiOSi\equiv + H_2O$$

Figure 02-6*:* Cross-linking reaction of RTV-1 Coatings (Cherney et al, 1999)

2) **Two-part system (RTV-2)**: crosslinker and inhibitor make Part B, but catalyst and polymer form Part A. This mechanism does not need moisture to cure and curing reaction

involves direct addition of crosslinker (Part B) to the functional polymer (Part A) forming an ethylene bridge (Figure 2-7). Unlike one-part moisture cure silicone; this mechanism does not include any leaving group that allows this system to cure in closed environment.

Both of these two mechanisms are based on curing by diffusion of atmospheric moisture. The touch-free curing time is fast while hardening of unexposed material can be quite long, especially when the thicknesses of coatings are high. For instances, it takes about 40 hours to be cured a coating with 4mm thickness. However, this fact can improve the adhesion of coatings to the surface because it allows a long spreading and wetting time of the silicone rubber on the substrate.

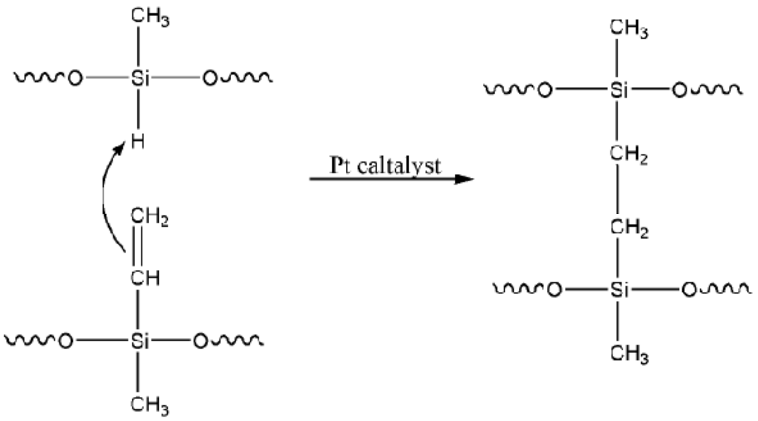


Figure 2-7: Cross-linking reaction of RTV-2 Coatings (Cherney et al, 1995)

A development based on water emulsions of silicones has been commercially introduced. The emulsion of silanol terminated polysiloxane and methyltrimethoxysilane makes the dispersion of precross-linked silicone particles. These water-based systems are blended with tin catalyst emulsions and are cured by the evaporation of water. These emulsions are easier to apply than solvent-base silicone rubbers while they have lower adhesion than them because the spreading of the precross-linked particles in emulsion system is more difficult (Cherney et al, 1995).

2-2-2 Pigments

Pigments are mixed with resins to make decorative effects like gloss and color or functional effects like corrosion protection. The distribution of pigments should be as uniform as possible to gain the optimal effects. Pigment is a material that is not dissolved in the coating and is used as a colorant in decorative, protective and functional coating systems like automotive finishes, marine paints, industrial coatings, traffic paint and conductive coatings. The main application of them is to give desired color, to increase hardness and durability, to confer protective properties to the paint film and to hide substrate. Pigments are classified to the two main groups that are inorganic and organic pigments. They will be discussed in the details in the following:

Inorganic pigments

They are related to various chemical classes including elements, oxides, sulphides, chromates, silicates, phosphates and carbonates. Commonly pigments are whites like titanium dioxide, zinc oxide and zinc sulphide; reds: cadmium sulphide selenide and iron oxide; yellows: cadmium sulphide, lead chromate and iron oxide; greens like chromium oxide green; blues: iron, ultramarine and cobalt blues; and blacks: carbon black and graphite. Also metallic pigments like aluminum, zinc and copper are used in paints. It is evident that inorganic pigments can be colored, colorless, black, white or metallic and they are usually composed of small particles that are insoluble or less soluble in the binders which are dispersed. Pigment selective absorption of visible light is attributed to color production. Also pigments can increase the opacity of resins because of light scattering from the large particles. They can provide protective functions like corrosion resistance, increase film durability by changing film permeability, make antistatic coatings and antifouling coatings. The properties of pigments are related to physical and chemical characteristics such as color, particle size, particle shape and surface area (Wicks, 2007).

The titanium dioxide (white pigment), chromate pigments, iron oxides, carbon black, graphite and carbon fiber are inorganic pigments that will be discussed. However, carbon black, graphite and carbon black were used in this work.

Titanium dioxide (white pigment)

It is the most important white pigment that is used for surface coatings. Titanium dioxide (TiO_2) is mainly found in three naturally crystallographic forms that are anatase (tetragonal), brookite (orthorhombic) and rutile (tetragonal). The rutile and anatase are manufactured on a large scale. The rutile has a much closer atomic packing in its crystal model and is more stable, so it has a higher specific gravity and a higher refractive index than anatase. As a result, rutile pigment is used more than anatase in coatings industries. Anatas also has very high photoactivity and therefore is not suitable for exterior coatings because it may degrade coating film quickly. Two processes are generally used to produce titanium dioxides that are the sulphate process and the chloride process. In the sulphate method, ilmenite ore ($FeTiO_3$ or $FeO.TiO_2$ or titanium slag) is used as the main raw material. This ore has 45-70% by weight of titanium dioxide and is ground and dissolved in concentrated suphuric acid to form titanyl sulphate. Titanium sulphate is purified by sedimentation and crystallization. Finally the titanium is percipated by hydrolysis. If the small nuclei of rutile (seed) are added before hydrolysis, the final product will have the rutile crystal form. On the other hand, if seeds are not used, the anatase form is obtained. Chloride process uses the natural rutile as raw materials while ilmenite and other titanium ores can also be used as source ores. In this method, coke is mixed with crude ore and product is reacted with chlorine at 900º C. The light scattering capacity of titanium dioxide is higher than all other white pigments like zinc oxide because it has higher refractive index (rutile n=2.8, anatase n=2.55) and therefore this pigment shows extremely good hiding power (Wicks, 2007).

Chromate pigments

They are used in coating industries because they show wide color ranges from greenish yellow to red and are relatively cheap. The various hue in chromate pigments depends on the interrelationships of three factors that include chemical composition, crystal structure and particle size. A partial replacement of chromium by sulphur and/or molybdenum makes crystal modifications that lead to the formation of greenish-yellow to red products. Chromates pigments are usually produced by precipitating soluble salts in aqueous media (Wicks, 2007).

Iron oxide pigments

These pigments include the oxide of trivalent iron or the hydroxide of trivalent iron and other oxides of different compositions. These pigments do not need any surface treatment because their fastness and resistance properties are so outstanding. They can be obtained from natural and synthetic sources. Natural iron oxides are made from different ores that they include hematite, limonite, siderite and magnetite and show a range of red, yellow, brown and black pigments. These shades of pigments are also obtained by synthetic routes (Wicks, 2007).

Carbon black

These pigments have the strongest absorbers of light over the entire visible spectrum and are used for jet black colors or for darkening of color that made by other pigments. They can impart the highest degree of reinforcement in rubber as fillers and this effect is essential for pneumatic tyers. Carbon black includes nearly pure carbon of colloidal dimensions. Carbon atoms like graphitic layers are arranged in polynuclear arrays containing dozens of 6-carbon aromatic rings. The colloidal units of carbon black are named aggregates due to they are composed of many spheroidal particles. The carbon black grades are different in particle sizes, in the structure of aggregates, in the surface chemistry and in the porosity of pigments. For instance, the carbon black that is used in jet-black colors has particle size between 5-10 nm while the coarser carbon black is 500nm. Carbon black can be manufactured in several ways while the furnace process is the most way that has been used because this method has higher efficiency. The natural gas is combusted in air in this process and then mixed with coal tar or crude oils. The reaction products are sent through filters that separate the carbon black from the tail gas. After that the size of large particles are reduced by hammer mills and then carbon black is transferred to a pelletizer and are mixed with water. The wet pellets are dried, screened and sent for storage in soils (Wicks, 2007).

The carbon blacks are also produced from the thermal decomposition of acetylene in the absence of oxygen. The product of this process is named acetylene black and it has higher conductivity than other carbon black grades. Carbon black from this process is very pure and has a high crystallinity degree. Furthermore, carbon black particles will aggregate in this method and produce high surface area agglomerate with very low density. The acetylene blacks are difficult to densify while they can improve the electrical conductivity and anti-static property of polymers and coatings (Wicks, 2007).

Graphite

There are two types of graphite that are used in industry: natural and synthetic. Natural graphite is obtained in three commercial forms that are: crystalline flake graphite, amorphous and vein graphite. Flake graphite is made from heat- and pressure-induced transformation of dispersed organic material in a metamorphic geological environment and it has flat, plate-like particles with hexagonal edge. Most commercial grade amorphous graphite is made from the contact metamorphism of anthracite coal. There are very fine grade. Vein or lump graphite is unique and it is occurred pyrolytic graphite. This type of graphite gets its name from the fact that it is found in the veins and fissures of the enclosing ore rock. The direct deposition of solid, graphitic carbon from subterranean (high temperature pegmatitc fluids) makes vein graphite. It has needle-like macro-morphology and flake-like micro-morphology. The vein graphite deposits are more than 90% pure because of the natural fluid-to-solid deposition process. Synthetic or artificial graphite is manufactured by heat treating amorphous carbons like calcined petroleum coke or pitch coke in a reducing atmosphere at temperatures above 2500º C. The pregraphitic structures present in these graphitizable carbons at high temperatures turn into aligned in three dimensions. Finally two-dimensionally ordered amorphous carbon is transformed into a three-dimensionally ordered crystalline carbon (Xanthos, 2005).

Graphite has a layered, planar structure that each layer includes carbon atoms which are arranged in a hexagonal lattice with separation of 0.142nm, and the distance between planes is 0.335nm (Figure 2-8). Alpha (hexagonal) and beta (rhombohedral) are two known forms of graphite that have very similar physical properties. The hexagonal graphite may be either flat or buckled. Also, the alpha form can be converted to the beta form by mechanical treatment while the beta form reverts to the alpha form when it is heated above 1300 ºC. Graphite can conduct electricity since it has enormous electron delocalization within the carbon layer and these electrons can move freely, so they are able to conduct electricity. However, graphite can only transfer electricity through the plane of the layers. Flake graphite is an effective coating additive and barrier filler in plastics because of its impermeable laminar structure. Also it is non-photo-reactive and is not affected by ultraviolet light. The flake graphite is laminar apart from particle size. Also expandable graphite is another form of graphite that is a synthesized intercalation compound that expands when it is heated. This material is manufactured when flake graphite is treated by various types of intercalation reagents. Expandable graphite has lower bulk density and higher surface area than other graphite and is used as a fire-suppressant additive.

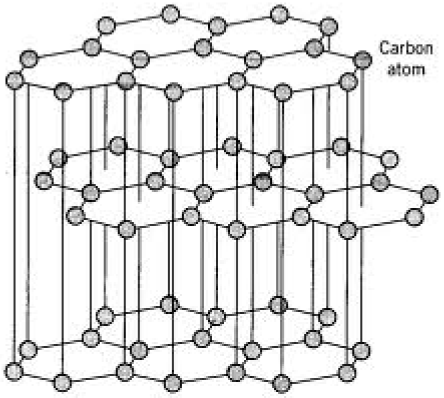


Figure 2-8: Graphite structure (Xanthos, 2005)

The synthetic graphite morphology is a function of particle size. The particles larger than 20μm have a morphology that is vey similar coke feed that is used to manufacture the graphite while the particles smaller than 20μm have the basic flaky structure. A single layer of graphite is named Graphene and has extraordinary electrical, thermal and physical properties. Graphite may be used in combination with metallic powders to reduce their costs. For istance, nickel coated graphite is produced from graphite powder which has been completely encapsulated with a layer of high purity nickel by the carbonyl decomposition process. The final product has a light weight and good conductivity and it can be dispersed in coatings better than nickel powder (Xanthos, 2005).

Carbon fiber

Micron-sized carbon fibers include at least 90% carbon and are prepared by heat treatment or controlled pyrolysis of different precursor fibers. A bundle of many thousands carbon filaments make carbon filament thread that has diameter of approximately 5 μm. The atomic structure of carbon fiber is similar to the graphite while the sheets in carbon fibers interlock. The most precursors that are used in the production of carbon fibers are polyacrylonitrile (PAN), cellulose fibers (like viscose or rayon), petroleum or coal tar pitch and certain phenolic fibers. The purcursor fiber materials such as PAN-based, mesophase or isotropic pitch-based and rayon based can classify micron-sized carbon fibers. The process of carbon fiber synthesizing includes a heat treatment of the precursor fibers to remove oxygen, nitrogen, and hydrogen. The crystallinity and orientation increasing with reducing defect in the fiber can improve the mechanical properties of the carbon fibers, so the best way to get this level of crystallinity is to start with a highly oriented precursor and then retain the initial high orientation during the carbonization and stabilization process. The carbon fibers that are made from the molten pitches spinning are of interest due to carbon yield on them that approaches to 99% and raw materials that have low cost. The carbon fiber shows high tensile strength, low weight and low thermal expansion, so they can be used in aerospace, military and motorsports (Xanthos, 2005).

They may be used in combination with metallic powders to reduce their costs. For instance, nickel coated carbon fiber is produced from graphite powder which has been completely encapsulated with a layer of high purity nickel by the carbonyl decomposition process. The final product has a light weight and good conductivity and it can be dispersed in coatings better than nickel powder or nickel coated graphite. Also nickel coated carbon fiber can be covered by gold. The 1 wt% gold is added to nickel carbon fiber that has the particle size of 30µm. The final product has high conductivity and has lower cost than gold (Xanthos, 2005).

Organic pigments

They also used to make color and/or cover a substrate. They have found more application recently because the use of some inorganic pigments containing heavy metals has been legally restricted due to environmental concerns. Inorganic pigments have a low light absorption with high scattering power while organic pigments have a high light absorption and a low scattering power. They also have a lower density, higher surface area, higher color purity and higher tinting strength compared with inorganic pigments. Table 2-3 exhibits the differences between the inorganic and organic pigments. Three important types of organic pigments include azo pigments, basic dye and phthalocyanine pigments.

Table 2-3**:** Differences between the inorganic and organic pigments (Paul, 1985)

Property	Inorganic pigments	Organic pigments
Solubility	Insoluble	Slightly soluble
Tinctorial strength	Low	High
Hiding power	High, opaque	Low, more transparent
Specific gravity	High	Low
Heat resistance	High	Low
Intensity	Low	High

In spite of high costs and poor light fastness, they are widely used for their high color strength in printing inks. The Malachite green is a basic dye pigment. The phthalocyanine pigments have excellent light fastness, intensity, bleed and chemical resistance, extreme stability to heat, exceptionally high tinting strength and low cost. They show only blue and green regions of the spectrum. The copper phthalocyanine blue is the main pigment in this class and it has two crystalline modifications that are a red-shade blue form and a more stable green-shade beta form. Finally the choice of organic pigment depends on the fastness, color and binder of the paint, so pigment manufacturers have produced data sheets for organic pigments that describe their properties and areas of application (Paul, 1985).

2-2-3 Fillers

Although they sometimes cannot be distinguished from pigment, they are referred as materials that are not soluble in the coatings and are used to improve some technical properties like reinforcing, to increase the flow properties and to reduce gloss and the cost of coatings. The most of fillers do not have scattering power like pigments, so they cannot be used solely in color coatings. The calcium carbonate, silica, aluminum trihydrate, glass bead and nanoclay are discussed in the following:

Calcium carbonate

Natural calcium carbonate is ($CaCo_3$) an abundant, largely inert, low cost, white filler with cubic, block-shaped or irregular particles of very low aspect ratio that is produced from chalk, limestone or marble. More than 90% of the calcium carbonate is made by conventional grinding method. After limestone was mined, the minerals are crushed and ground. Percipitated calcium carbonate (PCC) is a synthetic product that may involve several chemical operations in its manufacture. It is synthesized by a direct process that include calcinations of $CaCO_3$ at 900º C to produce quick lime, CaO, conversion into slaked lime, Ca(OH)2, by mixing with water and reaction with CO_2, the final recovered from the calcinations process. Then, the suspension is filtered and the collected solid is dried and deagglomerated in grinders. PCC has high purity with very fine, regular particle size and high surface area while it has higher cost than general calcium carbonates. The median particle size of PCC is 0.7-2.0 µm and its primary particle size is between 20 to 70 nm. A special PCC is nano or ultrafine precipitated calcium carbonate that has median particle sizes less than 0.1 µm and is used in nanocomposites. Calcium carbonate has different crystalline forms and the most widespread is calcite which may has a trigonal-rhombohedral or a trigonal-scalenohedral crystal lattice. Another form that is less stable and can be transformed to calcite by heating is orthorhombic aragonite. Also, the third form is vaterite that is unstable and over time will convert into the other two forms. The calcite and aragonite are white while aragonite has a higher density and a higher single refractive index. The primary function of calcium carbonate is to lower costs while it has moderate effect on mechanical properties. It is used in paint industries more than other extenders (Paul, 1985).

Silica

Silica is the name of silicone dioxide, SiO2 that has several crystalline and amorphous forms. It is chemically inert and has a good durability. Natural silica includes crystalline and amorphous form. Crystalline forms are sands, ground silica (silica flour) and a form of quartz (Tripoli). The amorphous silica includes diatomaceous earth (DE) or diatomite and is used as anti-blocks. The DE is a chalky sedimentary rock that is composed of the skeletons of single-cell aquatic organism or the diatomites that grew in a wide variety of shapes and vary in size from 10 µm to 2 mm. The amorphous synthetic silicas are made by two different processes: pyrogenic or thermal (fumed silica grade) and the wet process (precipitated or particulated silica). The fumed silica is made from the vapor-phase hydrolysis of silicone tetrachloride in a hydrogen/oxygen flame. Also silica can be precipitated by acidifying to a PH less than 10 from a sodium silicate solution. The hydrophilic fumed silica that contain hydroxyl groups on its surface is produced by aforementioned method while hydrophobic fumed silica is made by the treatment of hydrophilic silica by hydrophobic compounds like silanes and siloxanes. Both hydrophilic and hydrophobic silica are mixed with solvent-borne coatings to improve rheological properties like thixotropix additive to control settling and sag. They are also used in RTV silicone rubber to reinforce rubbers and to make hydrophobic coating. The diatomites are used in water thinned emulsion flat wall paints, flat varnishes and concrete finishes for controlling the gloss (Xanthos, 2005).

Aluminum trihydrate

Aluminum trihydrate (ATH) is one of the largest volumes flame retardant in the world and can be produced in a variety of particle sizes that are controlled by grinding or precipitation processes. It is the byproduct of aluminum metal process. The ATH precipitated grade has less particle size distribution and packing fraction than mechanically ground ATH, so it shows higher dusting, slower incorporation into the polymer matrix, and higher compound viscosity than ground ATH. Also the surface of ATH can be treated by surfactants, stearates and organofunctional silanes to enhance its overall performance. These chemical treatments can aid processing and improve mechanical properties, chemical resistance, flame retardance and hydrophobic properties. Alumina tri-hydrate (ATH) that has a higher thermal conductivity than silicone rubber is blended with RTV silicone rubber coatings to improve the tracking and erosion resistance. Furthermore, ATH begins to release water of hydration when the local hot spot temperature from dry arcing goes over 220 °C. This action is an important way to remove heat from the hot spots (Xanthos, 2005).

Glass beads

Glass spheres are made by firing crushed glass and cooling of the spheroid product or by melting the formulated glass batch and later the free-falling molten stream is broken-up to form small droplets. The commonly particle sizes may range from 35 to 200µm. The finer sizes are used in coatings to make texture in the surface. They are also used in anticorrosive coatings because they can reduce the water durability and increase the abrasion resistance. They may be used in combination with metallic powders to reduce their costs. For instance, silver coated glass sphere is produced from the glass powder which has been completely encapsulated with a layer of high purity silver and can be used in electromagnetic shielding coatings (Xanthos, 2005).

Nanoclays

Nanoclay is a clay mineral with a phyllosilicate or sheet structure with a thickness of 1 nm and surfaces of 50-150 nm in one dimension. The mineral base is hydrophilic and can be natural or synthetic and its surface can be modified with specific materials to turn into them organophillic and therefore makes it compatible with polymers. Many types of nanoclay are based on the smectite clay that is named montmorillonite. Montmorillonite is a hydrated sodium calcium aluminum magnesium silicate hydroxide $(Na,Ca)(Al,Mg)_6(Si_4O_{10})_3(OH)_6.nH_2O$. It is found throughout the world in small quantities in its natural geological state and in large deposits, it has mixed with a variety of other minerals that is named bentonite. The natural clay is mined and goes through purification and surface treatment that can be used in polymer composites or coatings. Silica and alumina are dominant constituents of clays. Clays have a sheet structure including two types of layers that are silica tetrahedral and alumina octahedral layers, so it is 2:1 clay. The Si_4O_{10} groups in silica tetrahedral layer linked together to form a hexagonal network of Si_4O_{10} repeating units. Two sheets of close-packed oxygens or hydroxyls form the alumina layer. The octahedrally coordinated aluminum atoms between these two sheets are embedded in such a position that they are equidistant from six oxygens or hydroxyls. The octahedral is sandwiched by the two tetrahedral layers and these two layers share their apex oxygens with the latter. One clay sheet is formed from these three layers. Figure 2-9 showed the montmorillonite structure. To make nanoclay compatible with organic polymers, an ion-exchange process is performed to treat the clay surface. An organic cation like a quaternary ammonium chloride is used to change the hydrophilic/hydrophobic characteristics of the clay (Xanthos, 2005).

Nanoclays are used to reinforce polymers and improve their mechanical properties. Also they can increase thermal, barrier properties and synergistic flame retardancy. The important factors responsible for the good performance of nanocomposites are intercalation, interfacial adhesion or wetting and exfoliation. During the dispersion of nanoclay in polymers, gallery spaces can be filled with monomer, oligomers or polymer. The clay is swollen when the distance between platelets increases. The clay platelets that are swollen by polymers are named to be intercalated. Exfoliate is when clay swells so much that it is no longer organized into stacks. The nanoclay can show the optimum property when it is exfoliated. Nanoclay also can improve the corrosion resistance and hardness of coatings and some type of nanoclay can improve the dispersion of pigments in coatings (Pinnavaia et al, 2000).

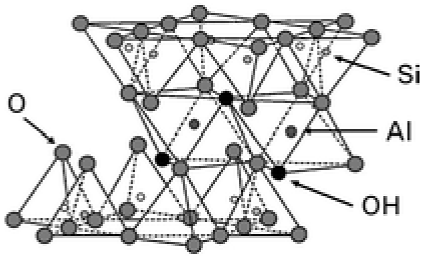


Figure 02-9: The montmorillonite structure (Xanthos, 2005)

2-2-4 Additives

Coating additives are ancillary products that usually added in small amounts to paints for improving some technical property or removing some defect of coatings. Paint additive are recalled by the name of their action. The additives are usually added in 0.01 to 1 wt% of total coating. The most important additives are discussed below:

Wetting and dispersing additives

The pigment or filler particles must be distributed as uniformly and finely as possible in binders to reach the final properties of coatings. The first step in dispersion process is the wetting of pigment agglomerates by resin solution. This process can be accelerated by using wetting additives because it mainly depends on the chemical nature of the pigments and binders. Wetting additives have a low molecular mass with a typical polar-nonpolar surfactant structure and can reduce the interfacial tension between the binder solution and the pigment surface. When the agglomerates have been broken down into smaller particles by grinding or milling, the pigment dispersion must be stabilized by dispersing additives to avoid reformation of larger pigment clusters by flocculation. These additives are absorbed onto the pigment surface via pigment-affinic groups and make repulsive forces between individual pigment particles. Stabilization is done by electrostatic charge repulsion or by steric hindrance because of molecular structures that come from the pigment surface into the resin solution. The second mechanism is remarkable in solventborne paints and the electrostatic charge repulsion is prevalent in waterborne emulsion systems. If the pigment surface do not absorb additive well, the stabilization process cannot work perfectly. This problem happens in many organic pigments due to their highly nonpolar surface. To solve this problem, a new group of dispersing additives was developed that they can stabilize organic pigments by their molecular structure and the large number of pigment-affinic groups (Florio et al, 2004).

Surface additives

The differences in interfacial tension can make many surface defects in coating films. For example, when the paint has a higher surface tension than the substrate to be coated, it shows poor substrate wetting. Also surface tension differences may develop during paint drying because the solvent evaporates and this change in composition can alter the surface tension which may result in visible surface defects like orange peel. Silicone additives that mainly include organically modified methylalkyl polysiloxanes can reduce the surface tension of coatings and minimize surface tension differences. These additives can also improve the slip properties of the dried coatings which can increase the scratch resistance. Another surface defect is poor leveling. The silicones can improve the leveling by suppressing eddy motion during drying. Moreover, the special blend of solvent can affect leveling and reduce the surface defects (Florio et al, 2004).

Texturing agents

They can modify the surface of the coating to make a coating finish that is not smooth and is texturized. Those finishes may be like sand paper, wrinkles or a hammered like surface. The most common compounds to obtain diverse textures are fine polypropylene powders and elastomeric polymer powders. These additives can increase the roughness of surface that is used to make hydrophobic coatings (Florio et al, 2004).

Rheology additives

The rheology of a coating depends on its viscosity and shear rate. The coating materials are pseudoplastic liquids and their viscosity will be thinned by shear. This effect is good for paints because their viscosity is fairly high at low shear rates which avoids sedimentation and gives good anti-sag properties. When the shear rate is increased, the viscosity is reduced that this effect allows easy handling and application of the material. It is possible sometimes in the coatings that the viscosity does not only depend on the shear rate, but it is time dependent. This type of coatings are thixotropic materials that their viscosity decreasing with the time of shearing (Stoye et al, 1998). Reological additives can modify the flow behavior of coating materials to get a better rheology. For instance, they can make pseudoplastic or thixotropic flow behavior to improve sag-resistance and anti-sedimentation properties.

Light stabilizers

The sever weathering in exterior application exposures high-quality industrial coatings like automotive paints. The exposure to UV light, oxygen, moisture, and atmospheric pollution in two-coat metallic coatings leads to decomposition of the polymer material in the automotive finishes. The loss of gloss, crack formation, color change and delamination effect is attributed to the coating decomposition. Each polymer material can be damaged easily at one or more wavelengths in the UV range, so light stabilization is usually essential (Florio et al, 2004).

Organofunctional silanes

Organofunctional silanes are used as coupling agents, surface treatments and protecting group reagents in organic synthesis. They also are monomers in the synthesis of organofunctional siloxane polymers. The main method for making organofunctional silanes are hydrosilylation, nucleophilic substitution of chloride and organometallic reagents, but the hydrosilylation is used commercially. This method includes the addition of silicone hydride moiety across an unsaturated linkage. This reaction may be done photochemically or by the use of transition metal complexes of rhodium or platinum (Xantos, 2005).

One of the main usages of organofunctional silanes is in the coupling agents. Silanes as adhesion promoter can join different phases present in a composite or coating. These phases are usually organic resins like polyester resin and inorganic fillers like ATH. These two weekly bonded surfaces are bound with strong, stable and water resistance molecular bridges that are formed by silanes. The organofunctional group in the coupling agent is bound to the polymer by chemical reactions (grafting or addition) and/or physicochemical interactions (hydrogen bonding and acid-base interaction). Also the alkoxysilanes in coupling agent is reacted with filler. These groups can be hydrolyzed and liberate the corresponding alcohol. This reaction continues with water or moisture that leads to the removing of alcohols and their replacement by hydroxyl moieties. These hydroxyl groups can make a reaction with surface hydroxyl groups to produce a stable covalent bond.

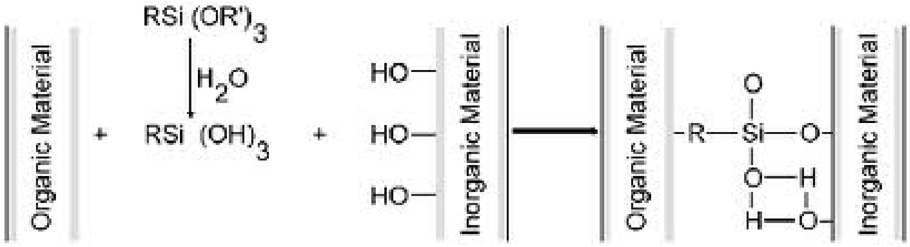


Figure 02-10: The reaction of coupling agent with polymer and inorganic material (Xanthos, 2005)

As a result, coupling agents are most effective on fillers with high concentrations of reactive hydroxyls like silica, glass and hydroxides. As a first step, the hydrogen bonding with the surface OH groups can fix the silanol on the filler surface. This reaction is reversible until the water molecule is removed from the reaction site. The silane on the filler surface is finally fixed by the covalent [silane-oxygen-filler] bond. Figure 2-10 indicated the reaction between a silanol and inorganic filler. Organofunctional silanes are also reacted with fluorocarbon compounds to make fluoroalkylsilanes that are used in surface treatment to make hydrophobic and oleophopbic surfaces (Xanthos, 2005).

2-2-5 Solvents

The most commonly solvents that are used in coatings are aromatic like toluene or xylene, aliphatic hydrocarbon like naphta, esters of acetic acid like butyl acetate, glycol ethers, alcohols, and some ketones like methyl ethyl ketone (MEK). They can improve pigment wetting and dispersion, control viscosity of coatings and control the drying behavior of coatings. The boiling point is an important property of solvents. The evaporation rate is also related to boiling point. For instances, some solvents like acetone will evaporate in seconds at room temperature while some solvents like butyl glycol will evaporate in half an hour. The choosing of solvents depends on the structure or resins. Each resin is compatible with special solvents, for instances epoxy resin is dissolved in ketone and esters, but it is insoluble in the toluene; in this case, we can have a mixture of solvents to control the evaporation rates of solvents in coatings and reduce the cost of paints. Also some solvents may make a reaction with resin and reduce the final properties of coatings; so it is important to know the solvent information of resins from manufacturer.

Table 02-4**:** The main solvents of some coatings

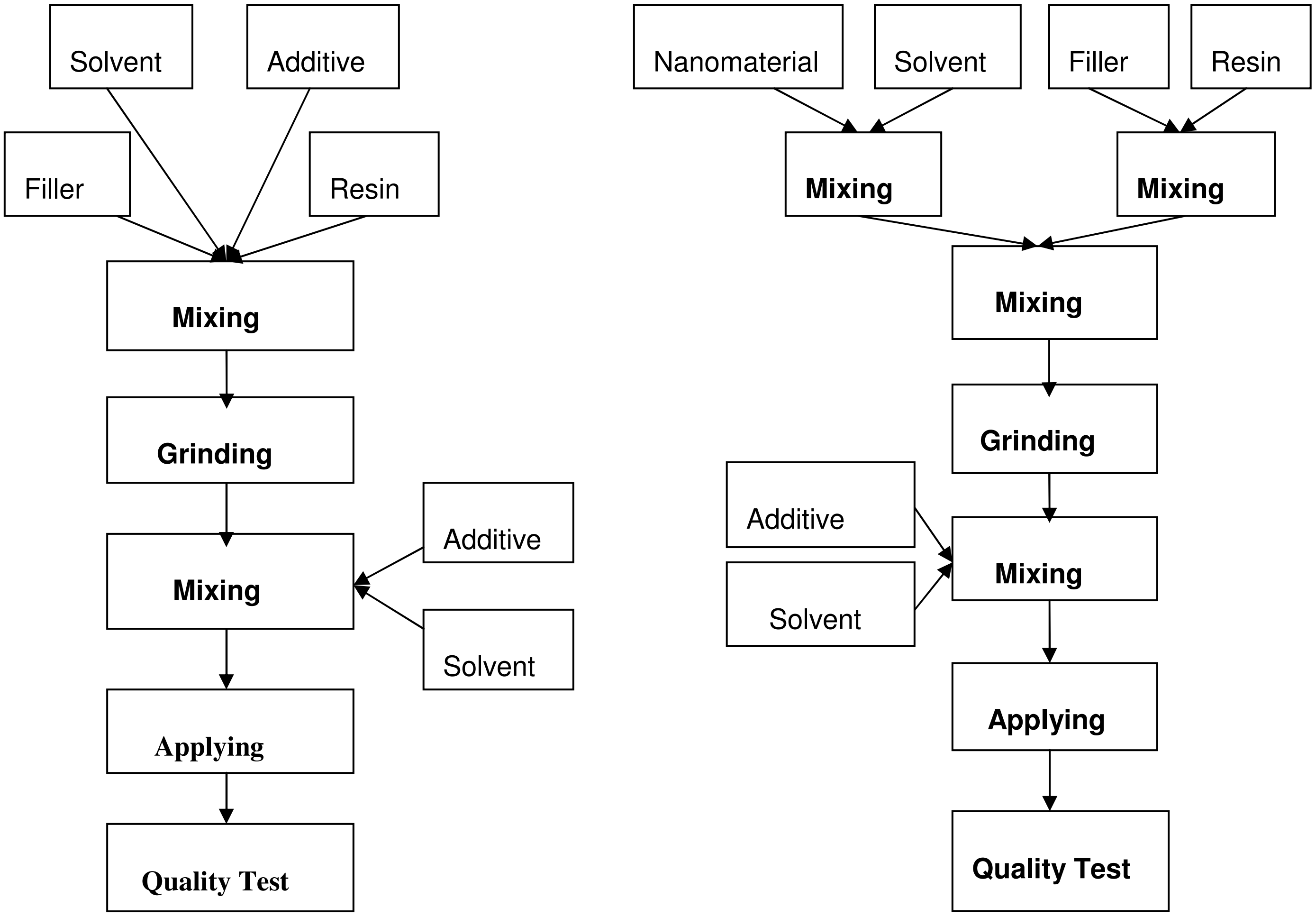
Coatings	**Solvents**
Epoxy	Esters and Ketones (Butyl acetate and Methyl Ethyl Ketone)
Polyurethane	Esters and Aromatic hydrocarbons (Butyl acetate and Xylene)
Silicone rubber	Aliphatic hydrocarbons (Mineral spirit)

For example, alcohol can react with polyisocyanates and reduce the amount of accessible hardener in polyurethane coatings. The water works as solvent in water base paints, so there is not any environment concern about these types of coatings. Table 2-4 demonstrates the main solvents for some coatings that are used in this project; it is possible to mix other solvents with main solvents to reduce the cost.

2-3 Production technology

The homogeneous, irreversible mixing of the liquid components is the main physical process involved in the production of coating materials. The complete wetting and a uniform, stabilized distribution of pigment particles in the liquid resin is one of the important factors that affect a coating performance. A properly dispersed coating shows higher performance than a poorly dispersed coating of similar composition. Satisfactory dispersions can make good optical and protective properties to the coatings. The complete process of pigments incorporation into liquid binder is named dispersion. The final dispersion includes fine pigment particle distribution throughout the medium. Pigment dispersion happens in three stages that are: wetting, grinding and dispersion (flocculation). Wetting is the dislocation of air or water that was adsorbed at the pigment surface with the binder. Also the dispersing agents like phosphates, organosilicone and inorganic alkalies are used to affect pigment wettings. The second step is grinding. The pigment particles exist as aggregates or agglomerates but instead as primary particles. In order to obtain optimum visual, economic and performance properties of pigments it is necessary to reduce these clusters to primary particles. The color strength of pigments is dependent on the exposed surface areas of the pigments, so the full reduction to primary particles is important. The mechanical breakdown and separation of particle clusters to isolated primary particles are referred grinding. When the pigment has been wetted, the grinding is started (Tracton, 2006; Paul, 1985).

The magnitude of forces holding the individual particles together in clusters that are related to physical character can affect the effectiveness of grinding. The surface treatments of pigments can reduce these physical interactions. When the pigment particle size reduces, the interparticle forces can affect more in controlling the packing and the pigment flow behavior. The smearing (shearing) or smashing (impact) types of are used to break down pigments; however, the exact clusters breakdown mechanism is not clear. The third stage of dispersion after wetting and grinding is flocculation. The movement of wetted particles into liquid vehicle to make permanent particle separation is named dispersion. Generally, the disruption of agglomerates and aggregates to secure a stable dispersion of primary particles is more important than flocculation.



Usual method **New method**

Figure 2-11: The usual and new method (for nanomaterials) of coating productions

Three major types of interaction can influence in colloidal stability that include: London-Van der Waals forces of attraction, the columbic forces associated with the charged particles and the repulsive forces arising from the salvation of adsorbed layers. The main process of coatings production include: mixing of resin, solvent and filler with some additives in the first steps; some of additives like surface leveling additives are sensitive to grinding and should be added at final stage of paint production. Secondly, paint mixtures are ground and dispersed in some mills like ball mills to crash down and distribute all the components in coatings uniformly. Then some additives are added to paints and its viscosity is adjusted by solvents. The flowcharts show the stages of coating productions. The new method of coating production can make possible to add higher fractions of nanomaterials to the coatings. Kanagasabapathy et al (2009) used a method to mix some nanoparticles with PDMS to make hydrophobic coatings. They dispersed nanoparticles in solvents and then added final dispersion to PDMS. Their method was modified and was used in this study as it can be seen in figure 2-11.

The apparatus that are used for making coatings are described below:

Mixers

A wide variety of tanks are used to mix paints materials. The materials of tanks are related to paint type. For instance, solvent borne coatings can be made in steel or aluminum container, but waterborne paints should be produced in stainless steel because of corrosion risk. The stirrers of mixer are usually of the flat-blade, disk, propeller or turbine type. When the pigments, fillers, the some parts of resin, the some part of solvent and dispersing additive are blended well in mixer, the final mixture are transferred to grinding mills to break down pigment of fillers clusters (Paul, 1985).

Grinding equipment

The grinding equipment can be divided mainly into three groups that are smearing or shearing type, smashing or impact type, and the hybrid type. In the hybrid type both the shearing and the impact effects are utilized. There are three different aspects of shearing and impact type grinders that include: 1) the motion optimum direction is perpendicular for the impact type while it is parallel to the particles in shearing types; 2) the mill base viscosity must be maximal for a shearing type nevertheless the mill base viscosity must be minimal for an impact type; and 3) A shearing type requires nominal velocity but for an impact type, the velocity is maximum (Paul, 1985). The most important grinders are discussed in the following:

Roller mills

The roller mills belong to smearing type grinders. The coating industry uses typically three roll mills whereas four-roll and five-roll mills are employed in ink industries. The space between the feed and the center rolls which are rotating inwardly at different speeds is used in three roll mills to charge the mill base. A knife edge pressing against the apron roll is used to discharge the final pigment dispersion at the takeoff apron. The shearing and mixing of dispersion continues until it is discharged. The equipment must be very robust due to tremendous forces that are involved in the operation of three-roll mills. The rolls are normally manufactured from chilled cast iron to have acceptable hardness and abrasion resistance (Tracton, 2006).

Ball and pebble mills

They belong to hybrid type mills. These mills include horizontally mounted cylindrical containers that are filled partially with pebbles or ceramic or metallic balls (the grinding medium). A charge consisting of pigment/vehicle mixture is added to the cylindrical container to acquire pigment dispersion. This charge is then subjected to rotation about the horizontal axis of the mill at a rate adequate to lift the pebbles or balls to one side and then cause them to roll, slide and tumble (cascade) to the lower side. Figure 2-11 indicates a lab scale ball mill that has been used in this study. The containers include baffles of either narrow metal bars in ball mills or ridged ceramic blocks in pebble mills to inhibit slippage or back-sliding of balls along the lower mill walls as the mill rotates. The pigments are put through both impact and intensive shear forces because of the cascading action. The required dispersion effect is prepared by highly turbulent mixing action on the mill base that is confined between the ball interstices. The optimum charging is usually 50% air space, 30% ball volume and 20% mill base volume (Tracton, 2006).

Figure 2-12: The lab scale ball mill

The main difference between ball and the pebble mills is that the former use from a metallic grinding medium consisting of the inside surface of an alloy steel or some other special metallic liner while the pebble mills use ceramic grinding medium with the inside surface of the mill being lined with a nonmetallic liner.

Sand mills

The difference of sand, bead and shot mills with ball mills mainly is related to the diameters of the spherical grinding media used. A homogeneous mixture of mill base is passed through the cylindrical bank of sand which agitates intensely. The shearing action between the sand particles disperses the pigments. The free flow of the pigment dispersion maintaining the sand particles happens when the dispersed mill base overflows consequently through an exit screen, sized. The rotational motion of the impeller conveys the centrifugal forces to the sand particles that theses forces give rise to the shearing forces within the sand mass (Paul, 1985).

2-4 Surface preparation

One of the important factors to obtain good protection by surface coatings is surface preparation. The preparation methods are different because they vary noticeably due to the substrate to be coated, the types of contaminant present on the surfaces and sometimes on the type of coating used. Contaminants usually include general dirt and dust, chemisorbed fluids, residual oil and grease from rolling or wire-drawing type of forming processes, cutting and grinding fluids from machining operations, residual metal powders or polishing powders. The preparation techniques are divided to four groups that are: mechanical methods, solvent cleaning, alkali cleaning and acid pickling.

Mechanical methods

These methods are usually useful in removing surface roughnesses and irregularities of edges that are made from primary production methods. However, they can not remove contaminants completely. They are the only feasible methods for large prefabricated structures such as bridge girders, ships hulls and etc. Wire brushing and abrasion may be done by hand or automatic machinery. Also for irregular surfaces the girt blasting is more effective. The kinetic energy of small hard particles is used to remove impurities in blasting methods like sandblasting, compressed air or water jet. Metallic like spherical cast iron shot or nonmetallic products like corundum are used as abrasives. The surfaces that are blasted and abraded are enormously dusty and must be cleaned by blowing, wiping or washing (Paul, 1985).

Solvent cleaning

Fats, oils, waxes and other organic material from surfaces are removed by these methods. However, they are ineffective against oxides, sulphides and other inorganic material. The cleaning may be done by immersion and agitation or by vapor condensation and washing. There must not be any solvent losses, and recovery circuits and systems should be an integral part of the process due to the toxicity of most of the organic solvents. Some solvents such as acetone and alcohols are cheap, flammable and moderate solvents, but aromatic solvents like toluene and xylene are good solvents and are moderately expensive, toxic and highly flammable. Also chlorinated solvents such as trichloroethylene are good and nonflammable solvents while are expensive and highly toxic. Methylene chloride is used for dissolving residual oil in old paintwork and is a paint stripper (Paul, 1985).

Alkaline cleaning

All types of surface contaminants can be removed effectively by this method and alkaline cleaners are applied by immersion or a spray process. The oil or grease can be saponified by an alkali salt such as hydroxide or carbonate and is converted to water-soluble soaps, glycerols and esters. The surface tension at the media/soil/solution interfaces is lowered by detergents and surfactants (Paul, 1985).

Pickling

The process of oxides removal by converting them into soluble compounds by treating the surfaces with acids or alkaline solutions or molten alkali salts is named pickling. The nature of the scale and the substrate can affect the selection of pickling media. The sulphuric (5-20%) or hydrochloric acid (1-10%) is used for steel (Paul, 1985).

2-5 Application methods

For applying a coating layer to the surfaces different methods can be used. The factors that can affects selecting the application methods are: whether the material to be applied is solid, liquid or powder; whether coated films are thick or thin, or are clear, metallic or wrinkled, or are water-borne or oil-based. Also the nature of surface can affect. For instance, the contoured surfaces may need a different method than the flat ones. The nature of coating substrate like wood or aluminum can vary the method of application. The main methods of coating application are discussed in the following:

Brushing

It is one of the oldest ways and it seems to be rather simple while its success relate to a great extent on the quality of the brushes and the rheological properties of the coatings. The length, shape and the mechanical properties of the bristles and the nature of the bristle tops can affect the bushes quality. The flow and the appearance of the coatings will be controlled by rheological properties. Brushing is a slow method and is used in the handicrafts sector, do-it-yourself sector or on building sites (Stoye et al, 1998).

Dip coating

It is used in the coating of large objects that protection is more important than decoration. Also it can be employed to obtain a high-class decorative finish on small objects such as pencils and paintbrush handles. The stages of dip coating are: lowering the article to be coated into a container containing the paint, lifting it out and hanging the coated article over the container or a drain board while the surplus paint drain off. This method has some weaknesses that are: paint may be kept in pockets which do not drain properly because of article shape; fatty edges (remaining paint along the edges) may form since improperly clean run-offs; the gaps and the threads in the objects are joint and the holes are blocked; refluxing (or solvent washing) may occur in enclosed or partially enclosed sections; the paints should be agitated to prevent settling and this issue can leads to variations from batch to batch; the thickening caused by the oxidation of the coating material may change viscosity and if paint viscosity are not fixed, film build varies; and there is fire hazards in the case of solvent-based coatings. These problems can be solved in the new method of dipping that is electrodeposition (Stoye et al, 1998).

Curtain coating

The catalyzed lacquers in the furniture industry are coated by this method and it is a substitute for spray applications. The advantages of this method are: the close controls of coating thickness without any material loss; low energy costs and the continuous nature of production; and rarely rejection due to faulty coating. However, this technique is generally limited to the flat surface coatings. It is used in the different fields of finishing from protective strippable lacquers for the sheet metal industry to the treatment and finishing in the leather trade (Stoye et al, 1998).

Roller coating

The most general method for coating flat surfaces is roller coating. This method is generally entailed surface coverage of at least 50% greater than other application method and it is very economical. Also, the method can control the film thickness accurately and hold uniform over long production runs. To apply ceiling and wall paints, hand rollers have extensive applications in do-it-yourself paints. The lamb wool rollers are used in this case, but it is difficult to get glossy finishes with hand rollers because they leave the slight texture on the surface (Stoye et al, 1998).

Spray coating

It is the most famous method of coating application because it has a high speed of application and it can be used to almost any condition, shape or size of article. However, the main drawback of this technique is the paint material wastage because of overspray. To achieve smooth coatings from rapidly setting paint compositions, and organic coatings which dry solely by solvent evaporation and where no cross-linking happens, the spray method is so effective. Spray guns include suction, pressure and gravity feed models. The length of the material hose from the tank to the gun should not be longer than is essential to reach the object. The air pressure is lost in longer hoses and they need more cleaning. The volatility of the solvents used can influence to a great amount in paint appearance. For instance, the orange peel is attributed to highly volatile solvents. There are different adoptions of standard head guns, for instances, for spraying the interiors of small necked vessels, cylindrical objects and tubes. Spray coatings are divided to two main groups that are air spraying and airless spraying. Air spray method includes suction feed-type spray guns where the air system is passed through a horizontal tube over the top of a vertical one which is immersed in the fluid. The fluid is drawn upwards by the air stream, is atomized and carried forward in the direction of the air stream. The compressed air flows through an annular gap that is made between a bore in the air cap and the concentric paint nozzle. Then jet shape is regulated by air jets from air-cap bores. Also the air jet assists outflow of the paint. The paint is atomized into particles due to the difference between the velocities of the compressed air and the exiting paint. These particles are conveyed as special droplets in the free jet. The paint material can be atomized extremely finely by the exiting air jets in the high-pressure process (0.2-0.7 MP). The liquid viscosity, the amount of delivered paint, and air pressure can vary the size of liquid droplets from 10 μm to 100 μm. The paint can be fed to the nozzle via a suction cup, a pressure cup, a flow cup, or pressure tank depending on the viscosity and throughput. The material loss because of overspray is slightly high and this method is rather inefficient. Airless spraying is another method of spray coating. It is used for high voltage insulator, shipbuilding, road and rail transport, maintenance and decorative coatings. The high application speeds and minimum material loss because of overspray are the main motive for its wide acceptance. The equipment includes a container, high-pressure fluid pump, a paint strainer, fluid hose, an airless spray gun and a compressed air supply to the pump motor. The output pressure is between 8 to 40 MPa. The releasing highly pressurized fluid through a small orifice in the spray cap can make atomization. A cloud of ultrafine particles that is made by atomized paint move slowly toward the surface to be coated. The air resistance is attributed to the slowing down and the cloud attacks the surface with very slow speed, so there is not any spray fog formation compared with air spray method (Stoye et al, 1998).

Coating applicators

Almost the layer thickness of the film can influence in all coating properties. The measurements have to be done on carefully prepared film with a specific layer thickness to get reproducible comparable test results. The large-scale industrial paint application methods are often simulated with simple coating equipment in the laboratory. The most commonly devices for producing coatings on glass slides are film applicator, film caster and wire-wound metering rods (Mayer bars). These devices produce a uniform layer thickness on the test panels when applied at a constant rate. The Mayer bar was used to apply conductive coatings in this project. The figure 2-13 indicated the Mayer bar that was employed. To make a Mayer bar, a tight spiral of wire made of stainless steel is wound around of a steel rod. For different coating thickness, the wires with diameters between 0.l8 mils to 13.5 mils are used.

Figure 2-13: The picture of Mayer bar

The initial shape of the coating is a series of stripes that are spaced apart according to the spacing of the wire windings when the metering rod is applied. The surface tension of the liquid film pulls these stripes together almost immediately and forms a flat and smooth surface. This flat surface is ready for the following drying and curing processes by heat or UV light sources. The wet film coating thickness can be controlled precisely within 0.1mil by using Mayer bar and it is 0.173 times the wire diameter according to mathematical calculations. It is accepted a ratio of 1:10 between the wet coating thickness and wire diameter by most users. The main pros of Mayer rods are: low cost and replacing worn or damaged rods to another are inexpensive and fast; and the coating thickness can be controlled accurately. Meanwhile, it has some cons, for instance, it can be used for low viscosity liquid or the coating speeds are not too much because striations formed required a certain amount of time to level out before the web is dried (Stoye et al, 1998).

2-6 Film formation

When the coating dries on the surface, a firm film is formed. Drying of the paint on the substrate can be physically or chemically:

1) Organic solvents evaporate from solvent base coatings
2) Water evaporates from water base coatings

3) Polymerization or cross-linking of low molecular resin with other low or medium molecular resin to form macromolecules.

The two first actions are related to physical drying and the third one is chemical drying. Theses two types of drying are explained below.

Physical drying

Coatings with high molecular polymers such as cellulose nitrate, cellulose esters, chlorinated rubber, vinyl resins, polyacrylates, styrene copolymers, thermoplastic polyesters, and polyamide and polyolefin copolymers dry physically. These materials have good flexibility and stability because of high molecular weight. To get sufficient hardness and scratch resistance, the glass transition temperature of resins should be above room temperature. The film formation can take place from solutions or dispersions in organic solvents or water in these polymers. When the solvent or water evaporates, leaves behind the chemically unchanged polymer film. Drying at elevated temperatures (forced drying) can accelerate film formation. The molecular mass of binder in solvent-based paints is relatively high, so these coatings have a low solid content. The dispersion of binder in water or in organic solvents can make high solid coatings. Physical drying happen when polymers dissolved in solvents (organic solvent or water) gradually sticks to make a solid film and then a network. The disadvantage of physical drying is that the films formed are sensitive to solvents. A special case of physically drying coatings systems are plastisols and organosols. The binders of these systems include finely dispersed poly (vinyl chloride) or thermoplastic poly (meth) acrylates suspended in plasticizers. The polymer particles are swollen by the plasticizer on drying at elevated temperatures. This process is named gelatin (Stoye et al, 1998).

Chemical drying

Chemically drying paint have resins which react together to form cross-linked macromolecules. These resins have a relatively low molecular weight, so their solutions have high solids content and a low viscosity. Polymerization, polyaddition or polycondensation can happen in chemical drying. In polymerization, reactive components like unsaturated polyesters with styrene monomer link together to form the film. In this example, styrene also behaves as a reactive solvent for polyesters. Cross-linking can be done in room temperature or by radiation curing. In polyaddition, low molecular weight reactive polymers such as alkyd resins or polyacrylates react with polyisocyanates or epoxy resin to make cross-linked macromolecules. This reaction can take place at room temperature, so the polymer components must be mixed shortly before application. The period of time that this mixture can be used is known as the pot life. These coatings are presented as two-pack coatings and differ from one pack coatings that can be stored for a long time. If one of the polyaddition binder components like the polyisocyanates is blocked chemically, a coating system that is stable at room temperature is formed. Heat enables cross-linking to happen and deblock the component. These types of resins are used in stoving coating and powder coating. Polycondensation needs the addition of catalysts or the use of higher temperatures. Acid-catalyzed coatings used in the furniture industry are cold-curing coatings, while industrial and automotive coatings are heat-curing and stoving coatings. The binding agents can be saturated polyesters or polyacrylates in combination with melamine resins or phenolic resins. Water, low molecular alcohols or other volatile components can be released after cross-linking.

Generally, the drying of coatings and paints does not occur only by one method. In solvent-containing and waterborne heat-curing coatings, chemical drying always can be accelerated by physical drying from organic solvent evaporation. The physical and chemical drying can take place simultaneously depending on the composition of the binder system (Stoye et al, 1998).

CHPTER 3

Materials and methods

This chapter will discuss about the materials and methods that have been used in this project to make superhydrophobic, icephobic and conductive coatings. Also the tests that have been down will be described.

3-1 Superhydrophobic coatings

Superhydrophobic coatings are made from the blending of RTV silicone rubber or fluorpolyol with hydrophobic additive, hydrophobic fillers or the combination of them. Also, dispersing additive and coupling agent were added to improve the dispersion and adhesion of coatings respectively. Solvent is used to adjust the viscosity too. The materials that were used in this project will be discussed in the following:

3-1-1 Materials

The polymers, fillers, additive and solvents that were used in this project will be described below:

Polymer systems

The RTV silicone rubber and Fluoropolyurethane polymers were used in this project. The brands name and the most important physical properties have been discussed in the following:

RTV Silicone Rubber

For the production of superhydrophobic RTV coatings, the RTV-1 silicone rubbers from Wacker Company (USA) were chosen. Its trade name was Elastosil E303.

Density:	0.9 (gr/cm^3)
Viscosity	600 (mPa.s)

Solvent content	50 w%

Fluoropolyurethane

The Fluoropolyurethane coatings were prepared from the mixing of fluoropolyol and its hardener that was polyisocyanates. Fluoropolyol was from AGC Company (Japan) and its trade name was Lumiflon LF-910LM.

Density	1.16 (gr/cm^3)
Viscosity	5800 (Pa.s)
Hydroxyl value	100 (mgKOH/g-polymer)
Solid content	66 w%

The polyisocyanates was from Bayer Company (Germany) and its trade name was Desmodure N75-BA.

Density	1.06 (gr/cm^3)
Viscosity	160 (mPa.s)
NCO content	16.5%
Solid content	75 wt%

Fillers

The fillers are added to coatings to reduce the cost and improve some mechanical properties. The alumina tri-hydrate (ATH), glass bead or nano calcium carbonate were employed in this work.

Alumina tri-hydrate (ATH)

Alumina tri-hydrate has higher thermal conductivity than silicone rubber and is added to superhydrophobic RTV silicone rubber coatings for high voltage insulator to improve their erosion and tracking resistance. Alumina tri-hydrate trade name was Hymod SB336 and it was a silane treated powder. Also, it was received from Huber Materials Company (USA).

Median particle size:	15.5 µm
Surface area	1.5 m^2/gr
Oil absorption	23

Glass beads

The glass bead is used to make texture in the surface, so it may improve the contact angles of coatings. It was prepared from Potters Industries Company (Canada) and its trade name was Spheriglass A.

Median particle size:	11 µm
Oil absorption	18
Density	2.5 (gr/cm^3)

Nnao calcium carbonate

The nano calcium carbonate was treated by fluoroalkyl silane (FAS) and it was added to coatings to increase the hydrophobicity of coatings. The nano calcium carbonate treated with FAS had been used to make superhydrophobic coatings by Wang et al (2007).

Median particle size:	20 nm
Surface area:	55 m^2/gr

Additives

The additives are added to coatings to improve some technical property or removing some defect of coatings. Also they can improve the hydrophobicity of coatings. Nnao silica treated with organosilane, nano fluoric particle, dispersing additive, polydimethylsiloxane, fluoroalkyl silane or coupling agent were used.

Dispersing additive

The dispersing or thixotropic additive was added to superhydrophobic coatings to improve the dispersion of hydrophobic additive or fillers in the coatings. The trade name of dispersing additive was Aerosil 200 from Degussa Company (Germany).

Specific gravity (water):	2.2
Median particle size:	12 nm
Surface area:	200 (m^2/gr)

Coupling agent

They are added to coatings to improve the binding between polymer and fillers. Also, they can improve the adhesion of coatings. The glycidoxypropyltrimethoxysilane is used as a coupling agent. Its trade name was Genosil GF 80 and made by Wacker Company (USA).

Boiling point	138 ºC
Density	1.07 (gr/cm^3)
Epoxy content	17.5%

Polydimethylsiloxane (PDMS)

It was added to RTV silicone rubber to improve the water durability and contact angles of coatings. Hackam et al (1996) exhibited that low molecular silicone fluid (PDMS) could increase the hydrophobicity of silicone rubber coatings. The PDMS was bought from Alfa Aesar Company (USA).

Density	0.97 (gr/cm^3)
Molecular weight	4200

Fluoroalkylsiane (FAS)

This material was utilized to make a hydrophobic treatment on the fillers (glass bead and nanocalcium carbonates). Perfluorodecyl triethoxysilane was used and its trade name was FAS-13. It was bought from Aldrich Company (USA).

Density	1.389 (gr/cm^3)
Boiling point	209-230 ºC

Solvents

They can improve pigment wetting and dispersion, control the viscosity of coatings and control the drying behavior of coatings. The solvents should be selected according to polymer structures. The mineral spirit, methyl ethyl ketone and toluene were used in this work.

Mineral spirit

It is used as solvent for RTV silicone rubber coatings. It was from Recochem Company (Canada).

Boiling point:	145-170 ºC
Density	0.78 (gr/cm^3)

Methyl ethyl ketone

It is the main solvent for polyisocyanates and will be used in the combination of toluene in Fluoropolyurethane coatings. It was from Alfa Aesar Company (USA).

Boiling point:	80 ºC
Density	0.85 (gr/cm^3)

Toluene

It is the main solvent for fluoropolyols and will be used in the combination of toluene in Fluoropolyurethane coatings. It was from Aldrich Company (USA).

Boiling point:	110.6 ºC
Density:	0.86 (gr/cm^3)

3-1-2 Preparation method

Superhydrophobic coatings are made by the new methods that described in chapter 2. First, the nano particles and dispersing additive were dispersed in the solvent by ultrasonic bath (figure 3-1), and then the dispersion was added to the mixture of silicone rubber or fluoropolyol and solvent that had been homogenized in a lab scale ball mill. Final mixture was blended in the ball mill too. Higher concentrations of nano particles could be blended in this new method compared with the usual way that all coating components were mixed together onetime. The final mixture of fluoropolyol and nanoparticles should be mixed with hardener (polyisocyanates) to make fluoropolyurethane coatings. The ratio of fluoropolyol to hardener was 3/1. To make superhydrophobic coatings with treated fillers, both usual and new method of mixing can be used. Also, for preparing superhydrophobic coatings with the combination of hydrophobic additives and fillers, the polymers were mixed in the ball mill with the fillers and the mixture was added to the dispersion of nanoparticle, hydrophobic additive and solvents that were made in the ultrasonic bath. Final mixture was mixed again in the ball mill. Superhydrophobic coatings are applied by spray gun on the substrate and were cured in room temperature.

Figure 03-1: The ultrasonic bath

Surface treatment of fillers (nano calcium carbonate and glass bead)

Ten gram of nano calcium carbonate were dispersed in 20 g isopropyl alcohol in a glass bottle (the method was based on the work of Wang et al (2007), but solvent was changed to isopropyl alcohol and treated powders were heated at 150 ºC). 0.4 g FAS-13 and 0.4 g acidic water (PH was adjusted by acetic acid in 3) were added to mixture and the final solution was stirred for 2 hours. Then mixture was poured into a glass vessel and dried at 80ºC in an oven. After drying, the treated powders were heated at 150 ºC in oven to improve the binding of FAS and nano $CaCo_{3.}$ The EDX material detection was used to find that the treatment of nano powder by FAS was successful or not.

3-1-3 Experimental formulations

The superhydrophobic coatings were made from the blending of RTV silicone rubber of fluoropolyurethane with hydrophobic additives, hydrophobic fillers or the combination of hydrophobic additive and fillers. Also the effect of coupling agent fraction on the adhesion of superhydrophobic coatings was evaluated. The role of PDMS in the contact angles of RTV silicone rubber was assessed too. The mixture of ATH and hydrophobic additives with RTV silicone coatings were prepared because the ATH can increase the resistance of this coating to track and erosion resistance. The experimental formulation for each polymer system is disclosed here.

RTV silicone rubber formulations

RTV silicone rubber and hydrophobic additive

The hydrophobic additives were nano silica and ultrafine fluoric particles. The formulations that were used to make superhydrophobic silicone rubber coatings are indicated in Table 3-1.The hydrophobic additive fractions in samples of 1 to 5 were 5%, 10%, 20%, 30% and 40% respectively.

Table 3-1: The RTV silicone coatings and hydrophobic additives

	Sample Number				
	1	**2**	**3**	**4**	**5**
Component	**Wt (g)**	**Wt (g)**	**Wt (g)**	**Wt (g)**	**Wt (g)**
RTV Silicone	83.6	81	76	70	63
Hydrophobic additive	2.4	5	10	16	23
Dispersing additive	0.6	0.6	0.6	0.6	0.6
Coupling agent	1.4	1.4	1.4	1.4	1.4
Solvent	12	12	12	12	12
Total weight:	100	100	100	100	100

RTV silicone rubber and hydrophobic fillers

The glass bead and nano calcium carbonate were treated by fluoroalkyl silane and treated powder were mixed with silicone rubber. The formulations were demonstrated in Table

3-2. The hydrophobic filler fractions in samples of 1 to 4 were 10%, 20%, 30% and 40% respectively.

Table 03-2: The RTV silicone coatings and hydrophobic fillers

	Sample Number			
	1	2	3	4
Component	**Wt (g)**	**Wt (g)**	**Wt (g)**	**Wt (g)**
RTV Silicone	81	76	70	63
Hydrophobic filler	5	10	16	23
Dispersing additive	0.6	0.6	0.6	0.6
Coupling agent	1.4	1.4	1.4	1.4
Solvent	12	12	12	12
Total weight:	100	100	100	100

RTV silicone rubber and the combination of hydrophobic additives and fillers

The combination of hydrophobic additives and fillers were added to RTV silicone rubber to make superhydrophobic coatings. The concentrations of hydrophobic additives were varied from 10 to 30 wt% while the fillers fractions (treated glass bead, treated nano calcium carbonate or ATH) were altered from 10 to 30 wt%. The Tables 3-3, 3-4 and 3-5 indicate the coating formulations. The highest combination fraction of hydrophobic additives and fillers was attained at 55 w%. The concentrations of hydrophobic additives in samples 1 to 4 (Table 3-3) were 10%, 20%, 30% and 40% respectively. Also the fractions in samples 1 to 3 (Table 3-4) were 10%, 20% and 30% respectively.

Table 3-3: The RTV silicone coatings with 10 wt% hydrophobic additive and hydrophobic fillers

	Sample Number			
	1	**2**	**3**	**4**
Component	**Wt (g)**	**Wt (g)**	**Wt (g)**	**Wt (g)**
RTV Silicone	76	70	63	56
Hydrophobic additive	5	5	5	5
Hydrophobic filler	5	11	18	25
Dispersing additive	0.6	0.6	0.6	0.6
Coupling agent	1.4	1.4	1.4	1.4
Solvent	12	12	12	12
Total weight:	100	100	100	100

Table 3-4: The RTV silicone coatings with 20 wt% hydrophobic additive and hydrophobic fillers

	Sample Number		
	1	**2**	**3**
Component	**Wt (g)**	**Wt (g)**	**Wt (g)**
RTV Silicone	70	63	56
Hydrophobic additive	5	12	19
Hydrophobic filler	11	11	11
Dispersing additive	0.6	0.6	0.6
Coupling agent	1.4	1.4	1.4
Solvent	12	12	12
Total weight:	100	100	100

The concentrations of hydrophobic additives in samples 1 to 2 (Table 3-5) were 10% and 20% respectively.

Table 3-5: The RTV silicone coatings with 30 wt% hydrophobic additive and hydrophobic fillers

	Sample Number	
	1	2
Component	**Wt (g)**	**Wt (g)**
RTV Silicone	63	56
Hydrophobic additive	6	13
Hydrophobic filler	17	17
Dispersing additive	0.6	0.6
Coupling agent	1.4	1.4
Solvent	12	12
Total weight:	100	100

The effect of PDMS on RTV superhydrophobic coatings

The superhydrophobic coatings including 30 wt% hydrophobic additives (nano silica) were mixed with PDMS. The PDMS may increase the hydrophobicity and water durability of coatings. The PDMS fractions in samples 1 to 3 was 5%, 10% and 15%. Table 3-6 displays the formulations that were prepared.

Table 3-6: The RTV superhydrophobic silicone coatings and PDMS

	Sample Number		
	1	**2**	**3**
Component	**Wt (g)**	**Wt (g)**	**Wt (g)**
RTV Silicone	67	64	61
Hydrophobic additive	16	16	16
Dispersing additive	0.6	0.6	0.6
Coupling agent	1.4	1.4	1.4
Silicone fluid (PDMS)	3	6	9
Solvent	12	12	12
Total weight:	100	100	100

The effect of coupling agent on RTV superhydrophobic coatings

The formulations are indicated in Table 3-7.

Table 3-7: The RTV superhydrophobic silicone coatings with coupling agent

	Sample Number		
	1	**2**	**3**
Component	**Wt (g)**	**Wt (g)**	**Wt (g)**
RTV Silicone	70	68.6	67.4
Hydrophobic additive	16	16	16
Dispersing additive	0.6	0.6	0.6
Coupling agent	1.4	2.8	4
Solvent	12	12	12
Total weight:	100	100	100

The coupling agent was mixed with superhydrophobic coatings containing 30 wt% hydrophobic additives (nano silica) to increase the adhesion of coatings to the substrate. The concentration of coupling agents in samples 1 to 3 was 2%, 4% and 6%.

Fluoropolyurethanes formualtions

Fluoropolyurethane coatings and hydrophobic additives

The hydrophobic additives were nano silica and ultrafine fluoric particles. The formulations that were used to make fluoropolyurethane coatings are indicated in Table 3-8.The hydrophobic additive fractions in samples of 1 to 4 were 10%, 20%, 30% and 40% respectively. The ratio of fluoropolyol to polyisocyanate (hardener) was 3 to 1.

Table 03-8: The fluoropolyurethane coatings and hydrophobic additives

	Sample Number			
	1	**2**	**3**	**4**
Component	**Wt (g)**	**Wt (g)**	**Wt (g)**	**Wt (g)**
Fluoropolyol	60	55	50	44
Polyisocyanate	20	18	16	14
Hydrophobic filler	6	13	20	28
Dispersing additive	0.5	0.5	0.5	0.5
Coupling agent	1.5	1.5	1.5	1.5
Solvent	12	12	12	12
Total weight:	100	100	100	100

Fluoropolyurethane coatings and hydrophobic fillers

The glass beads and nano calcium carbonate were treated by fluoroalkyl silane and treated powders were mixed with fluoropolyol. Final mixture was blended with hardener and applied on the surfaces. The hydrophobic additive fractions in samples of 1 to 4 were 10%, 20%, 30% and 40% respectively (Table 3-9). The ratio of fluoropolyol to polyisocyanate (hardener) was 3 to 1.

Table 03-9: The fluoropolyurethane coatings and hydrophobic fillers

	Sample Number			
	1	**2**	**3**	**4**
Component	**Wt (g)**	**Wt (g)**	**Wt (g)**	**Wt (g)**
Fluoropolyol	60	55	50	44
Polyisocyanate	20	18	16	14
Hydrophobic filler	6	13	20	28
Dispersing additive	0.5	0.5	0.5	0.5
Coupling agent	1.5	1.5	1.5	1.5
Solvent	12	12	12	12
Total weight:	100	100	100	100

Fluoropolyurethane coatings with the combination of hydrophobic nano silica and fillers

The combination of hydrophobic nano silica and fillers was added to fluoropolyol and the final mixtures were mixed with polyisocyanayes as hardener to make superhydrophobic coatings. The ultrafine fluoric particles with fluoropolyurethane coatings were not superhydrophobic, so these particles were not used in the combinations with fillers. The concentrations of hydrophobic additives were varied from 10 to 30 wt% while the fillers fractions (treated glass bead or treated nano calcium carbonate) were altered from 10 to 40 wt%. The following tables indicate the coating formulations. The highest combination fraction of hydrophobic additives and fillers was achieved in 50 w%. The Tables 3-10, 3-11 and 3-12 illustrate the coating formulations. The fractions of hydrophobic fillers in samples 1 to 4 (Table 3-10) were 10%, 20%, 30% and 40% respectively. The fractions of samples 1 to 3 (Table 3-11) were 10%, 20% and 30% respectively. The fractions of hydrophobic fillers in samples 1 to 2 (Table 3-12) were 10% and 20% respectively.

Table 3-10 : The fluoropolyurethane coatings with 10 wt% nano silica and hydrophobic fillers

	Sample Number			
	1	**2**	**3**	**4**
Component	**Wt (g)**	**Wt (g)**	**Wt (g)**	**Wt (g)**
Fluoropolyol	54	49.5	44.5	38.5
Polyisocyanate	18	16.5	14.5	12.5
Hydrophobic nano silica	7	7	7	7
Hydrophobic filler	7	13	20	28
Dispersing additive	0.6	0.6	0.6	0.6
Coupling agent	1.4	1.4	1.4	1.4
Solvent	12	12	12	12
Total weight:	100	100	100	100

Table 3-11: The coatings with 20 wt% nano silica and hydrophobic fillers

	Sample Number		
	1	**2**	**3**
Component	**Wt (g)**	**Wt (g)**	**Wt (g)**
Fluoropolyol	49.5	45	38.5
Polyisocyanate	16.5	15	12.5
Hydrophobic nano silica	13	13	13
Hydrophobic filler	7	13	22
Dispersing additive	0.6	0.6	0.6
Coupling agent	1.4	1.4	1.4
Solvent	12	12	12
Total weight:	100	100	100

Table 3-12: The coatings with 30 wt% nano silica and hydrophobic fillers

	Sample Number	
	1	**2**
Component	**Wt (g)**	**Wt (g)**
Fluoropolyol	45	38.5
Polyisocyanate	15	12.5
Hydrophobic nano silica	20	13
Hydrophobic filler	6	22
Dispersing additive	0.6	0.6
Coupling agent	1.4	1.4
Solvent	12	12
Total weight:	100	100

Fluoropolyurethane coatings with the combination of hydrophobic nano silica and ultrafine fluoric particles

As it emphasized before, the ultrafine fluoric particles could not make a superhydrophobic coating when used in fluoropolyurethane coatings. As a result, for improving the hydrophobicity of fluoropolyurethane coatings containing fluoric particles, the hydrophobic nano silica was mixed with coatings. The fractions of nano silica were varied from 10 to 30 wt% when the concentrations of ultrafine fluoric particle were changed from 10 to 30 wt%. The highest combination was got in 40% and after this point the dispersion of hydrophobic additives in coatings was not possible. The fractions of fluoric particles in samples 1 to 3 (Table 3-13) were 10%, 20% and 30% respectively. The fractions of fluoric particles in samples 1 to 2 (Table 3-14) were 10% and 20% respectively. The fractions of fluoric particles in sample 1 (Table 3-15) were 10%.

Table 03-13: The fluoropolyurethane coatings with 10 wt% nano silica and ultrafine fluoric particle

	Sample Number		
	1	**2**	**3**
Component	**Wt (g)**	**Wt (g)**	**Wt (g)**
Fluoropolyol	54	49.5	44.5
Polyisocyanate	18	16.5	14.5
Nano silica	7	7	7
Fluoric particle	7	13	20
Dispersing additive	0.6	0.6	0.6
Coupling agent	1.4	1.4	1.4
Solvent	12	12	12
Total weight:	100	100	100

Table 3-14: The coatings with 20 wt% nano silica and ultrafine fluoric particle

	Sample Number	
	1	**2**
Component	**Wt (g)**	**Wt (g)**
Fluoropolyol	49.5	45.5
Polyisocyanate	16.5	14.5
Hydrophobic nano silica	13	13
Hydrophobic filler	7	13
Dispersing additive	0.6	0.6
Coupling agent	1.4	1.4
Solvent	12	12
Total weight:	100	100

Table 03-15: The coatings with 30 wt% nano silica and ultrafine fluoric particle

	Sample Number
	1
Component	**Wt (g)**
Fluoropolyol	45.5
Polyisocyanate	14.5
Hydrophobic nano silica	20
Hydrophobic filler	6
Dispersing additive	0.6
Coupling agent	1.4
Solvent	12
Total weight:	100

The effect of coupling agent on fluoropolyurethane coatings

The coupling agent was mixed with fluoropolyurethane coatings containing 30wt% hydrophobic nano silica to increase the adhesion of coatings to the substrate. The concentration of coupling agents in samples 1 to 3 was 2%, 4% and 6%. The formulations in Table 3-16 were used to evaluate the role of coupling agents in RTV superhydrophobic coatings.

Table 3-16: Fluoropolyurethane coatings with coupling agents

	Sample Number		
	1	**2**	**3**
Component	**Wt (g)**	**Wt (g)**	**Wt (g)**
Fluoropolyol	50	48.5	47.5
Polyisocyanate	16	16	15.5
Nano silica	20	20	20
Dispersing additive	0.5	0.5	0.5
Coupling agent	1.5	3	4.5
Solvent	12	12	12
Total weight:	100	100	100

3-1-4 Characterization tests and methods

The most important tests for coatings are Contact and Sliding angles that demonstrate that the coating is superhydrophobic or not. Other tests like SEM picture, Immersion in water, Adhesion, UV durability, Hardness and Rubbing resistance were employed to evaluate the surface structure and mechanical/water durability of coatings. In addition, Inclined Plane Test (IPT) was used to evaluate the Erosion and Tracking resistance of superhydropobic RTV silicone rubber coatings. The methods with which these tests should be done will be discussed in the following:

Contact angles

Contact angles were measured by using Rame-Hart 100 Goniometer (Rame-Hart Instrument Compnay, USA) in this work. It has a horizontal microscope. A micrometric syringe was used to dispense a 10 μl droplet of deionized water on the coated surfaces. The slope of the tangent to the drop at the liquid-solid-air interface line indicated the contact angles. This method is named the sessile drop. Figure 3-2 displays the Goniometer that was used for this project. The contact angles of five different points on the coatings were measured and their averages were reported.

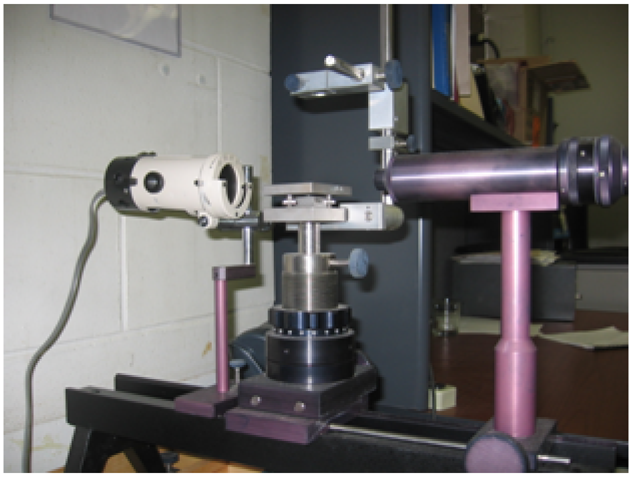


Figure 3-2: Contact angle goniometer

Sliding angles

Sliding angle exhibited the heterogeneity of surface and was measured by injecting a droplet on a surface and tilting the surface until the droplet starts to slide. The sliding angles of five different points on the coatings were measured and their averages were reported. Figure 3-3 indicates the angle instrument that was used.

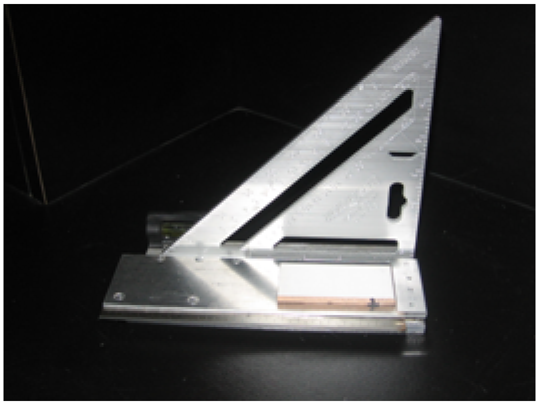


Figure 3-3: Sliding angle instrument

SEM pictures

The scanning electron microscopy (SEM) was utilized to verify the micro and/or nano structure of superhydrophobic coatings. The prepared samples were mounted on metal stubs by adhesive carbon tape and were sputter coated with (15 nm thick layer). A Hitachi S-2600 (Hitachi, Pleasonton, CA) SEM were used to examine gold-sputtered superhydrophobic coatings. Also the EDX (Energy Dispersive X-ray) was employed to identify the elemental composition of the specimens like treated nano calcium carbonate powder and superhydrophobic coatings.

Immersion in water

The samples of superhydrophobic coatings were immersed in water for 96 hours and then dried up in lab air to examine the durability of coatings with water immersion (Hillborg et al, 1999). The samples were naturally dried in lab air and their contact angles were measured after one and three days of air-drying to find the effect of water on hydrophobicity of coatings. For fluoropolyurethane coatings, the contact angles were demonstrated only after one day of air-drying because the fluoropolyurethane coatings cannot recover hydrophobicity like RTV silicone rubber coatings.

Adhesion test

Two different methods were used to measure the adhesion of superhydrophobic coatings. The first method was only for superhydrophobic RTV silicone coatings because these coatings should pass some special tests that can be used for high voltage insulators. Coated samples on ceramic tiles were immersed in boiling water for 100 hours and removed. Coatings that did not have good adhesion would show blisters at the interface of coating and ceramic substrate. This test was done according to IEEE STD 1523.

The other way to measure the adhesion of coatings to the substrate is based on ASTM D3359. In this method, the adhesion of coatings to the substrate was measured by using a Cross Hutch Cutter. It used a blade (11 mm by 1.5 mm) to cut the coatings that were applied on the metallic substrates. A grid of small squares was created by several perpendicular cuts. A standard adhesive tape was attached to the grid and it was withdrawn by a single smooth pull. As a result, some of the squares could be pulled off with the tape. The percentage of area that was removed from the cross cut surface indicated the adhesion of coatings. The best one should be at 0% and the worst one would be in higher than 65% according to standard. This method can be used for all types of coatings.

UV durability

It is one of the important factors that indicate how appropriate a superhydrophobic coating is for outdoor application. The coatings are exposed to natural and artificial sources of light. Weathering tests and UV durability of superhydrophobic coatings were done by Q-Sun Xenon Test Chamber (Q-Lab Company, USA). Following ASTM G155, this practice used xenon arc light and water apparatus to reproduce the weathering effects that happened when coatings are exposed to sunlight and moisture in actual use. The apparatus has one or more xenon-arc lamps. The light that is emitted by this instrument reproduces approximately the same spectrum of UV radiation received in the earth by means of a daylight filter. Also the intensity of light can be modified in the chamber.

Also the temperature, humidity and water flow should be controlled. Figure 3-4 illustrates the UV chambers that were utilized in this project.

Figure 3-4: UV test chamber

Before starting the test, the chamber radiometer and thermometer should be calibrated. Then the levels of irradiance, temperatures and spray times were programmed. The cycle takes two hours and when it finishes, it restarts again to continue the total process of exposure that is 1000 hours. Each cycle includes two steps that are: the first one is direct light with an irradiance of 0.35 $W/m^2/nm$ at a temperature of 63 ºC in dry conditions and takes 102 minutes. The second one is also direct light with an irradiance of 0.35 $W/m^2/nm$ at an uncontrolled temperature in water spray conditions and takes 18 minutes. Water spray is started for 20 seconds and stops for 40 seconds, and then the sequence is repeated, so this step is not continuous during 18 minutes. The light wavelength is 340 nm. The contact and sliding angles of coatings would be measured every 100 hours to find the hydrophobicity changes of coatings against UV radiation. The time 0 is the contact angle and sliding angle before starting the test.

Hardness

The ability of a coating to resist scratch from a hard object is referred to hardness. The test was done in accordance with ASTM D3363. Pencil test was employed to measure the hardness of coatings. A set of calibrated wood pencils with different scale of hardness was used which the softest was 6B and the hardest was 6H.

6B – 5B – 4B – 3B – 2B – B – HB – F – H – 2H – 3H – 4H – 5H – 6H

Firstly, 5mm to 6mm of wood were removed from the point of each pencil using a mechanical sharpener and then it was rubbed against an abrasive paper at a 90° angle until a flat smooth circular cross section was attained. The process was started with the hardest pencil and continued until a pencil did not scratch the paint film at all. The number of pencil in this point was reported as hardness. The angle of pencil with surface was 45º and a uniform pressure was applied forward and downwards to cut or scratch the coating. It was recommended that the stroke length to be 6.5 mm.

Rubbing resistance

The coating surfaces were rubbed by a 100% cotton cloth wrapped on a 1 cm × 1 cm ×1 cm cubic rubber head with 100 g normal force (Mozumder et al, 2008).

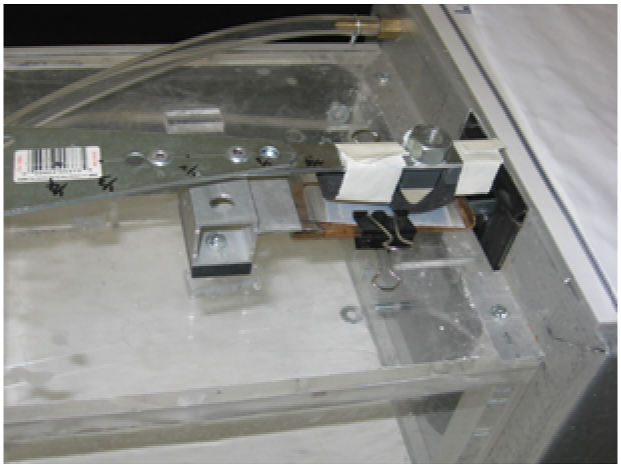


Figure 3-5: Rubbing durability instrument

The number of rubbing cycles performed before a remarkable alteration in water contact angle demonstrated the durability of superhydrophobic coatings. Figure 3-5 indicates the rubbing durability tester that was made in Dr Zhu`s group.

Inclined plane test

This test method is used to evaluate the relative tracking and erosion resistance of insulating solids by using the liquid contaminant, inclined-plane test. This test is consistent with ASTM- D2303. The erosion is defined as sever wearing of electrical insulation by electrical discharge and erosion resistance is the amount of electrical erosion. Also, the track is the conducting path of deterioration on the surface of insulators and track resistance is the amount of voltage and the time required to develop a track. This test method evaluates the resistance of electrical insulating material to the action of voltage stress along the insulator surface when it is contaminated with electrically conductive liquid. This test was used only for superhydrophobic RTV silicone rubber coatings that can be applied on the high voltage insulators. The voltage that is applied on the polymer is between 2 and 6 kV and a conductive liquid flows on the surface during the test. The coatings should pass the 3.25 kV that they can be used by industries. The conductive liquid includes 0.1% ammonium chloride and its flow rate is 0.15 mL/min. The six coated samples of each formulation were prepared. The ceramic slabs were 50 mm x 120 mm with about 0.2 mm thickness of coating.

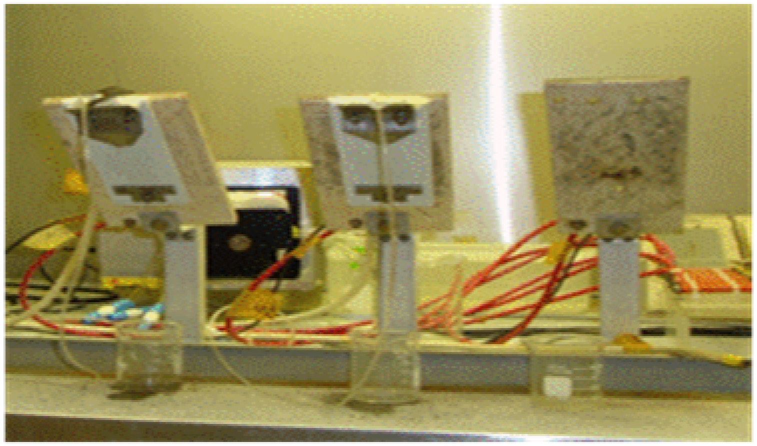


Figure 3-6: The samples in inclined plane test apparatus

The samples should be cleaned by isopropyl alcohol and washed with distilled water. The thicknesses of coatings were assured at 0.2 ± 0.02 mm. Inclined Plane Test was done by using the High Voltage Lab apparatus at the University of Waterloo. Figure 3-6 illustrates the samples in Inclined Plane Test Apparatus.

3-2 Icephobic coatings

For making icephobic coatings, fluorinated or silicone polymers that have shown lower ice adhesion than other coatings in the market were utilized. Also filler or additive and solvents were mixed by coatings.

3-2-1 Materials

The materials that were used in this study were:

Polymer systems

RTV silicone rubbers or fluoropolyurethane polymers that were used in superhydrophobic coatings were employed to make icephobic coatings. They were explained in the first part of this chapter.

Fillers or pigments

The graphite was mixed with coatings to reduce the adhesion of ice. Also, glass bead was added to coatings to break the ice. There was a big difference in the Coefficient of linear thermal expansions of glass bead and polymers, so this filler might inhibit ice formation. The physical properties of glass bead explained before and the specification of graphite are in the following:

Graphite

The trade name of used graphite was Timrex BNB90 and it was obtained from Timcal Company (Canada).

Density	2.2 (gr/cm^3)

Surface Area	12 m^2/gr

Additives

Deicers, fluorocarbon oil, silicone oil, Phase Change material (PCM), Super Absorbent Polymer (SAP) or hydrophobic additives were mixed by coatings as materials that might affect the adhesion of ice to the coatings. The materials properties are:

Deicers

They are used as deicers for roads and their advantage compared with salt is less corrosion. Cryotech CMA from Cryotech Company (USA) was used here. It is granulated calcium magnesium acetate and its density is 0.65 g/cm^3.

Fluorocarbon oil

It can reduce the adhesion of ice to the surface by establishing a weak boundary layer between ice and coatings. Its trade name was Kryotex 143 AD and was received from DuPont Company (USA).

Density	1.95 (gr/cm^3)
Viscosity	500 cSt
Molecular weight	8250

Silicone oil

It is used as mold release agent in the industry, so it may reduce ice adhesion. The trade name of silicone oil was TPR Silicone and it was got from Wacker Company (USA).

Density	1.02 (gr/cm^3)
Viscosity	325 mm^2/s

PCM

PCM or phase change materials were added to coatings because they made volume changes when they were converted from liquid to solid in their melting points.

The PCM that utilized here was n-Dodecane from Alfa Aesar Company (USA).

Density 0.749 (gr/cm^3)
Melting point: -10º
Boiling point: 215º

SAP (Super Absorbent Polymer)

These polymers can absorb a big volume of water and go through high volume changes, so they may break the ice on the coatings. Its trade name was Waste Lock 770 and was obtained from M2 Polymer Technology (USA). It could absorb distilled water 400-500 times its weight.

Solvents

The same solvents that were used in superhydrophobic coatings were blended by icephobic coatings. They described in the first part of this chapter.

3-2-2 Preparation method

The samples of coatings were made from the blending of RTV silicone rubber or fluoropolyol with fillers or additives. They were mixed in the ball mills and the solvents were used to adjust the viscosity. The final dispersion of fluoropolyol and fillers or additives should be mixed with hardener (polyisocyanates). Final coatings were applied by spray gun on the substrates and cured in room temperature.

3-2-3 Experimental formulations

Superhydrophobic coatings were made from the blending of hydrophobic nano silica and RTV silicone rubber or fluoropolyurethane coatings. Also other ice phobic coatings were made from the blending of hydrophobic nano silica with fillers or other additives like silicone oils. The icephobic coatings were made from SAP or glass bead (has higher coefficient of thermal expansion than polymers) too. The samples coated by ice phobic coatings were held in the freezer and cold water were sprayed on them. The coated samples were compared with bared samples. The icephobic coatings formulations that were prepared are in the following:

RTV silicone rubber or fluoropolyurethane coatings and hydrophobic nano silica

The hydrophobic nano silica exhibited higher contact angles compared with ultrafine fluoric particles in superhydrophobic coatings, so it was mixed in two concentrations (30 and 40 wt %) with RTV silicone rubber or fluoropolyurethane coatings. The formulations were same as superhydrophobic coatings that indicated in the first part of this chapter.

RTV silicone rubber or fluoropolyurethane coatings including nano silica and graphite, deicers, PCM or oils (fluoro or silicone oils)

The concentration of nano silica was 30% and other materials concentrations were 5%, 10% and 20 wt% in samples 1 to 3 respectively in dry film. The formulations of RTV silicone coatings are shown in Tables 3-17 and 3-18.

Table 03-17: RTV silicone rubber with nano silica and graphite or other additives

	Sample Number		
	1	2	3
Component	**Wt (g)**	**Wt (g)**	**Wt (g)**
RTV Silicone	68	64.5	58.5
Nnao silica	17	17	17
Dispersing additive	0.5	0.5	0.5
Graphite or other additives	2.5	6	12
Solvent	12	12	12
Total weight:	100	100	100

Table 3-18: Fluoropolyurethane coatings with nano silica and graphite or other additives

	Sample Number		
	1	2	3
Component	**Wt (g)**	**Wt (g)**	**Wt (g)**
Fluoropolyol	48	45.5	40
Polyisocyanates	16	15	13.5
Nnao silica	20	20	20
Dispersing additive	0.5	0.5	0.5
Graphite or other additives	3.5	7	14
Solvent	12	12	12
Total weight:	100	100	100

RTV silicone rubber or fluoropolyurethane coatings and glass bead

There is a big difference in the Coefficient of Linear Thermal Expansion of polymers and glass bead, so it is possible that the coatings containing glass bead break the ice. The concentration of glass bead in coatings was 40 wt%. Tables 3-19 and 3-20 display the formulations that were prepared.

Table 03-19: RTV silicone rubber and glass bead

	Sample Number
	1
Component	**Wt (g)**
RTV Silicone rubber	65.5
Dispersing additive	0.5
Glass bead	22
Solvent	12
Total weight:	100

Table 03-20: Fluoropolyurethane and glass bead

	Sample Number
	1
Component	**Wt (g)**
Fluoropolyol	45.5
Polyisocyanates	15
Dispersing additive	0.5
Glass bead	27
Solvent	12
Total weight:	100

Icephobic coatings with Super Absorbent Polymers (SAP)

The samples are prepared from two following methods:

1) Mix fluoropolyurethane coatings and SAP

The samples were made according to Table 3-21. The concentration of SAP is between 20 to 30% in samples 1 and 2.

Table 3-21: Fluoropolyurethane coatings with SAP

	Sample Number	
	1	**2**
Component	**Wt (g)**	**Wt (g)**
Fluoropolyol	55	50
Polyisocyanate	18.5	16.5
Filler (SAP)	14	21
Dispersing additive	0.5	0.5
Solvent	12	12
Total weight:	100	100

2) The RTV silicone coatings (without any filler or additive) as second coatings were sprayed on the fluoropolyurethane coatings with SAP (they prepared according to Tables 3-21). The samples that had two layers of coatings (one layer is fluoropolyurethane coating with SAP and the second one is RTV silicone coating) were put in the freezer.

3-3 Conductive coatings

The conductive coatings were made from the blending of epoxy resins or polyurethane resins with conductive fillers. First, different conductive fillers were mixed by epoxy resin to find the range of resistivity of final coatings. Second, the nano clay was mixed with conductive coatings. Also mesh coatings were made from silver ink or graphite ink. The materials used are described below:

3-3-1 Materials

The resins, conductive pigments, additives and solvents were used to make conductive coatings. Also conductive inks were used in this study. The materials are discussed in the following:

Resins

The polyurethane and epoxy resins that are used in the market for making conductive coatings were utilized here.

Epoxy resins

The epoxy coatings were made from the blending of epoxy resin with polyamine hardener. The trade name of epoxy resin was Araldite GZ471-X75 from Huntsman Company (Germany).

Epoxy value	1.89-2.22 eq/kg
Viscosity	4500-9000 cPs
Density	1.8 gr/cm^3
Solid content	75 wt%

The polyamine trade name was Aradur 283 from Huntsman Company (Germany).

H active equivalent	133g/eq
Density	1 gr/ cm^3
Solid content	100 wt%

Polyurethane resins

Polyurethane coatings were prepared from the mixing of polyols and polyisocyanates. The polyols trade name was Desmophen A-160 SN from Bayer Company (Germany).

Specific gravity	1
OH content	1.6%
Viscosity	2800 mPa.s
Solid content	60%

The polyisocyanates trade name was Desmodure N75-BA from Bayer Company (Germany).

Density	1.06 (gr/cm^3)
Viscosity	160 (mPa.s)
NCO content	16.5%
Solid content	75 wt%

Pigments or fillers

Conductive carbon black, conductive graphite, nickel coated carbon fiber, nickel graphite, silver coated glass spheres, silver coated nickel and gold nickel coated carbon fiber were used as conductive pigments and nano clay as filler. These materials are noted below:

Conductive carbon black

The trade name was Ensaco 350G from Timcal Company (Canada).

Surface Area	770 m^2/gr
Oil absorption	320ml/100gr

Conductive graphite

The trade name of used graphite was Timrex BNB90 and it was obtained from Timcal Company (Canada).

Density	2.2 gr/cm^3
Surface Area	12 m^2/gr

Nickel coated carbon fiber

Its trade name was E-Fill 2901 from Sulzer Metco Company (Canada). This pigment includes 67% nickel.

Particle Density	3.8 gr/cm^3
Average particle size	70 µm

Nickel graphite

It was from Novamet Company (USA).

Particle Density	3.6 gr/cm^3
Average particle size	80 µm

Silver coated glass spheres

Its trade name was GL-0279 from MO-SCI Specialty Products (USA).

Specicfic Gravity	2.5 gr/cm^3
Softening temperature	650 ºC

Silver coated nickel

It was from Novamet Company (USA).

Particle Density	5 gr/cm^3
Average particle size	40 µm

Gold nickel coated carbon fiber

It was from Sulzer Metco Company (Canada).

Particle Density	4 gr/cm^3
Average particle size	70 µm

Nano clay

It was added to conductive coatings to improve its electrical and mechanical properties. Two grades of nano clays from Southern Clay Products (USA) were used. The trade name of first clay was Claytone HT. It is a modified montmorillonite.

Specific Gravity	1.7
Average particle size	25 µm

The trade name of second nano clays were Cloisite 30B. It is a natural montmorillonite modified with a ternary ammonium salt.

Density	1.98 gr/cm^3
Average particle size	6 µm

Additives

Dispersing aid, polypropylene, hammer finishes and surfactant were used as additives. They are discussed below:

Dispersing aid

The trade name of dispersing additive was Aerosil 200 from Degussa Company (Germany).

Specific gravity (water): 2.2

Median particle size: 12 Nanometer

Surface area:	200 m^2/gr

Polypropylene

It was added to conductive ink to make mesh coatings and was from Aldrich Company (USA).

Density	0.9 gr/cm^3
Viscosity	6 poise
Melting Point	157 ºC

Hammer finishes

They were added to conductive ink to make mesh coatings. Its trade name was Tego Hammer 300000 and was from Tego Company (Germany).

Color	clear, colorless liquid
Active matter content	100%

Surfactant

It was used to make emulsion conductive mesh coatings. Its trade name was Arlacel P135 from Croda Company (UK).

Molecular weight	4400
HLB	5-6

Solvents

The solvents should be selected according to polymer structures. Methyl ethyl ketone, acetone, toluene, Methyl isobutyl ketone and reatrder were used in this project that will be discussed below (methyl ethyl ketone and toluene were discussed before):

Acetone

It was from Aldrich Company (USA).

Density	0.792 gr/cm^3
Boiling point	56.5 ºC

Methyl isobutyl ketone

It was from Sun Chem Company (USA) and its trade name was reducer E-25.

Density	0.8 gr/cm^3
Boiling point	117 ºC

Retarder

It was from Sun Chem Company (USA) and its trade name was Retarder- E10. It was used to reduce the evaporation rate of solvents in mesh conductive coatings.

Conductive inks

Two types of conductive inks from Sun Chem Company (USA) were used here. The first one was Silver ink and its trade name was E-8205.

Specific gravity	2.3
Viscosity	70Poise
Sheet resistivity	<0.04 Ω/sq

The second conductive ink was graphite ink and its trade name was E-8203.

Specific gravity	1.2
Viscosity	90Poise
Sheet resistivity	< 40 Ω/sq

3-3-2 Methods

The conductive coatings were made from the blending epoxy resin or polyols resins with conductive pigments, additives and solvent in a wet lab ball mill. Final dispersion was mixed with polyamine or polyisocyanates as hardener. Final coatings were sprayed on the metallic or glass surfaces and cured in room temperature. Nano clay conductive coatings were made by the mixing of nano clay and conductive coatings too.

To make conductive mesh coatings, conductive inks that had finer particles were used to make better meshes. Mesh coatings were prepared from following methods:

1) Conductive inks were mixed with polypropylene and final coatings sprayed on glass and cured at 150 ºC for 15 minutes.
2) Conductive ink was thinned with solvent and hammer finishes additive was added to it. Final coatings were applied by Mayer bar and cured at 120 ºC for 15 minutes.
3) Conductive ink was thinned with solvents. Then surfactant was added to them. When the surfactant was dissolved in coating, water was added drop wise to the coatings. Final coatings were applied by Mayer bar and cured at 120 ºC for 15 minutes.

3-3-3 Experimental formulations

The conductive coatings with epoxy resins and conductive pigments were prepared to find the range of conductivity with each pigment. Also nano clay conductive coatings were made from the mixing of polyurethane resins with nickel coated carbon fiber. The properties of nano clay polyurethane conductive coatings were compared with epoxy conductive coatings including nano clay. Also the effect of nano clay on polyurethane coatings with two different conductive pigments was evaluated. The effect of mixing time and resin to hardener ratio in nano clay polyurethane conductive coatings were examined too. The conductive mesh coatings were made from the mixing of silver or graphite ink with polypropylene, hammer finishes additives or water (emulsion). Also, the effect of surfactant concentration, retarder concentration, solvent type and the effect of curing process in emulsion conductive mesh coatings were evaluated. The formulations of continuous conductive coatings and mesh coatings will be discussed in the following:

Continuous conductive coatings

Epoxy resin coatings with conductive pigments

The samples that should be prepared are in Table 3-22. The concentration of conductive pigments (in dry film) in samples 1 to 6 were 10%, 20%, 30%, 40%, 50% and 60% respectively.

Table 3-22: The formulations of epoxy conductive coatings

	Sample Number					
	1	**2**	**3**	**4**	**5**	**6**
Component	**Wt (g)**	**Wt (g)**	**Wt (g)**	**Wt (g)**	**Wt (g)**	**Wt (g)**
Epoxy resin	62	55	48	43	37	30
Hardener	15	14	12	11	9	8
Pigment	7	15	24	30	38	46
Dispersing additive	1	1	1	1	1	1
Solvent	15	15	15	15	15	15
Total weight:	100	100	100	100	100	100

Conductive coatings with nanoclay

The polyurethane coatings including 35 wt% nickel coated carbon fiber were mixed with different nano clay fractions. Nano clay concentrations were varied from 2 to 8 wt% in samples 1 to 4. Two different sizes of nano clay (5 and 25 µm) were used. Nickel coated carbon fiber was selected in accordance with the results of epoxy conductive coatings that showed metal (nickel or gold) coated carbon pigments were dispersed better than other pigments in the coatings. Also, the point of 35% chose to find that how much nano clay could improve the electrical properties of coatings. Table 3-23 illustrats the formulations of polyurethane conductive coatings with nano clay. Also the results of polyurethane conductive coatings with nano clay compared with the results of epoxy conductive coatings with nano clay.

Table 3-23: The formulations of polyurethane conductive coatings with nano clay

	Sample Number			
	1	**2**	**3**	**4**
Component	**Wt (g)**	**Wt (g)**	**Wt (g)**	**Wt (g)**
Polyol	50	49	48.5	47.5
Polyisocyanates	12.5	12	11	10.5
Nanoclay	1.5	3	4.5	6
Pigment	23	23	23	23
Dispersing additive	1	1	1	1
Solvent	12	12	12	12
Total weight:	100	100	100	100

Conductive mesh coatings

Conductive ink with polypropylene or hammer finishes additive

The polypropylenes were added in two fractions: 20 and 25 wt%. Also, the hammer finishes additive was mixed with conductive ink in two concentrations: 0.05 and 0.1wt% of total formulations.

Conductive emulsion coatings

These coatings were prepared from the mixing of water and surfactant in conductive ink. The water concentrations in samples 1 to 3 were 40, 45 and 50 vol% respectively. Table 3-24 demonstrats the formulations that were used.

Table 03-24: Conductive emulsion coatings

	Sample Number		
	1	**2**	**3**
Component	**Wt (g)**	**Wt (g)**	**Wt (g)**
Conductive ink	48	45	42
Solvent	15	15	15
Retarder	2	2	2
Surfactant	5	5	5
Water	30	33	36
Total weight:	100	100	100

3-3-4 Characterization tests and methods

The most important test for conductive coatings is surface resistivity which demonstrates that the coating is conductive or not. Other tests like SEM picture, high magnification microscope, adhesion, corrosion resistance, hardness and impact resistance were employed to evaluate the surface structure and mechanical durability of coatings. The methods that these tests should be done will be discussed in the following:

Resistivity

The material`s intrinsic surface resistance to current flow multiplied by that ratio of specimen surface dimensions is named surface resistivity. According to Ohm`s law for circuit theory, the resistance of a material is calculated by following equation:

$$R = V/I$$

Where: R is resistance (ohms), V is voltage (volts) and I is current (amperes). This electrical resistance is related to sample`s length, resistivity and sample`s cross sectional area in accordance with below equation:

$$R = \rho\, l/A$$

Where: ρ is the resistivity, l is length and A is cross sectional area. This resistivity is defined as volume resistivity and its unit is Ωm. The volume resistivity of coatings does not change with thickness, but surface resistivity is changed by thickness. The unit of surface resistivity is Ω/sq. A square sheet with sheet resistance 1 ohm/square has an actual resistance of 1 ohm, regardless of the size of the square and it is the reason for the name of ohm per square. The resistivity is the reciprocal of conductivity (σ) and the unit of conductivity is Siemens per meter (S/m).

One of the common methods for measuring resistivity that was used in this work is four point probe method. It was done according to ASTM D4496-04. The probes aligned linearly or in a square pattern that contacts the surface of coatings were used. The resistivity was checked in five different points and their average was reported. The resistivity error range was ±5 Ω/sq. Figure 3-7 displays the four point probe instruments that were used in this work. It was made by Four Probes Tech Company (China).

Figure 3-7: Four point probe instrument

SEM picture

The scanning electron microscopy (SEM) was utilized to evaluate the cross section of conductive coatings. The instrument was explained before in superhydrophobic coatings.

High magnification microscope (Optical)

It was used to evaluate the shape of meshes in conductive mesh coatings. An optical microscope (Opti-Tech, Canada) was utilized.

Adhesion

The adhesion of conductive coatings was measured in accordance with ASTM D3359 – 09. The method of test was described before in superhydrophobic coatings.

Corrosion resistance

This test evaluates the ability of conductive coatings to withstand a specific corrosive environment. This was utilized to assess the effect of nano clay fraction on the corrosion resistance of conductive coatings. A sealed chamber which is filled with a saturated fog of a particular corrosive solution was used to hold the test panels. The corrosive solution was made of sodium chloride (NaCl) in water and the levels of exposure were 500 hours. The test was done according to ASTM D1654 – 08. 5 ± 1 parts by mass of sodium chloride in 95 parts of distilled water were dissolved to prepare salt solution. The salt that used included maximum of 0.1% sodium iodide and a maximum of 0.3% of total impurities and was free of nickel and copper. Also compressed air was used to feed the nozzle that atomizes the salt solution into the testing section of the chamber. The air pressure was set at 103 KPa. The salt spray instrument was made by Associated Environmental Systems (USA) and its model was MX-9204. It included a fog chamber, a salt solution tank, a distilled water tower, an atomizing nozzle, an air line to supply compressed air, panel supports, a space heater for the chamber, a heater for the water tower, a pressure gauge and thermometer for the water tower and a thermometer for the chamber. Figure 3-8 illustrates the slat spray instrument that was utilized in this work.

The chamber had an exhaust to remove the excess fog from it and was equipped with independent drains for the testing compartment, salt solution reservoir and water tower. The coated samples should be prepared before salt spray test. A sharp object was used to scribe two lines in form of an X on the surface and to expose the bare surface. Then samples were placed in the test chamber and suspended from the holding bars.

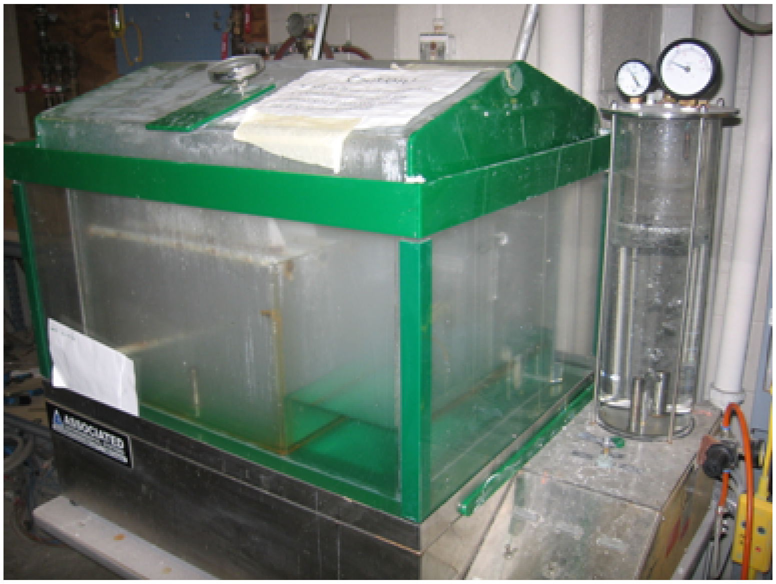


Figure 3-8: Salt spray chamber

The angle of samples from the vertical was 20º. Also they were placed in a way that the free settling of the fog on their surface was possible and no condensation dripped onto another panel. The adhesion test and resistivity test were used after 500 hours salt spray test to evaluate the corrosion resistance of conductive coatings with nano clay.

Impact resistance

This test was used to give an indication of conductive coatings behavior when it is subjected to an object of considerable mass. After applying impact to the sample panels, cracks in the coating and spots where the paint had chipped off the testing panel were evaluated. The test was done regarding to ASTM D2794. The name of used apparatus was variable height impact tester. It had a slot lengthwise acting as a guide for the free falling cylindrical weight and consisted of a vertical guide tube 0.6m to 1.2m long. The cylinder weight was 1.82 kg. For doing test, the coated panel was placed on the panel support and then, the weight was lifted up to the desired height using the scale. Once the weight arrived to desire height, it felt freely on the panel making an indentation on it. The conductive coatings samples were tested with the height in 20mm.

CHAPTER 4

Superhydrophobic RTV silicone rubber coatings

4-1 Introduction

In chemistry, hydrophobicity (from the combining form of water in Attic Greek hydro- and for fear phobos) refers to the physical property of a molecule (known as a hydrophobe) that is repelled from a mass of water. Hydrophobic molecules tend to be non-polar and thus prefer other neutral molecules and nonpolar solvents. Hydrophobic molecules in water often cluster together forming micelles. Water on hydrophobic surfaces will exhibit a high contact angle. Examples of hydrophobic molecules include the alkanes, oils, fats, and greasy substances in general. Hydrophobic materials are used for oil removal from water, the management of oil spills, and chemical separation processes to remove non-polar from polar compounds. Hydrophobic molecules are also called lipophilic because they will dissolve in oils and other lipids. They tend to be electrically neutral and nonpolar and work better with neutral and nonpolar solvents. The highly hydrophobic surfaces such are named superhydrophobic surfaces (Hill, 1998).

There are many surfaces in the nature that exhibits superhydrophobic property. For examples, the wings of butterflies and the leaves of plants such as cabbage and Indian cress. Also the wetting of some detrimental plants such as gorse or common yard weeds with water-based herbicides is very difficult because they have waxy leave surfaces. To solve this problem, trisiloxane superwetters were developed for their significant ability to wet such hard-to-wet surfaces and improve herbicide efficacy (Hill, 1998). One of the best examples of the superhydrophobic surfaces in the nature is the leaves of lotus plant. Figure 4-1 indicated the water droplet on the lotus leaf. The variability of cell shapes, micro- and nanostructures on the cell surfaces, and the formation of multicellular structures define the multiplicity of plant surface structure. The outermost cell layer of all primary plant surfaces is the epidermal cells. The cuticle is the outermost layer of the epidermis. The cuticle is absent in roots and secondary tissues while it covers nearly all aerial tissues of land living plants as a continuous extracellular membrane. The cuticle includes an epicuticular wax that has an important role in surface structure. The lignin and cutin form the cuticle network. The next layer is pectin that is a complex polysaccharide and connects the cuticle to the much thicker underlying cellulose wall. The plasma membrane is the last layer and separates the living section of the water-containing cell from the outer non-living part of the epidermis (Koch et al, 2009).

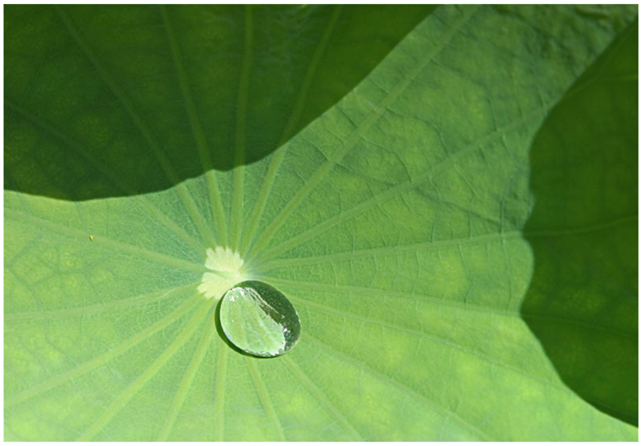


Figure 4-1: The water droplet on the lotus surface

(Source: http://www.pbase.com/image/32993464)

The single epidermal cell is the basic unit for plant surface structuring. The basic cell curvature can be tabular (flat), convex (arced to the outside) and concave. However, the convex form is the common cell shape. Convex cells can be segregated into several subtypes, such as hemisphere, cupola, cone, papilla, hair papilla and hair (Bhushan et al, 2008). The epicuticular waxes and cuticular patterns are two kinds of cell surface structuring in plants. A white or bluish coloration of leaves and fruits, such as grapes and plums is related to epicuticular waxes. The mixture of aliphatic and cyclo hydrocarbons forms plant waxes (Muller et al, 2005). It has been shown that the water-repellant plants have hierarchical surface structures that are formed by convex to papillose epidermal cells and a very dense arrangement of three-dimensional epicuticular waxes of different shapes. The hairs, convex or papillose epidermal cells, and superimposed three-dimensional waxes form the multiple-length-scale roughness on the plant surfaces. The self-cleaning of plant surfaces can protect them against particle accumulation. The gas exchanges reduce dramatically because Superhydrophobicity prevents the formation of water films on the surface. The uptake of CO_2 for photosynthesis on wet leaves is reduced because CO_2 diffuses 10000 times more slowly through water than air. As a result, superhydrophobicity can protect terrestrial plant surfaces against pathogen by self-cleaning or by the reduction of water availability for the micro-organism. An intrinsic hierarchical surface structure built by randomly oriented small hydrophobic wax tubules on the top of convex cell papillae is attributed to superhydrophobicity of lotus leaf. The air is trapped in the cavities of the convex cell sculptures and it minimizes the wetting of such hierarchical surfaces. Also the solid–water interface is reduced while the hierarchical roughness enlarges the water–air interface. The contact area and the adhesion to these surfaces are considerably reduced and water gains very little energy through absorption and forms a spherical droplet on them (Extrand, 2005; Li et al 2008). The Lotus effect refers to the very high water repellency (superhydrophobicity) exhibited by the leaves and flowers of lotus plant. Lotus flower is known in several Asian countries as a symbol of purity. This definition is related to self-cleaning property of its leaves. “This property has been studied intensively by the two botanists Barthlott and Neinhuis from the University of Bonn. They discovered the reason for this self-cleansing effect” Before their founding, people thought that smoother surfaces have less dirt and adhesion of water. By using SEM (Scanning Electron Microscopy) they discovered that the surface of lotus leaf is not smooth. The lotus leaf has a nano and microstructure that makes the surface rough. Dirt particles are picked up by water droplets due to this structure (Wang et al, 2006).

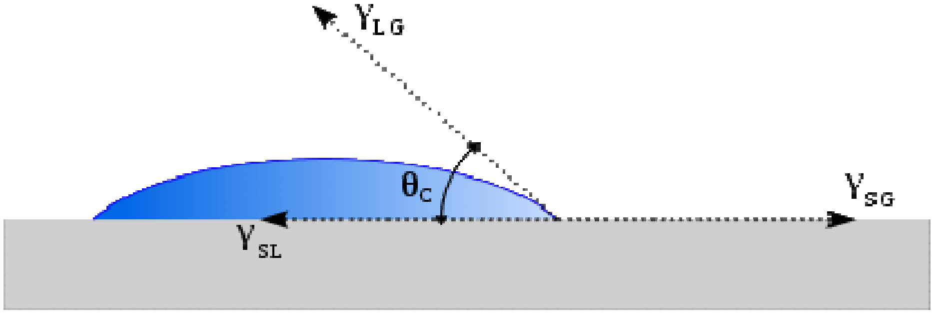
To understand superhydrophobic properties, it is necessary to look at Young theory (Erbil, 2006). In 1805 Thomas Young defined the contact angle θ by analyzing the forces acting on a fluid droplet resting on a solid surface surrounded by a gas (Figure 4-2).

$$\gamma_{SG} = \gamma_{SL} + \gamma_{LG} \cos\theta$$

Where: $\gamma_{SG} =$ Interfacial tension between the solid and gas

$\gamma_{SL} =$ Interfacial tension between the solid and liquid

γ_{LG} = Interfacial tension between the liquid and gas



.svg)

The shape of drop on the surface is related to these forces. The roughness can decrease the wettability for hydrophobic surfaces (θ>90). Hydrophobic surface can increase water-repellency. The droplet on a superhydrophobic surface (θ>130) rolls off and can clean surface from contamination; because the force of contamination absorption to droplet is higher than static force between contamination and surface. This property is named self-cleaning and have a lot of application in the industries.

There are apparent contact angles in the superhydrophobic surfaces that were introduced by Wenzel (1936) and Cassie-Baxter (1944) to define the topography and roughness of surfaces. Wenzel determined that the θ will be converted to θ* (apparent contact angle) when the liquid fills the voids below the liquid and thus occupies more surface area. He stated when the contact angle is higher than 90º the surfaces become more hydrophobic and there is a relation between apparent contact angle and roughness (r) as in the following:

$$\cos\theta^* = r \cos\theta$$

This equation indicates that microstructuring a surface magnify the natural tendency of the surface. The droplet in Wenzel state is in intimate contact with the solid asperities and the contact angle of surface will rise when the roughness increases. However, Cassie-Baxter demonstrated that if the droplet rests on the top of solid asperities, θ will change to θ_{CB} as in the below equation:

$$\cos\theta_{CB}{}^{*} = \varphi(\cos\theta + 1) - 1$$

The φ is the area fraction of the solid that touches the liquid. In this state, the gas left in the voids below the drop and the surface area is less than a drop of the same volume and apparent contact angle on a flat surface or a rough surface in a Wenzel state. Liquid in Cassie state is more mobile than Wenzel and shows better superhydrophobicity (Bormashenko, 2008). The Figure 4-3 indicates the Wenzel and Cassie-Baxter.

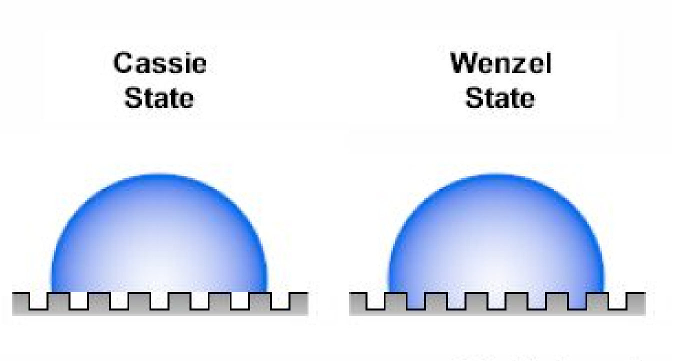


Figure 4-3: The droplet resting on a solid in Wenzel and Cassie-Baxter state

(Source: http://www.ramehart.com/newsletters/2008-09_news.htm)

Contact angle is a static measure, but contact angle hysteresis (CAH) and slide angle are dynamic measure. Surface heterogeneity is evaluated by Contact angle hysteresis. When a pipette injects a liquid onto a solid, the liquid will form a contact angle. When increase the amount of liquid by pipette, the volume of droplet and its contact angle will increase, but its boundary will remain constant until it suddenly advances outward. The contact angle of the droplet immediately before advancing outward is named advancing contact angle. The receding contact angle is measured when we pumped liquid from the droplet. In this case, the volume and contact angle of droplet will reduce, but its boundary will remain constant until it suddenly recedes inward. The difference between these two angles is named contact angle hysteresis (CAH). The slide angle also is measured by injecting a droplet on a surface and tilting the surface until the droplet start to slide. Superhydrophobic surfaces have low contact angle hysteresis and sliding angle. The self-cleaning property is attributed to Superhydrophobicity in combination with a low contact angle hysteresis. Water droplets on these surfaces can pick up dirt particles and remove contaminations. The surfaces in Cassie state indicates CAH less than 10 while the surfaces in Wenzel state shows CAH between 20 and 50, so the surfaces in Cassie situation exhibits self-cleaning properties. As a result, for fabricating self-cleaning property, the contact angles should be higher than 130º and Contac Angle Hysteresis or sliding angle less than 10º. The fabrication of super hydrophobic surfaces, mimicking the special nature of lotus leaf property, with contact angles higher than 140° has been found growing interest among many researchers around the world. It has been shown by the electron microscopy of the surface of lotus leaves that there are protruding nubs about 20–40 μm apart each covered with a smaller scale rough surface of epicuticular wax crystalloids. The combination of micrometer-scale and/or nanometer-scale roughness, along with a low surface energy material leads to self-cleaning properties in lotus leaf (Barthlott et al, 1997). As a result, fabricating self-cleaning surfaces requires low surface energy materials along with micro and/or nano scale roughness on top of the surface.

4-2 The fabricating methods of superhydrophibc surfaces

The enormous works has been made to develop lotus leaf superhydrophobic surfaces. The most important methods have been discussed below:

Roughening of organic or inorganic materials

The silicone and fluoropolymers have been used in producing superhydrophopbic surfaces due to extremely low surface energies. Zhang et al (2004) stretched a poly tetrafluoroethylene (Teflon) film to attain a superhydrophobic film. They increased the axial extension ratio perpendicular to the fibrous crystals from 5 to 190% of the teflon tape and found that contact angle raised from 118 to 165º. The high water contact angle is attributed to the fibrous crystals and the rising distance between the fibrous crystals. Also Singh et al (2005) produced poly [bis(2,2,2-trifluoroethoxy)phosphazene] by electrospinning from solutions in tetrahydrofuran, methylethyl ketone, and acetone. The changes in the concentration of the polymer solution can vary the fiber diameter from 80 nm to 1.4 μm. The contact angles changed in the range of 135°−159° when the fiber diameter and surface morphology varied. The PDMS is another well known low surface energy material. Khorasani et al (2005) used a CO2-pulsed laser as an excitation source to treat PDMS. The contact angle reached 175º because of both the porosity and chain ordering on the polymer surface. Ma et al (2005) employed electrospining to make a superhydrophobic membrane in the form of a nonwoven fiber mat from PS-PDMS block copolymer blended with PS homopolymer. The surface roughness because of small fiber diameters (150 nm to 400 nm) and the combination of enrichment of PDMS component on fiber surfaces lead to the contact angle of 163º. The membrane should have good flexibility, breathability and free-standing feature to be used in textile and biomedical applications. Lu et al (2004) fabricated a highly porous superhydrophobic surface of polyethylene (PE) by controlling its crystallization behavior. It was a simple and inexpensive method. They added nonsolvent (cyclohexanone) to the PE/xylene solution to form nanostructured floral-like crystal structures. The contact angle of up to 173º was achieved from this way. Lee et al (2004) used nanoporous anodic aluminum oxide as a replication template to produce vertically aligned PS nanofibers in a heat- and pressure-driven nanoimprint pattern transfer process. When the aspect ratio of the PS nanofibers enlarged, the nanofibers could not stand upright and formed twisted bundles that lead to a three-dimensionally rough surface. This surface indicated contact angle hysteresis of 4º. Also some inorganic material has been employed to produce superhydrophobic surfaces. Feng et al (2005) synthesized the TiO_2 nanorods from a two-step solution method. They employed a low-temperature hydrothermal approach to deposit TiO_2 nanorod films on glass substrates. The supersaturated titanium trichloride aqueous solutions with sodium chloride were heated at 160 ºC for 2 hours. Then the films were deposited on glass wafers and were rinsed thoroughly with deionized water and ethanol. Finally, the samples dried at room temperature. The nanorod films exhibited contact angle of 154º owing to the surface roughness and the low surface energy.

Etching and lithography method

Etching is employed to make a rough surface. Plasma etching, laser etching and chemical etching have all been used in the past years to fabricate superhydrophobic surfaces. Teshima et al (2005) utilized selective oxygen plasma etching that is followed by plasma-enhanced chemical vapor deposition using tetramethylsilane (TMS) as the precursor to make a transparent superhydrophobic surface from a poly(ethylene terephthalate) (PET). The contact angles of PET films were higher than 150º. Qian et al (2005) used simple chemical etching for the fabrication of superhydrophobic surfaces on three polycrystalline metals, namely aluminum, copper, and zinc. The etching was done by dislocation etchant that preferentially dissolves the dislocation sites in the grains. Then etched metallic surfaces were hydrophobized by fluoroalkylsilane and showed contact angles larger than 150º and sliding angles less than 10º. Another technique that has been utilized to create large area micro-/nanopatterns is Lithography. It may include photolithography, electron beam lithography, X-ray lithography, soft lithography and nanosphere lithography. Callies et al (2005) described a conventional photographic method to make silicon wafer patterns. The wafers were pre-heated at 125 ºC for 1 min before exposing to UV radiation for 15 seconds. Finally, the samples were developed. The surfaces demonstrated contact angles higher than 150º. Also Martines et al (2005) employed electron beam lithography and plasma etching to fabricate ordered arrays of nanopits and nanopillars. They hydrophobized surfaces including tall pillars with cusped tops by octadecyltricholorosilane and attained surfaces with CA of 164º and contact angle hysteresis of 3º.

Sol-Gel method

Water-repellent coatings derived from the sol–gel process have been investigated in recent years because of their high commercial and industrial importance. They are typically produced by Sol-Gel treatments with Fluoroalkylsilane (FAS) or Polydimethylsilicone (PDMS). The sol-gel process is a wet-chemical technique (Chemical Solution Deposition) for the fabrication of materials starting either from a chemical solution (sol short for solution) or colloidal particles (sol for nanoscale particle) to produce an integrated network (gel). The dispersions of colloidal particles in a liquid are sols and gel is an interconnected, rigid network with pores of submicrometer dimensions and polymeric chains that their average length is greater than a micrometer (Larry et al, 1990). Taurino et al (2008) made superhydrophobic coatings from fluorpolymer, TEOS and tetraethyl orthotitanate (TEOT). They sprayed coatings on glass slides. The samples were subjected to heat at 100°c and the contact angles of coatings were 157°. Daoud et al (2006) prepared coatings containing hexdecyltrimethoxysilane (HDTMS), TEOS and 3-glycidoxypropyltrimethoxysilane (GPTMS). Their results showed that the contact angle of coating on the cellulosic substrate is 141° and on the glass is 120°. These founding demonstrated the effect of surface type on superhydrophobicity. Shang et al (2005) fabricated superhydrophobic coatings from TEOS, MPS (methacrylloxypropyltrimethoxysilane) and MTES (methyltriethoxysilane). They found that these coatings have contact angles between 125-165°. All coatings were applied on the glass substrate and heat treated at 110°C. Hikita et al (2005) prepared a sol-gel film with super-liquid repellency from colloidal silica particles and fluoroalkylsilane. The colloidal silica (heptadecafluoro-1,1,2,2-tetrahydrodecyl) triethoxysilane (FOETES) were added to the mixture of TEOS and 0.1 N HCl solution. A magnetic stirrer was used to stir mixture for half an hour. The final solutions are applied on the surface by spin coatings and the films were cured at 160 ºC for 1 hour. The final coatings indicated contact angle of 150º.

Superhydrophobic polymeric coatings

These coatings are prepared from the mixing of polymeric materials with hydrophobic additive or fillers. They can be fabricated more easily compared with other methods that sometimes need complicated processes. They can be applied on the surface by similar ways for paints like spraying, so they can be utilized by customers without difficulty. Super hydrophobic powder coating was fabricated in Dr Zhu`s group (Mozumder et al, 2008). They usually are more durable than liquid coatings and they eliminate the use of toxic solvents that are responsible for the hazardous emissions of Volatile Organic Compounds (VOC) and hence make them less expensive than the conventional liquid coatings. The superhydrophobic powder coatings were prepared from the blending of polyester powder resin and silica or ultrafine fluoric additive in an extruder. The powder coatings applied by electrostatic spray on the metallic surfaces. These coatings are cured at 200°C in the furnace and demonstrated contact angle of 160º. Wang et al (2007) made superhydrophobic coatings from the mixing of nano-calcium carbonate treated by FAS-17 (heptadecafluorodecyl trimethoxysilane) with synthesized acrylic resin. The coatings were cured at 120º for 10 min and displayed contact angle of 150º. Also Cao et al (2009) made superhydrophobic coatings from the mixing of synthesizes acrylic resin, silicone resin and organosilane-modified silica particles (20 nm). The coatings applied on the surfaces and cured in oven at 80 ºC for 2 hours. The superhydrophobic coatings showed contact angle hysteresis less than 5º.

Most of the superhydrophobic coatings in the literature are cured in ovens and hard to be used for maintenance or be applied at the work places. This study demonstrates the development of superhydrophobic coatings that can be cured at room temperature and applied in plant and on field.

4-3 Application of superhydrophobic coatings

Superhydrophobic coatings are useful for many applications. Following are some major example areas:

Marinre: They can reduce frictional drag and can be used for friction reduction in pumping of liquid through pipes, cruise ship, boat bottoms, marine vessels and submarines. Also they have potential to slow down the growth of the algae on the surface and can be used as antifouling coatings to reduce the cost of maintenance.

Corrosion resistance: The superhydrophobic coatings cause water to bead off of surfaces, so these coatings can increase the corrosion resistance of metallic surfaces. They can be used for vehicle bodies, bridges, pipe exterior and steel structures.

Self-cleaning: They can work as self-cleaning surfaces, causing rain and other precipitated moisture to bead up. They can be used for building protection. For vehicles, aided by airflow caused by wind or vehicle motion, the resulting beads of water run off the surface of vehicle.

Icephobic coatings: Ice and snow build up on outdoor surfaces is a major problem for power transmission line, aircrafts and boats. Super hydrophobic surfaces have the lowest ice adhesion and they can reduce the speed of ice forming. These coatings will be discussed in second part of this chapter.

High voltage insulator coatings: One of the important applications of super hydrophobic coating is for outdoor insulator maintenance. Environmental contamination of outdoor insulation has caused power losses and reduced reliability of electric distribution systems since their inception. Losses arise from the reduction of surface resistance and increase in leakage currents from phase to phase or ground. This results in wasted power on the distribution system and is sometimes measured as “Watt Loss” of individual insulators or device housings. Increases in these leakage currents cause instability over the surface that can lead to arcing and flashover of the entire insulator, causing an outage and possibly damaging equipment. Despite important progress in technologies for removing pollution, contamination is one of the main reasons in system outages. Surface contamination comes from different sources. They can include costal salt water carried in fog, industrial vapors, cement dust, high-way road salt and tire dust (Cherney et al, 1999).

Over time, three classes have been categorized for contaminations mitigating that are cleaning, design and surface modifications of insulators. For surface modifications, different forms of silicones are commonly used, because they can maintain and recover hydrophobicity. The hydrophobic materials interrupt the flash over mechanism and limit leakage currents due to preventing of forming conductive water film. The most usual silicone materials in the market are silicone greases and Room Temperature elastomeric (RTV) coating due to that elastomeric coatings have better properties are more popular (Cherney et al, 1999). As it was discussed in chapter 2, RTV silicone rubber can retain the water repellency under outdoor weathering. On polluted surfaces, these coatings can release low molecular weight silicone fluid that diffuses from the bulk of coating, surrounds contaminants and recover hydrophobicity. Researchers have studied silicone rubber coatings for insulators and tried to improve these coatings. For example, Deng et al (1999) and Hackam et al (1996) evaluated RTV silicone rubber liquid coatings. Their results showed the contact angles of coatings are between 100 to 120°. Also solvent and substrate type could affect the electrical properties of coatings. Moreover, their results demonstrated that ATH (Alumina tri-hydrate) had better electrical properties than SiO_2 and there was an optimum point for the concentration of filler. Also, Jahromi et al (2008) and Liao et al (2007) worked with RTV silicone coatings and indicated that the thickness of coatings could affect the electrical performance of coatings and contact angle of them. They also illustrated nano silica filler and carbon black could increase the erosion resistance and hydrophbicity of silicone coatings respectively. Meyer et al (2004) evaluated the effect of ATH in silicone RTV coatings. They indicated that ATH can remove heat from the hot spots and can improve the erosion and tracking resistance of coatings. Despite the significant properties of these coatings, they cannot fully prevent the accumulation of dust on surfaces due to unsatisfactory water repellency. The water contact angles of current RTV coatings are smaller than 120 degrees. Also these coatings do not show satisfactory performance during cladding ice season, so they cannot reduce the ice adhesion considerably. However superhydrophobic coatings can remove contaminations much more effectively and reduce ice adhesion to the insulator surfaces because of their self cleaning properties.

This study will discuss about superhydrophobic coatings that are synthesized from RTV silicone rubber or fluoropolyurethane polymers and have been shown the best water repellency properties. These coatings are prepared from three following approaches:

1) Silicone rubbers or Fluoropolyurethane are mixed with hydrophobic additives (nano silica or nano fluoric particles). These materials were used in Dr zhu`s group to make superhydrophobic powder coatings.

2) Silicone rubbers or Fluoropolyurethane are mixed with glass bead or nano calcium carbonates. These fillers were treated by fluoroalkylsilane.
3) Silicone rubbers or Fluoropolyurethane are mixed with the combination of hydrophobic additives and treated fillers (glass bead or nano calcium carbonates).

This chapter analyzes the results of superhydrophobic RTV silicone rubber coatings and the results of superhydrophobic fluoropolyurethane coatings will be evaluated in next chapter.

Superhydrophobic RTV silicone rubber coatings

The superhydrophobic coatings were made from the blending of RTV silicone rubber with hydrophobic additives, hydrophobic fillers or the combination of hydrophobic additives and fillers. Contact angle and sliding angle measurements were conducted to evaluate the coatings hydrophobicity. Also SEM pictures were used to exhibit the topography of surfaces. Water immersion test, adhesion test, hardness, rubbing durability and UV durability tests were utilized to check the mechanical and the weathering durability of coatings. Inclined planed test was another test that was done to assess the track and erosion resistance of superhydrophobic RTV silicone rubber coatings. Some factors that could influence in the hydrophobicity or the mechanical properties of coatings were evaluated too. They were: the effect of PDMS fraction on RTV silicone rubber coatings; the role of coupling agents in adhesion of superhydrophobic coatings; the effect of production method, solvent type, resin type and thickness on hydrophobicity of coatings; the role of dispersing additive in coatings dispersion; and the effect of hydrophobic additives on the silicone fluid releasing in RTV silicone rubber coatings.

4-4 Results

Contact angles

The contact angles were measured by using Rame-Hart 100 Goniometer. The contact angle results for RTV silicone coatings with hydrophobic additives, hydrophobic fillers or the combination of them were noted in Figures 4-4 to 4-10.

Figure 4-4 demonstrates the changes of contact angles with hydrophobic additive fractions. The results indicated that with rising hydrophobic additive fractions, the contact angles of coatings increase. The highest contact angle (152º) was achieved with nano silica at 40 wt%. The highest concentration was got at 40 wt% and after this amount; the dispersion of hydrophobic additives in RTV silicone coatings was not possible.

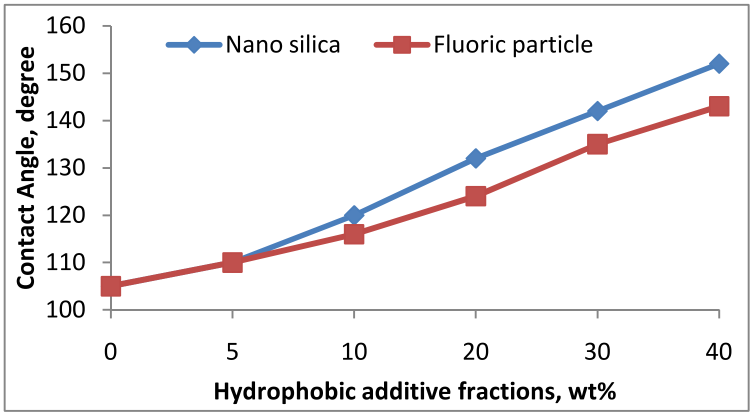


Figure 04-4: The Contact angles of RTV superhydrophobic coatings with hydrophobic additives

As it can be seen in Figure 4-5, the contact angles of RTV silicone coatings raise with increasing treated nano $CaCO_3$ (NC) or treated glass bead (G) fractions. The highest contact angle was at 40 wt% hydrophobic fillers and nano calcium carbonate could increase contact angles more than glass beads. However, the treated fillers could not make superhydrophobic coatings. The contact angle of RTV silicone coatings with 50 wt% was similar to 40 wt% and is not shown in Figure 4-5. Also, the dispersion of hydrophobic additives in RTV silicone coatings was not possible, when the hydrophobic filler fraction increased more than 50 wt%.

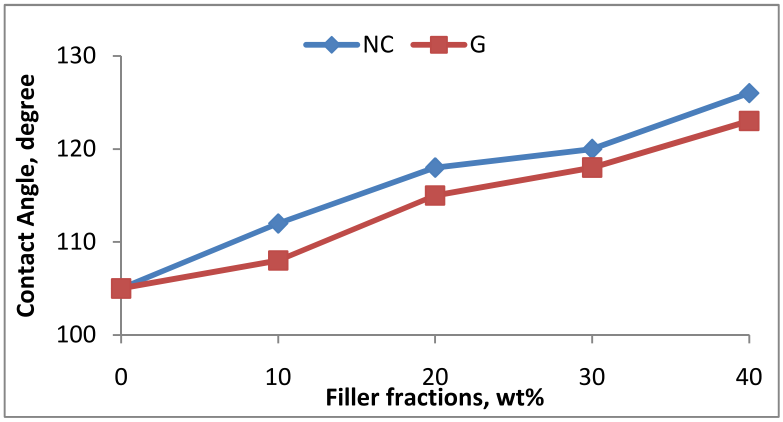


Figure 4-5: The Contact angles of RTV superhydrophobic coatings containing hydrophobic fillers

Figure 4-6 illustrates the contact angle changes of RTV silicone rubber coatings with the combination of nano silica and treated nano calcium carbonate (NC) concentrations.

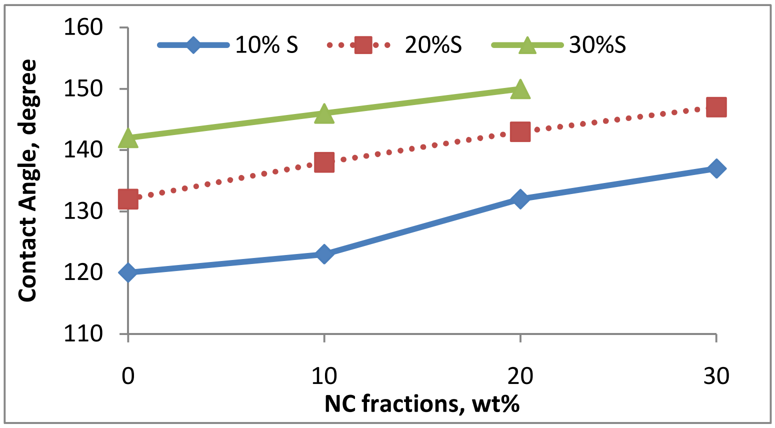


Figure 4-6: The Contact angles of RTV superhydrophobic coatings with the combination of nano silica (S) and nano calcium carbonate

The fraction of nano calcium carbonate was changed from 10 to 40 wt% in each of nano silica (S) concentrations that were altered from 10 to 30 wt%. The highest fraction was achieved at 50 wt%. The results showed that the combinations of nano silica and nano calcium carbonate could make RTV superhydrophobic coatings. The highest contact angle (150º) was obtained at the point including 30 wt% nano silica and 20 wt% nano $CaCO_3$. The dispersion of filler and additive combinations in coating was not achievable after this point.

As it can be observed in Figure 4-7, the contact angles of RTV silicone coatings could increase when the concentration of two materials (ultrafine fluoric particle and nano calcium carbonate (NC)) combination enlarged.

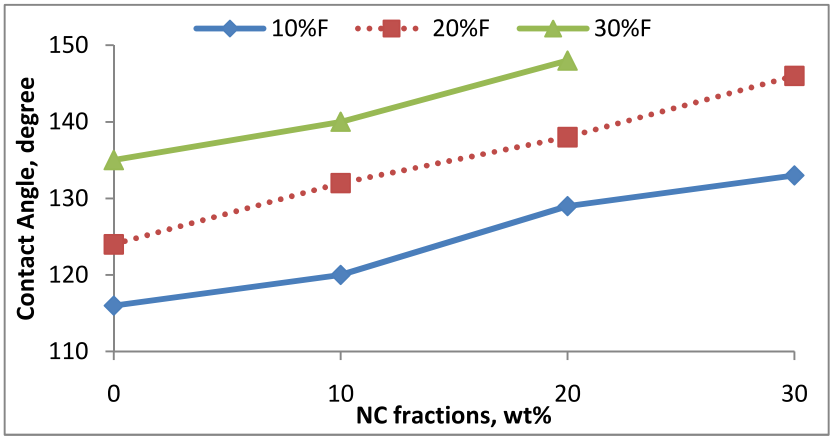


Figure 04-7: The Contact angles of RTV superhydrophobic coatings containing ultrafine fluoric particle (F) and treated nano $CaCO_3$ (NC)

The fraction of nano calcium carbonate was changed from 10 to 40 wt% in each of ultrafine fluoric particle (F) concentrations that were altered from 10 to 30 wt%. The highest contact angle was attained at 148º at the fraction that contains 30 wt% fluoric particle and 20 wt% nano calcium carbonate. The highest concentration was got at 50 wt% and after this amount, the dispersion of two material combinations in RTV silicone coatings was not possible.

Figure 4-8 demonstrates the alteration of contact angles of RTV silicone coatings containing the combination of nano silica and treated glass beads (G). The fractions of nano silica were changed from 10 to 30 wt% when the concentrations of glass beads were varied from 10 to 40 wt% in each nano silica fraction.

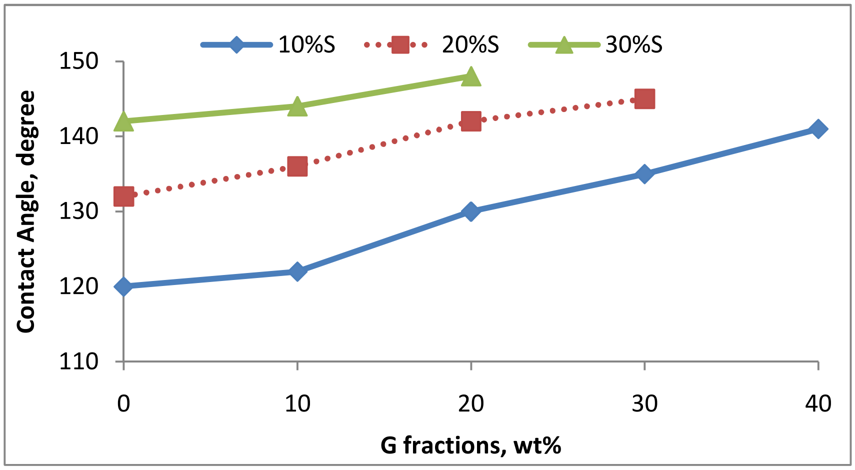


Figure 4-8: The Contact angles of RTV superhydrophobic coatings including the combination of nano silica (S) and treated glass bead (G)

The maximum contact angle was 148° and the highest fraction of nano silica and glass beads combination was 50 wt%. Also, the dispersion of aforementioned materials in coating was not possible after this amount.

Also, Figure 4-9 indicates that the contact angles of RTV silicone coatings would rise with increasing the concentrations of ultrafine fluoric particle and glass beads (G) fractions. The fractions of fluoric particles were varied from 10 to 30 wt% when the concentrations of glass beads were altered from 10 to 40 wt% in each fluoric particle fraction. The highest contact angle was attained at 146° in the point including the combination of 30 wt% fluoric particle and 20 wt% treated glass bead. The maximum concentration of fluoric particle and glass bead combination was 50 wt% and after this point, the dispersion of materials in the RTV silicone coatings was not achievable.

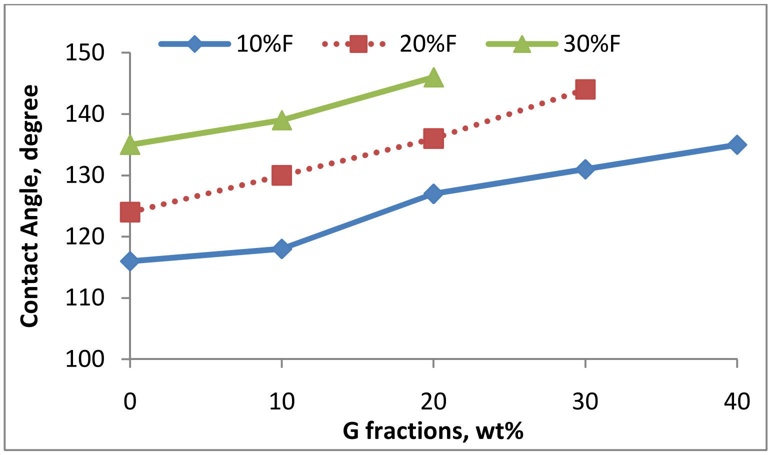


Figure 04-9: The Contact angles of RTV superhydrophobic coatings including the combination of ultrafine fluoric particle (F) and treated glass bead (G)

As it can be observed in Figure 4-10, the contact angles of RTV silicone coatings would increase with raising the concentrations of ultrafine fluoric particle and ATH (alumina tri-hydrate) combination. The concentrations of ATH were varied from 10 to 40 wt% in each fraction of ultrafine fluoric particles. The fluoric particle concentrations were altered from 10 to 30 wt%. The highest contact angle was achieved at 152° when the ultrafine fluoric particle fraction was 30 wt% and ATH fraction was 20 wt%.

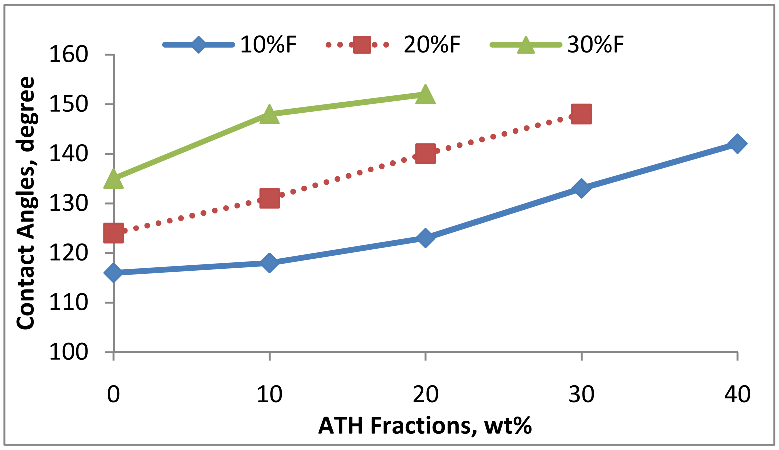


Figure 04-10: The Contact angles of RTV superhydrophobic coatings with the combination of ultrafine fluoric particle (F) and ATH

The maximum concentration of fluoric particle and ATH combination was 55 wt% and the dispersion of fluoric particle and ATH combination in coating was not possible after this point. The contact angle result of coatings with 55 wt% ATH and fluoric particle was similar to the point with 50 wt% and were not displayed in Figure 4-10. The combinations of nano silica and ATH cannot be used for superhydrophobic RTV silicone insulator coatings because they cause cracks in the coatings when the coatings have thickness higher than 120 µm.

Figure 4-11 compares the contact angles of two superhydrophobic RTV silicone rubber insulator coatings (A and B) that fabricated at University of Western Ontario with the commercial RTV silicone rubber coating from Dow Corning Company (USA). The formulation A includes 10 wt% ultrafine fluoric particle and 45 wt% ATH while the formulation B contains 13 wt% ultrafine fluoric particle and 35 wt% ATH. The results demonstrated that UWO superhydrophobic coatings made much higher contact angles than commercial RTV coatings that were not superhydrophobic and included only ATH.

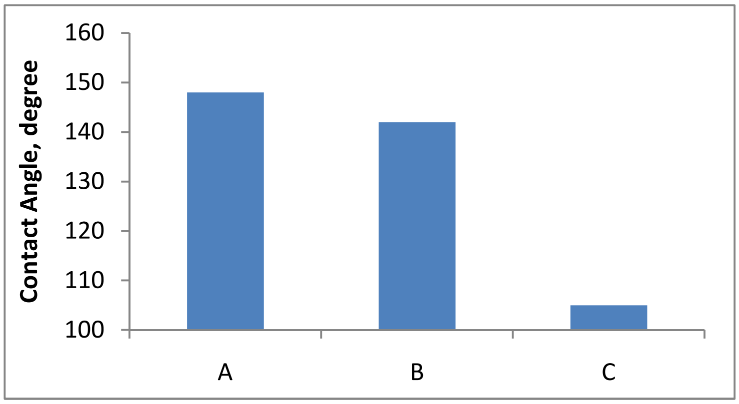


Figure 4-11: The contact angle comparison of UWO superhydrophobic RTV coatings (A and B) with the commercial coating (C)

Sliding angles

Sliding angle exhibits the heterogeneity of surface and was measured by injecting a droplet on a surface and tilting the surface to find the angle of the surface to the horizontal plain when the droplet starts to slide. The sliding angle results for RTV silicone coatings with hydrophobic additives, hydrophobic fillers or the combination of them were noted in Figures 4-12 to 4-19.

Figure 4-12 demonstrates the changes of sliding angles with hydrophobic additive fractions. The results indicated that with rising hydrophobic additive fractions, the sliding angles of coatings reduce. The lowest sliding angle was 3º at 40 wt% nano silica.

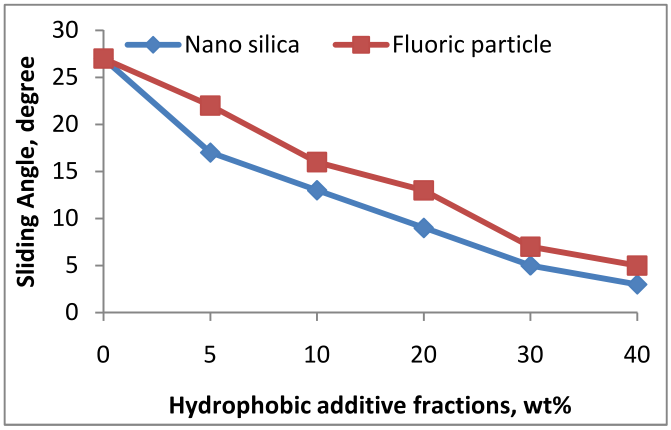


Figure 04-12: The sliding angles of RTV superhydrophobic coatings with hydrophobic additives

As it can be seen in Figure 4-13, the sliding angles of RTV silicone coatings could decrease with increasing hydrophobic treated nano $CaCO_3$ (NC) or treated glass beads (G) fractions. The lowest sliding angle was at 40 wt% hydrophobic filler and nano calcium carbonate could reduce sliding angles more than glass beads. However, the treated fillers could not make superhydrophobic coatings.

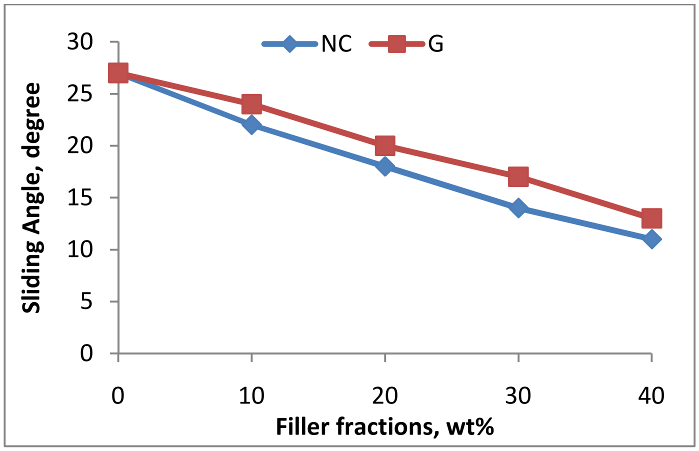


Figure 4-13: The sliding angles of RTV superhydrophobic coatings with hydrophobic fillers

Figure 4-14 indicates the sliding angles changes of RTV silicone rubber coatings with the combination of nano silica and treated nano calcium carbonate concentrations (NC). The fraction of nano calcium carbonate was changed from 10 to 40 wt% in each of nano silica (S) concentrations that were altered from 10 to 30 wt%. The minimum fraction was achieved at 50 wt%.

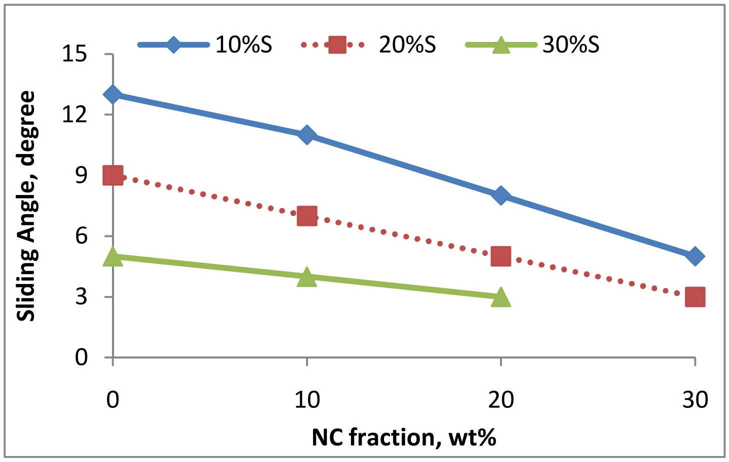


Figure 4-14: The sliding angles of RTV superhydrophobic coatings containing the combination of nano silica (S) and nano $CaCO_3$ (NC)

The results showed that the combination of nano silica and nano calcium carbonate could make RTV superhydrophobic coatings. The lowest sliding angle (3°) was obtained at the point including 30 wt% nano silica and 20 wt% nano $CaCO_3$.

As it can be observed in Figure 4-15, the sliding angles of RTV silicone coatings could decrease when the concentrations of two materials (ultrafine fluoric particle and nano calcium carbonate) combination would rise. The fraction of nano calcium carbonate (NC) was changed from 10 to 40 wt% in each of ultrafine fluoric particle (F) concentrations that were altered from 10 to 30 wt%.

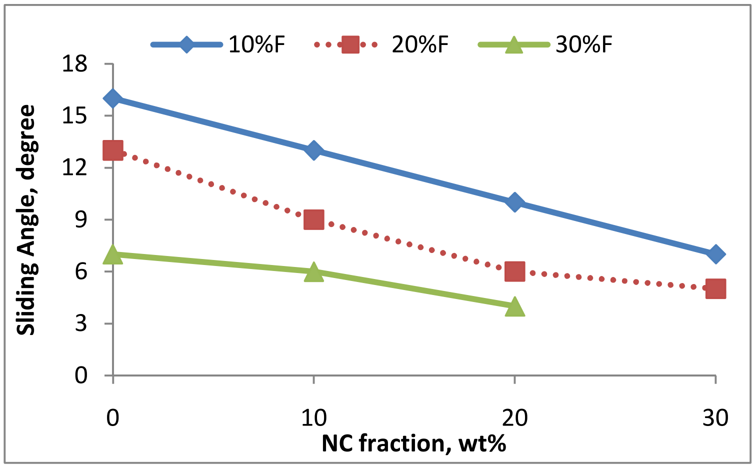


Figure 04-15: The sliding angles of RTV superhydrophobic coatings containing the combination of ultrafine fluoric particle (F) and nano $CaCO_3$ (NC)

The lowest sliding angle was attained at 4° at the fraction that contains 30 wt% fluoric particle and 20 wt% nano calcium carbonate. The lowest concentration was got at 50 wt% and after this amount, the dispersion of two materials in RTV silicone coatings was not possible.

Figure 4-16 demonstrates the alteration of sliding angles of RTV silicone coatings containing the combination of nano silica and treated glass bead (G). The fractions of nano silica were changed from 10 to 30 wt% when the concentrations of glass bead were varied from 10 to 40 wt% in each nano silica fraction. The maximum sliding angle was 4° and the highest fraction of nano silica and glass bead combination was 50 wt%.

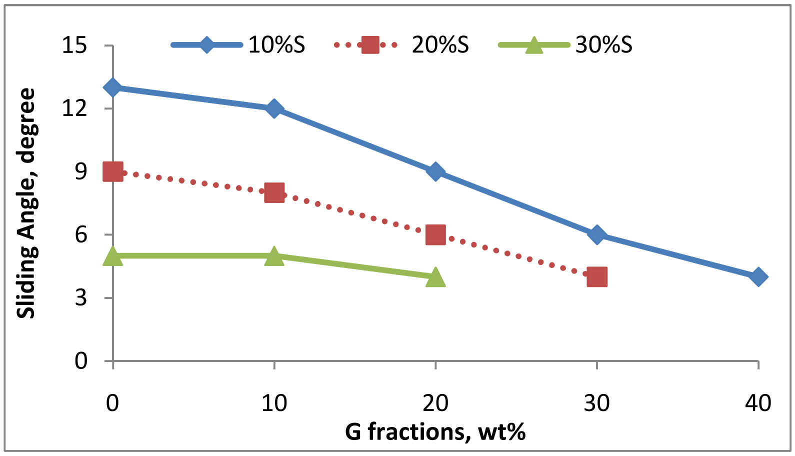


Figure 04-16: The sliding angles of RTV superhydrophobic coatings containing the combination of nano silica (S) and glass beads (G)

Also, the Figure 4-17 indicates that the sliding angles of RTV silicone coatings would rise with increasing the concentrations of ultrafine fluoric particle and glass beads (G) fractions.

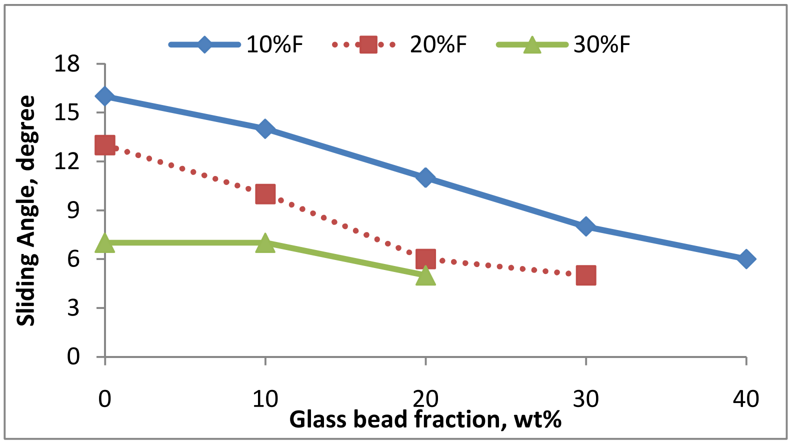


Figure 4-17: The sliding angles of RTV superhydrophobic coatings containing the combination of ultrafine fluoric particle (F) and glass bead (G)

The fractions of fluoric particle were varied from 10 to 30 wt% when the concentrations of glass bead were altered from 10 to 40 wt% in each fluoric particle fraction. The highest sliding angle was attained at 4° in the point including the combination of 30 wt% fluoric particle and 20 wt% treated glass bead. The maximum concentration of fluoric particle and glass bead combination was 50 wt% and after this point, the dispersion of materials in the RTV silicone coatings were not possible.

As it can be observed in Figure 4-18, the sliding angles of RTV silicone coatings would reduce with raising the concentration of ultrafine fluoric particle and ATH (alumina tri-hydrate) combination. The concentrations of ATH were varied from 10 to 40 wt% in each fraction of ultrafine fluoric particles. The fluoric particle concentrations were altered from 10 to 30 wt%.

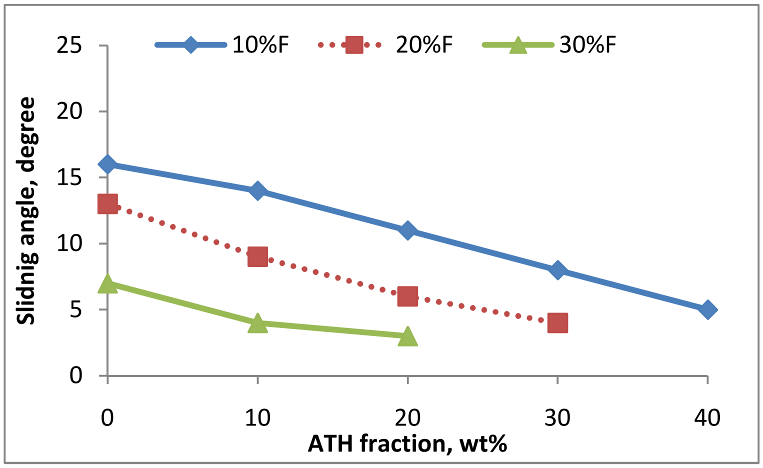


Figure 4-18: The sliding angles of RTV superhydrophobic coatings containing the combination of ultrafine fluoric particle (F) and ATH

The lowest sliding angle was achieved at 3° when the ultrafine fluoric particle fraction was 30 wt% and ATH fraction was 20 wt%. The maximum concentration of fluoric particle and ATH combination was 55 wt%.

Figure 4-19 compares the sliding angles of two superhydrophobic RTV silicone rubber insulator coatings (A and B) that were fabricated at University of Western Ontario with the commercial RTV silicone rubber coating from Dow Corning Company (USA).

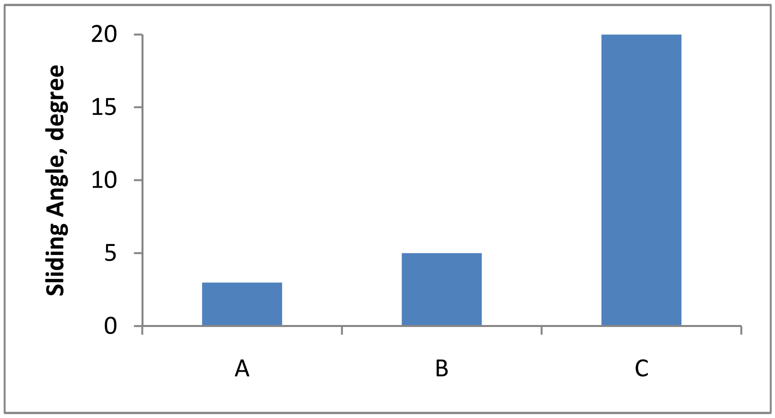


Figure 04-19: The sliding angle comparison of UWO superhydrophobic RTV coatings (A and B) with the commercial coating (C)

The formulation A includes 10 wt% ultrafine fluoric particle and 45 wt% ATH while the formulation B contains 13 wt% ultrafine fluoric particle and 35 wt% ATH. The results demonstrate that UWO superhydrophobic coatings made lower sliding angles than commercial RTV coatings that were not superhydrophobic.

SEM pictures

The SEM pictures were utilized to evaluate the topography of coated surfaces.

Figure 4-20 exhibited the SEM picture of superhydrophobic RTV silicone rubber coatings including 10 wt% ultrafine fluoric particle and 45 wt% ATH (Formulation A).

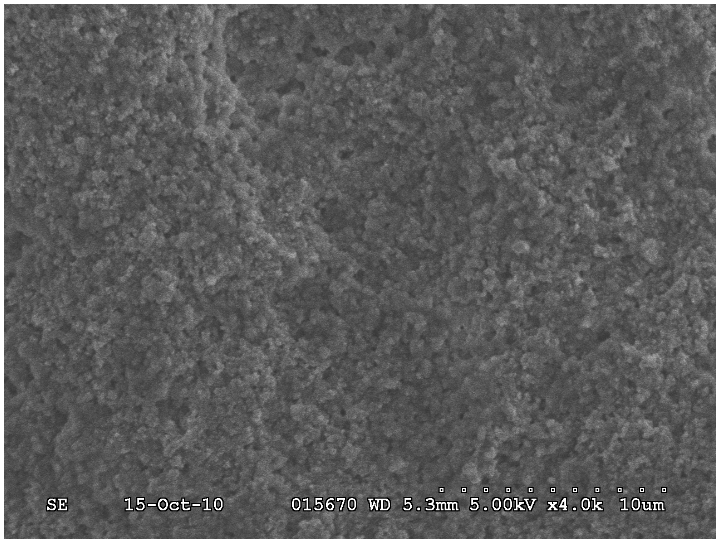


Figure 04-20: The SEM picture of superhydrophobic RTV silicone rubber coating

Figure 4-21 demonstrated the SEM picture of commercial RTV hydrophobic coatings (Dow Coning). The picture confirmed that commercial coating had a smooth surface that can not make superhydrophobic coatings.

Figure 4-21: The SEM picture of commercial RTV silicone rubber coating

EDX (Energy Dispersive X-ray) was employed to identify the elemental composition of the specimens like treated nano calcium carbonate or glass bead. Two methods were used to make a treatment by fluoroalkylsilane (FAS) on the surface of these powders. In the first method, ten gram of nano calcium carbonate was dispersed in 20 g of acetone in a glass bottle. 0.4 g FAS-13 and 0.4 g acidic water (PH was adjusted by acetic acid to 3) were added to mixture and the final solution was stirred for 2 hours. Then mixture was poured into a glass vessel and dried at 80ºC in an oven (Wang et al, 2007). In the second method, isopropyl alcohol was used instead of acetone and after drying, the treated powders were heated at 150 ºC in oven to improve the binding of FAS and nano $CaCO_3$. Table 4-1 compares the distributions of element concentrations in nano calcium carbonate treated with FAS by method one or two.

Table 4-1: EDX results of treated nano calcium carbonate

	Method 1	**Method 2**
Elements	**Concentrations wt%**	
Carbon	37.8	39.4
Oxygen	36.4	35.3
Fluorine	0.9	1.8
Calcium	24.1	23.2

Water immersion test

This test assesses the water durability of superhydrophobic coatings. The coated samples were immersed in water for 96 hours and then dried up in lab air to examine the durability of coatings with water immersion (Hillborg et al, 1999). The contact angles of superhydrophobic RTV coatings before immersion in water were compared with contact angles after one and three days drying in lab air.

Figure 4-22 indicates how the contact angles of RTV silicone coatings change before immersion in water (Zero), after one day (One) and three days (Three) drying in air against increasing nano silica fraction. The fractions were raised from 5 to 40 wt%. The coatings with 40 wt% nano silica could recover hydrophobicity sooner than other coatings.

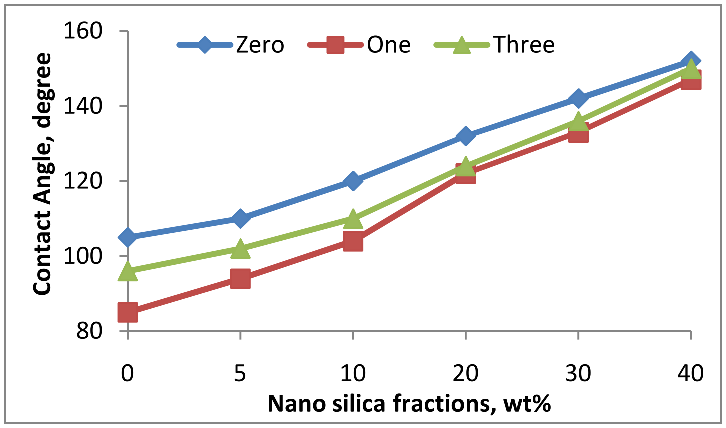


Figure 04-22: The contact angle changes of RTV silicone rubber coatings including nano silica after immersion in water

As it can be seen in Figure 4-23, the contact angle of RTV silicone rubber coatings with different fractions of ultrafine fluoric particle were changed after immersion in water. The fluoric particle concentrations were varied from 5 to 40 wt%. The coatings containing 40 wt% fluoric particles could recover hydrophobicity sooner than other coating formulations. The RTV silicone rubber coatings with fluoroalkylsilane treated fillers (nano calcium carbonate or glass bead) were not superhydrophobic, so their water durability was not tested in this project.

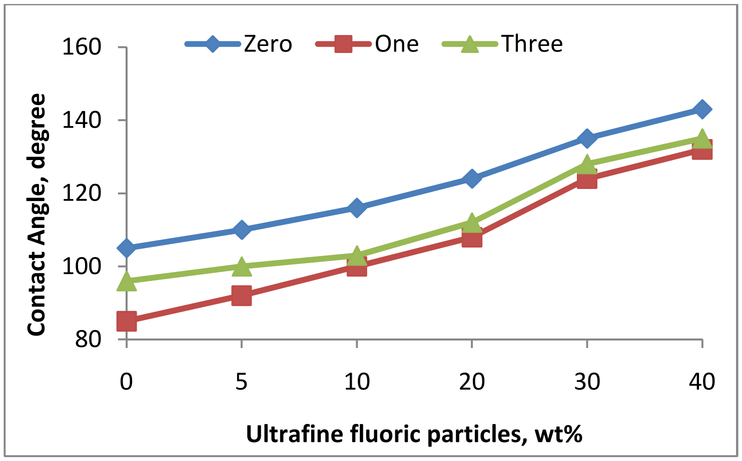


Figure 04-23: The contact angle changes of RTV silicone rubber coatings including ultrafine fluoric particle after immersion in water

Figures 4-24 and 4-25 demonstrate the contact angle changes of RTV silicone coatings with the combination of nano silica and nano calcium carbonate (NC). In figure 4-24, the concentration of nano silica was 20 wt% and nano calcium carbonate fractions were changed from 10 to 30 wt%. The RTV coating including 20 wt% nano silica and 30 wt% nano calcium carbonate could recover hydrophobicity faster than other fractions.

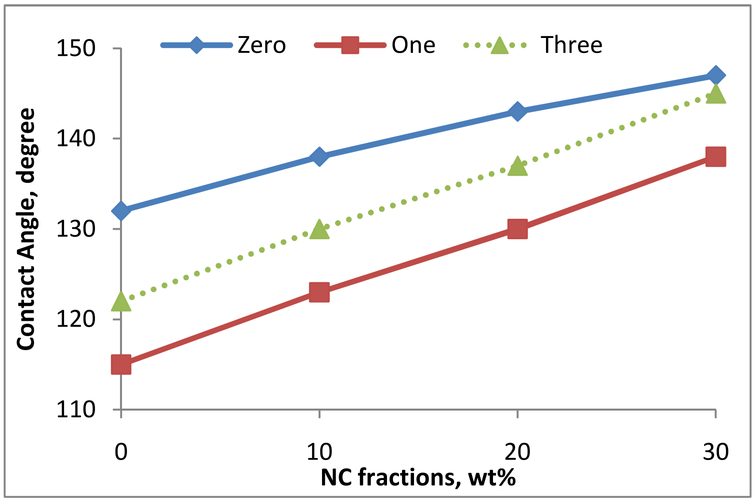


Figure 4-24: The contact angle changes of RTV silicone rubber coatings with 20 wt% nano silica and nano $CaCO_3$ (NC) after water immersion

Also in Figure 4-25, the concentration of nano silica was 30 wt% and nano calcium carbonate (NC) fractions were altered from 10 to 20 wt%. The RTV coating containing 30 wt% nano silica and 20 wt% nano calcium carbonate showed fewer changes in contact angle.

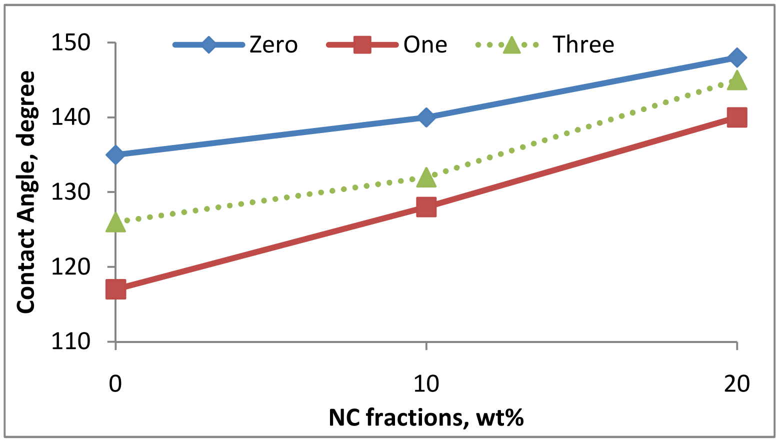


Figure 4-25: The contact angle changes of RTV silicone rubber coatings with 30 wt% nano silica and nano $CaCO_3$ (NC) after water immersion

As it can be seen in Figure 4-26 and 4-27, the contact angles of RTV silicone coatings including the combination of ultrafine fluoric particle and nano calcium carbonate (NC) were altered after immersion in water.

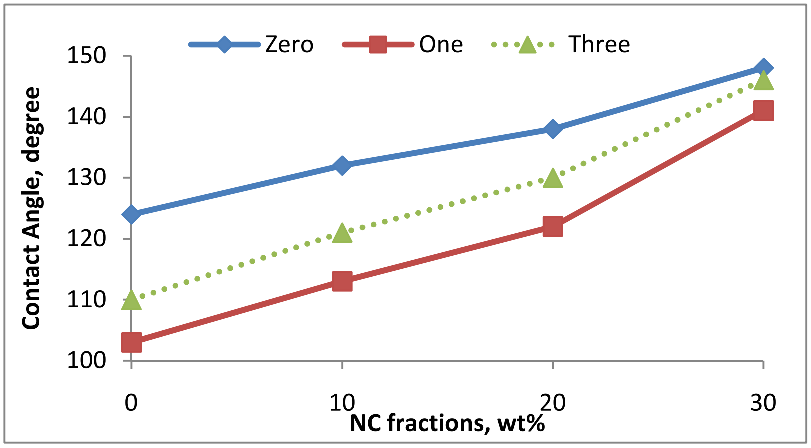


Figure 4-26: The contact angle changes of RTV silicone rubber coatings including 20 wt% fluoric particle and nano $CaCO_3$ (NC) after water immersion

Figure 4-26 shows the results of RTV silicone coatings with 20 wt% fluoric particle and nano calcium carbonate (NC). The fractions of nano $CaCO_3$ were varied from 10 to 30 wt%. The point including 20 wt% fluoric particle and 30 wt% nano calcium carbonate could recover hydrophobicity sooner. Also in Figure 4-27, the concentration of fluoric particle was 30 wt% and nano calcium carbonate fractions were altered from 10 to 20 wt%. The RTV coating containing 30 wt% fluoric particle and 20 wt% nano $CaCO_3$ indicated less changes in contact angle.

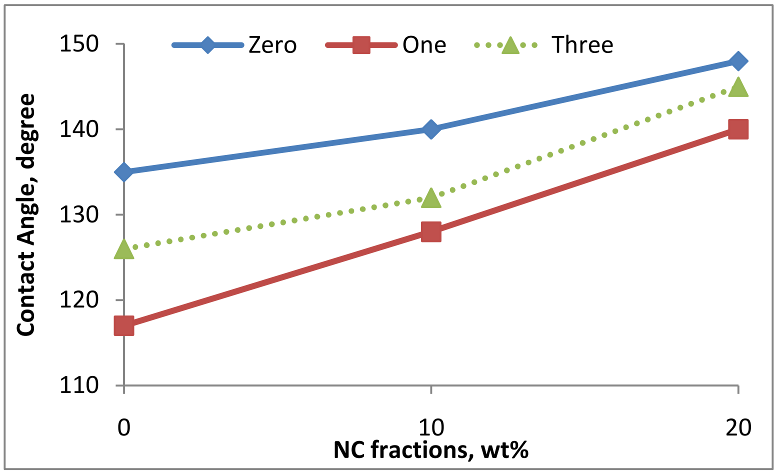


Figure 4-27: The contact angle changes of RTV silicone rubber coatings with 30 wt% fluoric particle and nano $CaCO_3$ (NC) after water immersion

Figures 4-28 and 4-29 display the contact angle changes of RTV silicone coatings including the combination of ultrafine fluoric particle and ATH. In figure 4-28, the concentration of fluoric particle was 20 wt% and ATH fractions were changed from 10 to 30 wt%. The RTV coating including 20 wt% fluoric particle and 30 wt% ATH could recover hydrophobicity faster than other fractions. Also in Figure 4-29, the concentration of fluoric particle was 30 wt% and ATH fractions were altered from 10 to 20 wt%. The RTV coating containing 30 wt% fluoric particle and 20 wt% ATH indicated less change in contact angle.

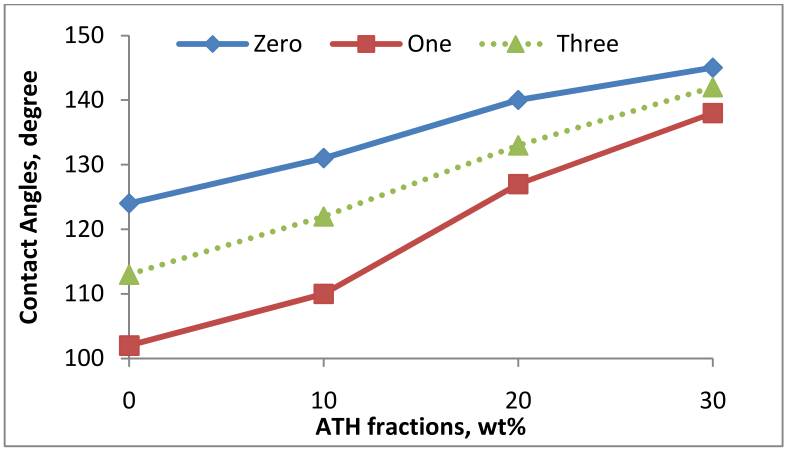


Figure 4-28: The contact angle changes of RTV silicone rubber coatings with 20 wt% fluoric particle and ATH after water immersion

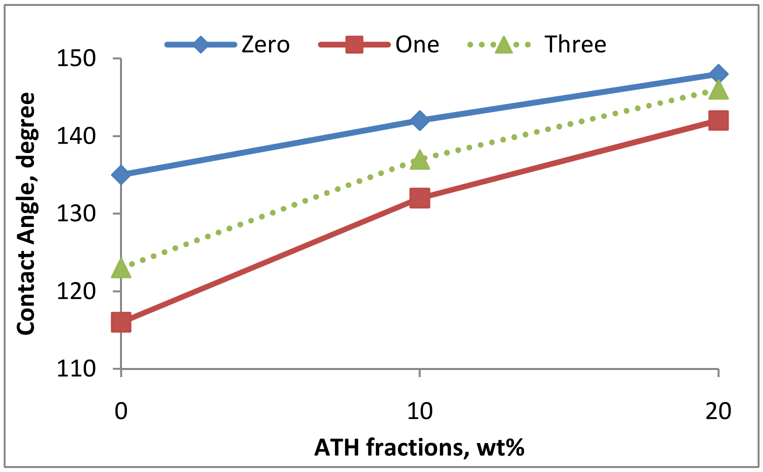


Figure 4-29: The contact angle changes of RTV silicone rubber coatings with 30 wt% fluoric particle and ATH after water immersion

The results of immersion tests for RTV silicone rubber containing the combination of hydrophobic additive (nano silica or fluoric particles) and glass beads were similar to the results of RTV silicone rubber with the combination of hydrophobic additives and nano $CaCO_3$, so they are not repeated again here.

Adhesion

The adhesion of superhydrophobic RTV silicone rubber coatings was assessed by methods described in IEEE STD 1523. The samples coated with superhydrophobic RTV silicone rubber coatings including hydrophobic additive, hydrophobic fillers or the combination of hydrophobic additive and hydrophobic fillers (nano calcium carbonate, glass beads or ATH) did not show blisters in their surfaces, so increasing the concentration of fillers did not reduce adhesion to the substrate. The results of adhesion tests were same as RTV silicone rubber commercial coatings.

UV Durability

The UV durability test of superhydrophobic coatings was conducted with Q-Sun Xenon Test Chamber (Q-Lab Company, USA) in accordance with ASTM G-155. The total exposure time was 1000 hours; the contact and sliding angles of coatings were assessed every 100 hours to evaluate the effect of UV radiation on coatings.

Figures 4-30 and 4-31 illustrate the contact and sliding angles changes against UV radiation for RTV silicone coatings including 30 wt% and 40 wt% hydrophobic additives (nano silica (S) or fluoric particles (F)).

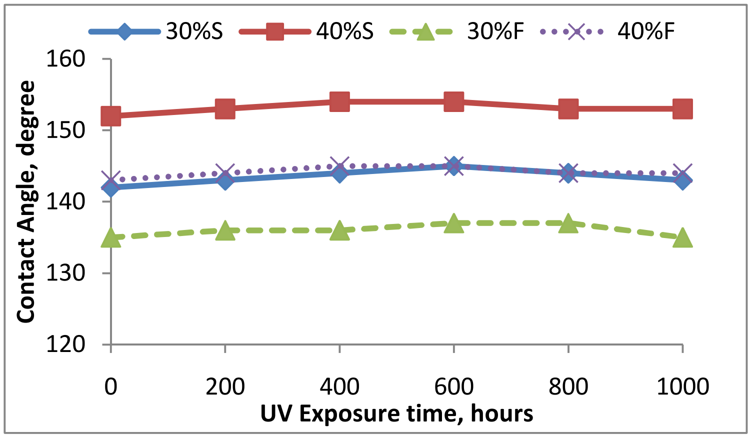


Figure 04-30: The contact angle changes of RTV silicone rubber with hydrophobic additives against UV exposure time

The time zero was before starting UV test. There was not any reduction in contact and sliding angles of coatings after 1000 hours, so superhydrophobic RTV silicone rubber coatings had a good UV and weathering durability.

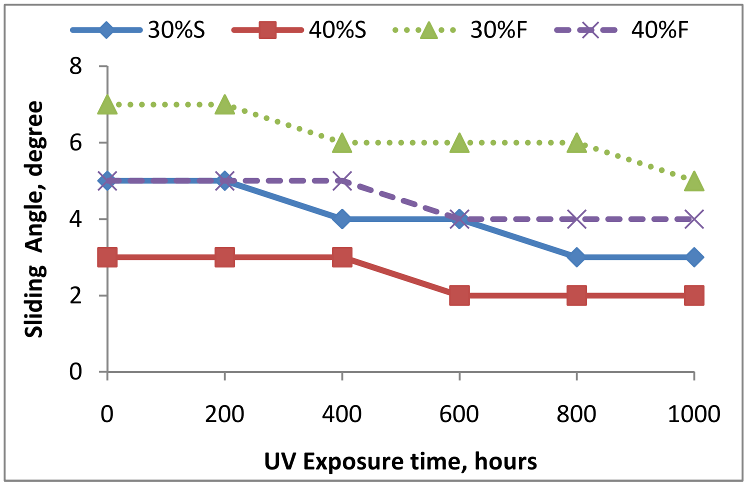


Figure 04-31: The sliding angle changes of RTV silicone rubber with hydrophobic additives against UV exposure time

As it can be seen in Figure 4-32 and 4-33, the UV durability of two superhydrophobic RTV coatings (A and B) containing the combination of ultrafine fluoric particle and ATH were compared with RTV silicon rubber commercial insulator coatings (C).

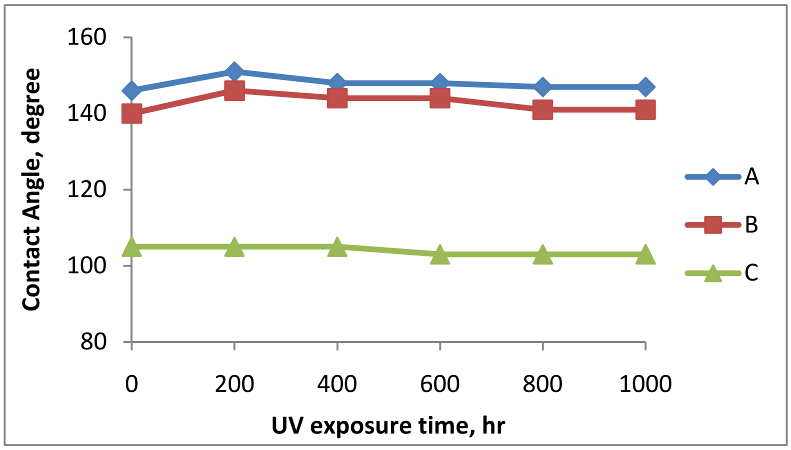


Figure 04-32: The contact angle changes of superhydrophobic and commercial RTV silicone rubber coatings against UV exposure time

Formulation A includes 10 wt% ultrafine fluoric particle and 45 wt% ATH while formulation B contains 13 wt% ultrafine fluoric particle and 35 wt% ATH. There was not reduction in contact angles of superhydrophobic RTV coatings including the combination of fluoric particles and ATH as well as RTV commercial coating.

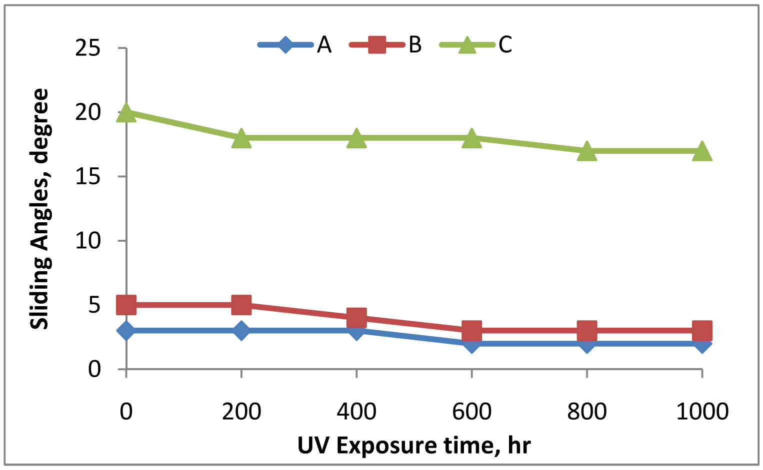


Figure 04-33: The sliding angle changes of superhydrophobic and commercial RTV silicone rubber coatings against UV exposure time

Hardness

The test was done in accordance with ASTM D3363. Pencil test was utilized to assess the hardness of coatings. A set of calibrated wood pencils with different scale of hardness was used which the softest was 6B and the hardest was 6H.

The hardness of RTV silicone rubber coatings with hydrophobic additives, hydrophobic fillers or the combination of them were around 6B to 5B, so their results were not mention here. The RTV silicone rubber is so soft that the addition of additives or fillers could not improve its hardness.

Rubbing resistance

The coating surfaces were rubbed with a 100% cotton cloth by a self made rubbing instrument. Table 4-2 demonstrates the results of rubbing properties of RTV silicone coatings with hydrophobic additives (nano silica or fluoric particles). The coatings with higher contact angles showed better durability. The highest one was 2500 rubs.

Also, the rubbing results of RTV silicone coatings with the combination of hydrophobic additives and hydrophobic fillers indicated that formulations with 10 wt% nano silica or fluoric particle and at least 30 wt% hydrophobic filler could pass 2000 rubs.

Table 4-2: The rubbing durability of RTV silicone rubber coatings including hydrophobic additives

Material	**Rubbing**	
	30 wt%	40 wt%
Nano silica	2000	2500
Fluoric particle	2000	2500

Inclined plane test

This test was done to evaluate the track and erosion resistance of RTV superhydrophobic coatings that were used for high voltage insulator. It was done by using the High Voltage Lab apparatus at the University of Waterloo in accordance with ASTM D-2303. Four different formulations were prepared (Table 4-3). The ATH and fluoric particle fractions were changed in the formulations A to E respectively. The thicknesses of coatings were assured at 0.2 ± 0.02 mm. The nano silica could not be used in RTV silicone coatings with thickness higher than 120 µm because it cause some cracks in the coating films.

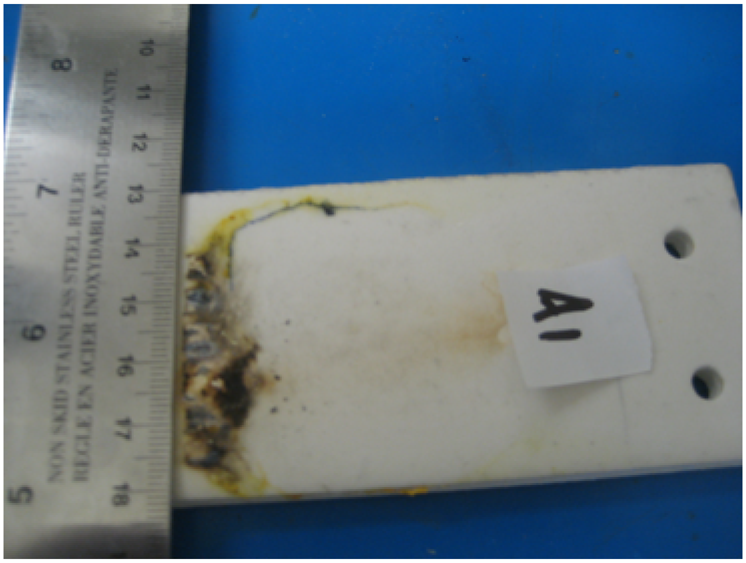
Table 4-3: RTV silicone rubber coating formulations

Formulation	**ATH wt%**	**Fluoric particles wt%**
A	45	10
B	35	13
D	10	30
E	0	40

Table 3-4 indicates that only RTV silicone rubber coatings with ATH fraction higher than or equal 35 wt% can pass the 3.25 KV that was accepted by industry as minimum acceptance voltage. They can also reduce the length of track. Also picture 4-34 displays the length of track for ceramic tile samples coated with formulation A.

Table 4-4: Erosion and track resistant of the superhydrophobic RTV Coatings

	2.75 KV	**3 KV**	**3.25 KV**	**4 KV**	**Length of Track(mm)**
A	Pass	Pass	Pass	Pass	8
B	Pass	Pass	Pass	Pass	9
D	Pass	Fail	Fail	Fail	23
E	Fail	Fail	Fail	Fail	27



4-5 Discussion

The contact angle results of RTV silicone rubber coatings with hydrophobic additives indicated that coatings including at least 30 wt% nano silica or ultrafine fluoric particles could show contact angles more than 130°. However, nano silica could improve the contact angle more than fluoric particle. The RTV silicone rubber with hydrophobic fillers (treated nano calcium carbonate or treated glass beads) were not superhydrophobic and they should be used in combination with hydrophobic additives to make superhydrophobic coatings. Meanwhile, nano calcium carbonate could increase the contact angles more than glass bead. The results of the combination of hydrophobic additives and hydrophobic fillers exhibited that RTV coating containing higher than 30 wt% of the combination of hydrophobic additives and hydrophobic fillers could have contact angles higher than 130°. Though, the combination of nano silica and hydrophobic fillers demonstrated higher contact angles than the combination of fluoric particles and hydrophobic fillers. Also, the combination of fluoric particle and ATH could make superhydrophobic coatings with contact angles higher than 130° while the commercial coatings containing ATH could have contact angles around 105°.

The RTV silicone rubber coatings with at least 30 wt% hydrophobic additives demonstrated sliding angles less than 7°. Though, the nano silica could reduce the sliding angle of these coatings more than fluoric particles. The RTV silicone rubber coatings with hydrophobic fillers could not show sliding angles less than 11° and they were not superhydrophobic. However, RTV silicone rubber coatings containing the combination of hydrophobic additives and hydrophobic filler showed sliding angles smaller than 7° when the fraction of the combination were higher than 40 wt%. The coatings with the combination of nano silica and hydrophobic filler indicated smaller sliding angle compared with the coatings containing the combination of fluoric particles and treated fillers. Also, RTV silicone rubber coatings with the combination of nano silica and ATH demonstrated smaller sliding angles than commercial RTV silicone rubber coatings that contained only ATH. The contact angle hysteresis (CAH) of RTV silicone rubber coatings with sliding angles smaller than 7º were around 5º to 7º, so these coatings could show self cleaning properties due to low CAH.

The SEM picture confirmed the micro/or nano structure in superhydrophobic coatings while the commercial coatings shows a smooth surface and that is why the commercial coatings had a low contact angle. Also the EDX elemental analysis in nano calcium carbonate treated by fluoroalkylsilane indicated that method 2 that was a modification from method 1 could deposite more fluor on the powder surfaces.

The contact angle changes of RTV silicone coatings with hydrophobic additives or the combination of hydrophobic additives and hydrophobic fillers against water immersion test indicated that RTV silicone coatings lost hydrophobicity, but they can recover it. The silicone fluid in these coatings can migrate to the surface of coatings and recover hydrophobicity. However, the RTV silicone coatings that had contact angles higher than 145º could recover hydrophobicity faster than other coatings.

The superhydrophobic RTV silicone coatings and commercial RTV coatings showed good adhesion to the ceramic tiles. There were not any blisters on the surfaces of these coatings after 100 hours boiling in water. Though, RTV silicone rubber coatings were soft and could be used only for applications that were not touched by hands like high voltage insulators.

The RTV silicone coatings hardness was not good with all different formulations because silicone rubber is so soft and reinforcing it with additives or fillers could not increase its hardness. They should be used in some applications that hardness is not important like antifouling or high voltage insulator coatings.

The rubbing resistance of RTV silicone coatings with contact angles higher than 140º was about 2500 rubs, so they exhibited good durability.

The results of Inclined Plane tests of superhydrophobic RTV silicone rubber coatings demonstrated that only coatings with ATH fractions higher or equal 35 wt% could pass the erosion and track resistance test that is important for high voltage insulator coatings. Moreover, the results confirmed the findings of other researchers that ATH could improve track and erosion resistance.

In addition to the tests that were done on the superhydrophobic RTV silicone rubber coatings, some factors that could influence in the coating properties were evaluated. They included: the effect of PDMS fraction on RTV silicone rubber coatings; the role of coupling agents in adhesion of superhydrophobic coatings; the effect of production method, solvent type, resin type and thickness on hydrophobicity of coatings; the role of dispersing additive in coatings dispersion; and the effect of hydrophobic additives fractions on the diffusion rate of silicone fluid in RTV silicone rubber coatings. The results of theses parameters will be discussed below:

PDMS and RTV silicone rubber coatings

The superhydrophobic coatings with 30 wt% hydrophobic additives were mixed with PDMS (silicone fluid). The PDMS fractions in samples 1 to 3 was 5%, 10% or 15%. The results of contact angles are displayed in table 4-5. The results indicated that adding

PDMS to the RTV silicone rubber coatings could not improve the contact angles and they had a negative effect on coatings.

Table 4-5: The effect of PDMS in contact angles of RTV silicone rubber coatings with hydrophobic additives

	Contact Angle, degrees			
Hydrophobic additive	0% PDMS	5% PDMS	10% PDMS	15% PDMS
Fluoric particle	135	130	126	122
Nano silica	142	138	135	132

Coupling agents and superhydrophobic coatings

The coupling agent (silicone agent) was mixed with superhydrophobic coatings containing 30 wt% nano silica to increase the adhesion of coatings to the substrate. The concentrations of coupling agents in samples were 2%, 4% and 6%. Figure 4-35 showed the effect of coupling agent fraction on RTV silicone rubber coating adhesions.

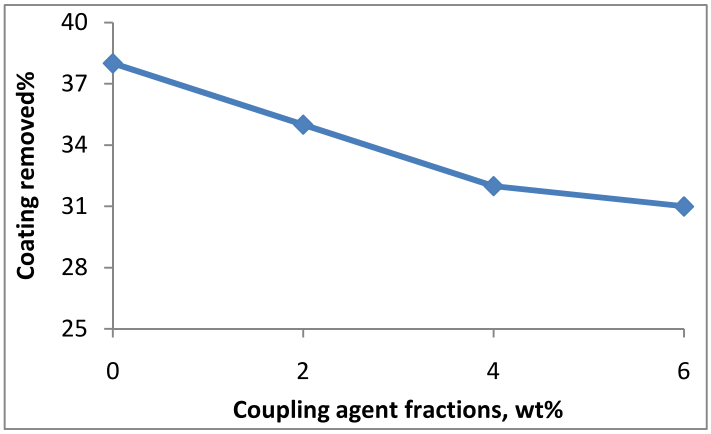


Figure 04-35: The effect of coupling agent fraction on adhesions of superhydrophobic coating with nano silica

The results indicated that increasing the coupling agent fraction could increase the coating adhesions. The optimum point was between 4 to 6wt%.

Production method and solvent type

The effect of production method, solvent type and silicone rubber types on the contact angles of superhydrophobic coatings including 30 wt% nano silica were evaluated. The RTV superhydrophobic silicone rubber coatings with nano silica were prepared by usual method and new method of coatings production (they were discussed in chapter 2). The contact angles of two coatings were compared in table 4-6. The results indicated that new method of production can increase the contact angles of silicone rubber coatings more than usual method. Moreover, the dispersion of higher than 30 wt% nano silica in silicone rubber coatings were not possible in usual method while in new method, the addition of higher nano silica up to 50 wt% were achievable.

Table 04-6: The effect of production method in RTV silicone rubber coatings

	RTV silicone rubber coatings	
	New method	Usual method
Contact Angle, degree	142	133

Another factor that could affect the hydrophobicity of coatings was solvent type. For the mixing of nano silica in RTV silicone rubber, aromatic solvents should not be used because they can influence the hydrophobicity of nano silica and reduce the contact angles of coatings (Kanagasabapathy et al, 2009). Also, solvents that evaporate very fast like acetone or methyl ethyl ketone should not be used in silicone rubber alone, because they can cause crack in final coating films. Table 4-7 compared the contact angles of RTV silicone coatings including nano silica with two different solvents that were toluene and mineral spirit. The results showed that coatings with mineral spirit had higher contact angles than coatings with toluene.

Table 4-7: The effect of solvent type in the contact angle of RTV silicone rubber coatings with nano silica

	RTV silicone rubber coatings	
	Toluene	Mineral spirit
Contact Angle, degree	128	142

The type of silicone rubbers also could influence in the contact angles and water durability of coatings. The trade name of RTV silicone rubber that was used in this project was Elastosil E303. Another RTV silicone rubber with a trade name of Elastosil A316 was used to make RTV silicone rubber coatings with 30 wt% nano silica. The main difference of these two silicone rubbers was in the existence of silica filler. Elastosil E303 did not contain this filler while Elastosil A316 had this it. Tables 4-8 compared the contact angles of coatings with two different rubbers. The results indicated that coatings with silicone rubber without silica filler could have higher contact angles. Also the data given in table 3-9 indicated water durability of two coatings before immersion in water and after immersion. The sample coatings were immersed for 96 hours in water and let dry three days in lab air. The coatings with rubber without silica filler could recover hydrophobicity sooner than rubber with silica filler.

Table 04-8: The effect of rubber type in the contact angle of RTV silicone coatings with nano silica

	RTV silicone rubber coatings	
	Rubber with silica filler	Rubber without silica filler
Contact Angle, degree	131	142

Table 4-9: The effect of rubber type in the water durability of RTV silicone coatings with nano silica

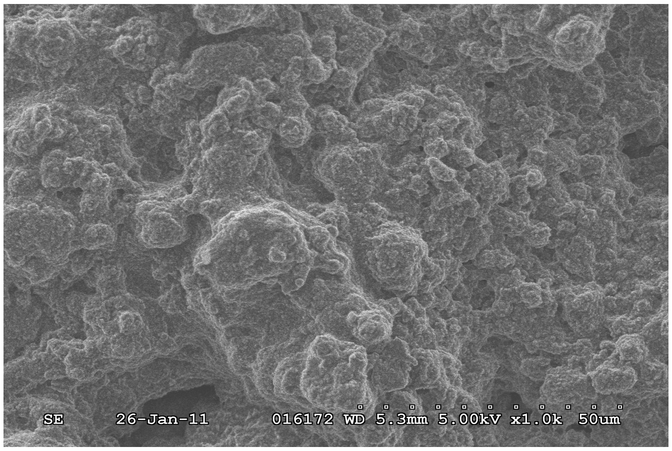
Contact Angle, degrees	**RTV silicone rubber coatings**	
	Rubber with silica filler	Rubber without silica filler
Before immersion	131	142
After immersion	118	136

The role of thickness in superhydrophobic coatings

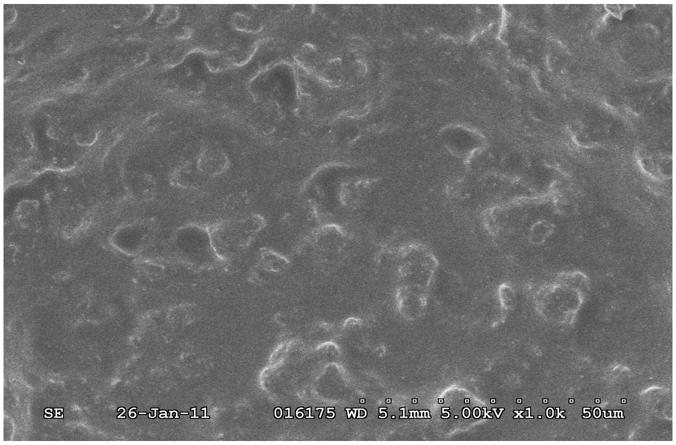
The thickness effect of RTV silicone rubber coatings with 30 wt% fluoric particles on contact angles was evaluated. As it can be observed in table 3-10, the contact angles of coatings were reduced by increasing thickness. Also the results of RTV silicone coatings containing 30 wt% nano silica were the same as that with fluoric particles. However, the nano silica in the RTV coatings with thickness higher than 120 µm could cause cracks and they could not be used in thick coatings like high voltage insulators. One method to improve the contact angles of RTV silicone rubber coatings in high thickness is that coatings should be sprayed in multiple layers. The last layer should have low thickness and are applied when the under layers were dried.

Table 4-10: The contact angle changes of RTV silicone rubber coatings against coating thickness

	Thickness			
	40 µm	80 µm	120 µm	160 µm
Contact Angle, degree	135	130	121	115



40 µm coating thickness



160 µm coating thickness

Figure 4-36: The SEM pictures of RTV silicone coating with two different thicknesses

The SEM picture was used to examine the surface of RTV silicone coatings including 30 wt% fluoric particles in two different thicknesses. Figure 4-36 compared the SEM surface pictures of 40 µm coatings with coatings of 160 µm thicknesses. The results demonstrated that coatings with low thickness had more surface roughness than coatings with high thickness.

Dispersing additives

A dispersion additive was added in a low concentration (1-3 wt %) to the super hydrophobic RTV coatings. The RTV silicone coatings with 13 wt% fluoric particles and 45% ATH were used for evaluating the effect of dispersing aid in the superhydrophobic coatings. The EDX analysis of coating cross section was employed to find the fraction of nano particles in three different areas of coating that were: (1) Top of the coating (Area 1), (2): in the bulk of coating (Area 2) and (3): near the substrate (Area 3). Figure 4-37 indicated the SEM picture of superhydrophobic coating cross section.

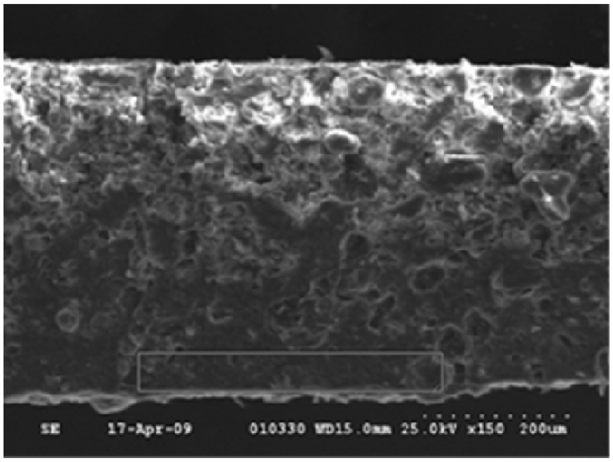


Figure 4-37: Cross section SEM picture of Superhydrophobic RTV silicone coating

Table 4-11 compares the distributions of fluor concentrations across the thickness of coating film with and without dispersing additives. More fluor on the top area of the superhydrophobic RTV silicone coatings with additive were detected comparing with that without additive, so it was be found that the dispersing aid could improve the dispersion of fluoric particle in superhydrophobic coatings.

Table 4-11: EDX results of the super-hydrophobic RTV coating

	Fluor fraction wt%	
	With Additive	Without Additive
Area 1	11.7	5.5
Area 2	14.5	10.8
Area3	7.7	12.6

Releasing silicone fluid from RTV silicone rubber coatings

RTV silicone rubber coating can release low molecular weight silicone fluid that comes from the bulk of coating surrounding contaminants and recovering hydrophobicity. An extraction technique was used to determine the amount of silicone fluid that can come from the bulk to the surface of coatings (Hackam et al, 2000). RTV silicone rubber coatings including nano silica or fluoric particle samples were immersed in hexane for 96 hours. Then, samples were dried in air for 12 hours that hexane could be completely removed from the coatings. The mass of silicone fluid that could go to the surface was determined by the difference between the weights of coated sample before immersion in hexane and after they were completely dried in air. The hydrophobic additives fractions were varied from 20 to 40 wt%. Table 4-12 displays the dependence of silicone fluid amounts that diffused from coating, to hydrophobic additives fractions. The results demonstrated the amount of silicone that could go to the surface would reduce with increasing additive fractions. This is because firstly the fillers had large surface area and they would absorb more silicone when their concentration increased. Secondly, the fraction of silicone rubber in formulation with higher filler fraction was smaller than formulation with lower filler fraction. For instance, RTV silicone coatings including 40 wt% nano silica had less silicone rubber than formulation containing 20 wt% nano silica.

The results indicated that nano silica could absorb more silicone fluid than fluoric particles.

Table 4-12: Silicone fluid weight loss from RTV silicone coatings including hydrophobic additives

	Weight loss (gr/ m^2)		
	20 wt%	30 wt%	40 wt%
Nnao silica	3.68	2.41	1.75
Fluoric particle	4.13	2.92	2.05

Chapter 5

Superhydrophobic fluoropolymeric and icephobic coatings

This chapter will discuss about the results that were obtained from the tests that carried out to determine the different properties of coatings. The first part is related to the results of superhydrophobic fluoropolyurethane coatings and the second part dealt with icephobic coatings.

5-1 Superhydrophobic coatings

The fluoropolyurethane superhydrophobic coatings were made from the blending of fluoropolyurethane polymers with hydrophobic additives, hydrophobic fillers or the combination of hydrophobic additives and fillers. The contact angles and sliding angles were conducted to evaluate the coatings hydrophobicity. Also SEM pictures exhibited the topography of surfaces. Water immersion test, adhesion test, hardness, rubbing durability and UV durability tests were utilized to check the mechanical and the weathering durability of coatings. Some factors that could influence hydrophobicity or mechanical properties of coatings were evaluated too. They were: the role of coupling agents in adhesion of superhydrophobic coatings; the effect of production method and solvent type.

5-1-1 Results

Contact angles

The contact angles were measured by using Rame-Hart 100 Goniometer. The contact angle results for fluoropolyurethane coatings with hydrophobic additives, hydrophobic fillers or the combination of them were noted in Figures 5-1 to 5-5.

As it can be seen in Figure 5-1, the contact angles of fluoropolyurethane coatings raised with increasing hydrophobic additive fractions. The highest contact angle was attained at 148°. The results indicated that only nano silica could make superhydrophobic coatings when it was mixed with fluoropolyurethane polymers and ultrafine fluoric particles could not increase the contact angle of coatings to higher than 125º.

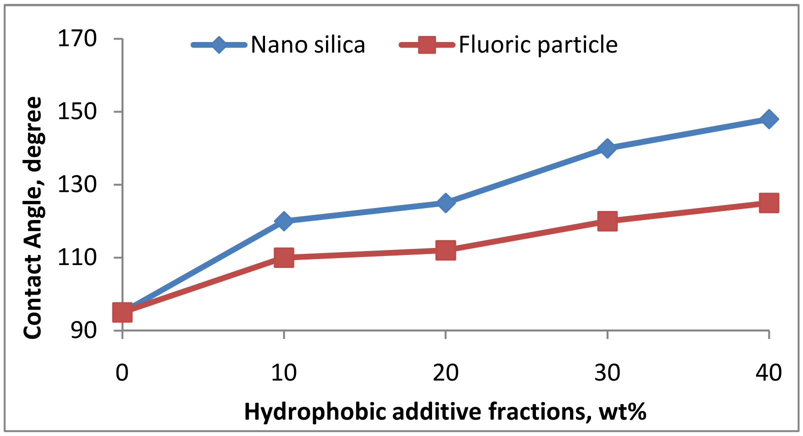


Figure 5-1: The Contact angles of fluoropolyurethane coatings with hydrophobic additive

Figure 5-2 displays the contact angle changes of fluoropolyurethane coatings containing hydrophobic treated calcium carbonate (NC) or treated glass beads (G). The contact angles rose with increasing hydrophobic filler concentrations. The highest contact angle was achieved at 40 wt% and it was 125º. As it can be found, the hydrophobic fillers could not make superhydrophobic coatings.

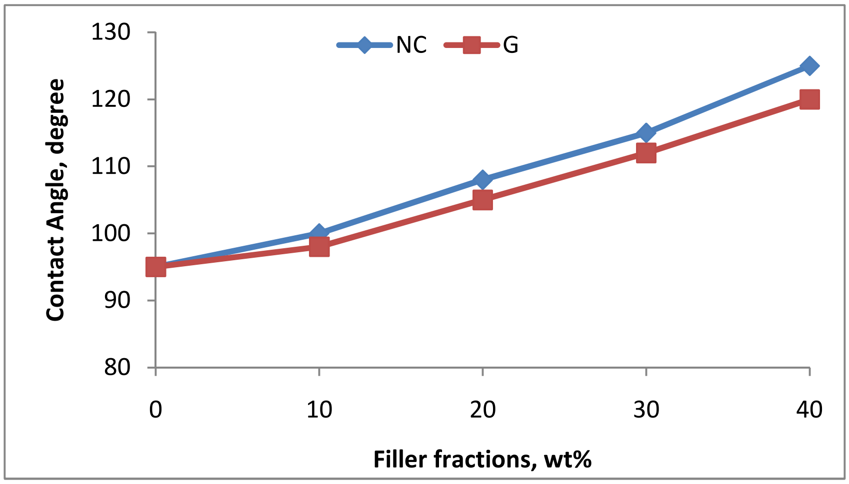


Figure 5-2: The Contact angles of fluoropolyurethane coatings with hydrophobic fillers

As it can be seen in Figure 5-3, the contact angles of fluoropolyurethane coatings raise with increasing the fraction of nano silica and ultrafine fluoric particle combination. The concentrations of nano silica were varied from 10 to 30 wt% while the fractions of fluoric particle were changed from 10 to 30 wt% in each nano silica concentration. The maximum contact angle was attained at the point containing 30 wt% nano silica and 10 wt% fluoric particles. The highest angle reached 146º. The highest fraction of nano silica and fluoric particle was 40 wt% and after this point, the dispersion of these materials in coatings were not possible.

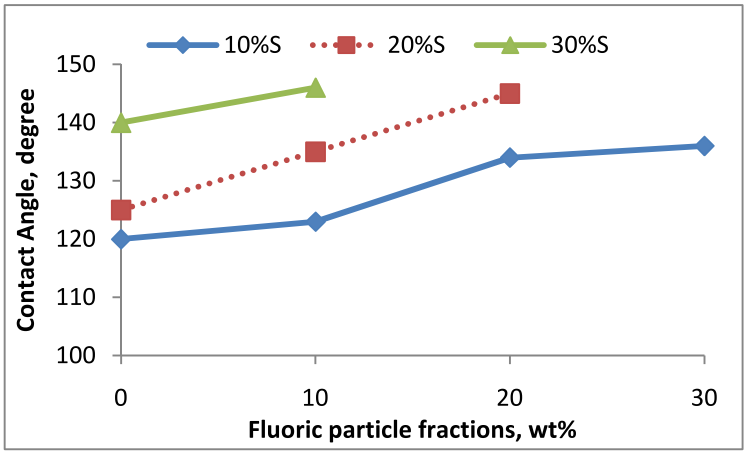


Figure 05-3: The Contact angles of fluoropolyurethane coatings with the combination of nano silica (S) and fluoric particles

Also, Figure 5-4 shows the contact angles of fluoropolyurethane coatings were enlarged when the fraction of nano silica and nano calcium carbonate (NC) combination were increased. The concentrations of nano $CaCO_3$ were altered from 10 to 40 wt% while the nano silica fractions were varied from 10 to 30 wt% in each nano calcium carbonate fraction. The maximum contact angle was 148º and the highest fraction of nano silica and nano calcium carbonate combination was achieved at 50 wt%.

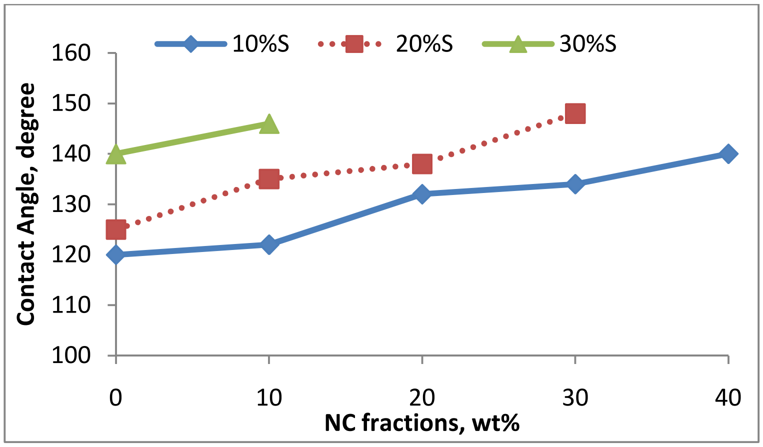


Figure 05-4: The Contact angles of fluoropolyurethane coatings with the combination of nano silica (S) and nano calcium carbonate (NC)

As it can be observed in Figure 5-5, the contact angles of fluoropolyurethane coatings increased when the concentration of nano silica and glass beads (G) combination were raised. The fractions of nano silica were varied from 10 to 30 wt% when the concentrations of treated glass bead were changed from 10 to 40 wt% in each nano silica fraction. The highest contact angle was 148° and the maximum fraction of nano silica and glass bead combination in fluoropolyurethane coatings was 50 wt%.

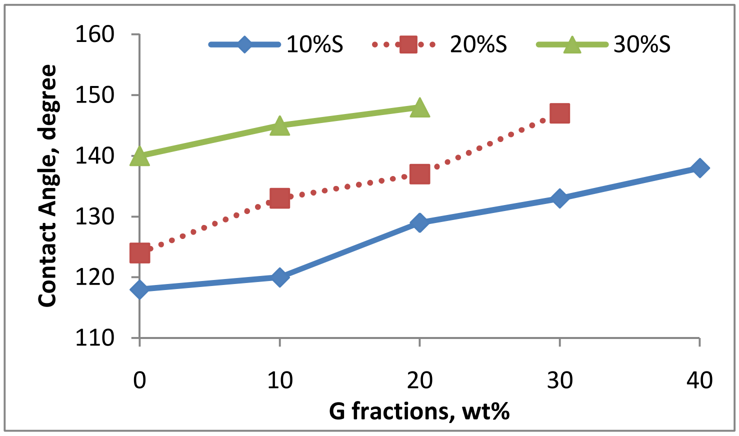


Figure 05-5: The Contact angle of fluoropolyurethane coatings including the combination of nano silica (S) and treated glass bead (G)

Sliding angles

Sliding angle shows the heterogeneity of surface and was measured by injecting a droplet on a surface and tilting the surface to find the angle of the surface to the horizontal plain when the droplet starts to slide. The sliding angle results for fluoropolyurethane coatings with hydrophobic additives, hydrophobic fillers or the combination of them were noted in the figures 5-6 to 5-10.

As it can be seen in Figure 5-6, the sliding angles of fluoropolyurethane coatings reduced with increasing the hydrophobic additive fractions. The minimum sliding angle was attained at 4°. The results indicated that only nano silica could make superhydrophobic coatings when it was mixed with fluoropolyurethane polymers and ultrafine fluoric particle could not decrease the sliding angle of coatings less than 15º.

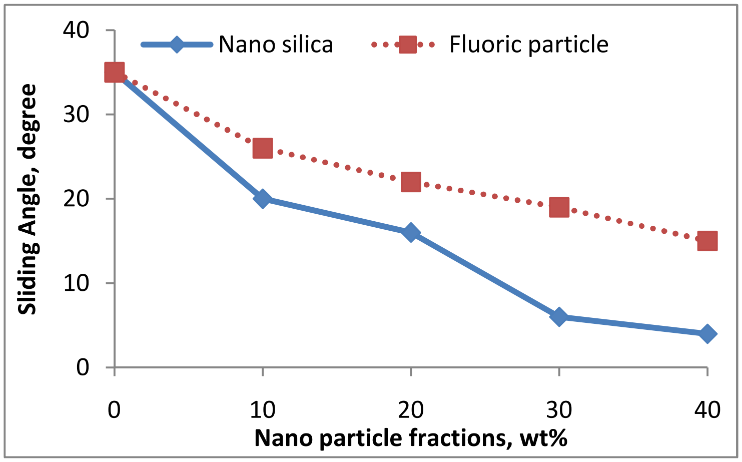


Figure 5-6: The sliding angles of fluoropolyurethene coatings with hydrophobic additives

Figure 5-7 illustrates the sliding angle changes of fluoropolyurethane coatings containing hydrophobic treated calcium carbonate (NC) or treated glass bead (G). The sliding angles reduced with increasing the hydrophobic filler concentrations. The lowest sliding angle was achieved at 40 wt% and it was 13º. As it can be found, the hydrophobic fillers could not make superhydrophobic coatings.

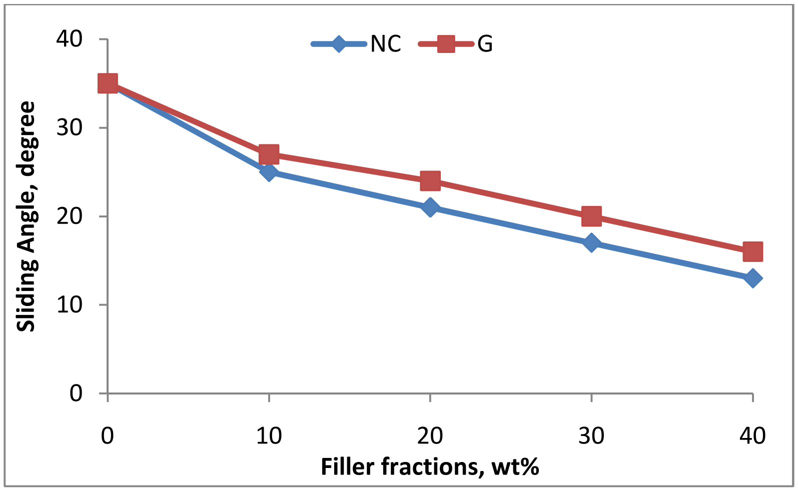


Figure 5-7: The sliding angles of fluoropolyurethane coatings including hydrophobic fillers

As it can be seen in Figure 5-8, the sliding angles of fluoropolyurethane coatings decreased with increasing the fraction of nano silica and ultrafine fluoric particle combination. The concentrations of nano silica were varied from 10 to 30 wt% while the fractions of fluoric particle were changed from 10 to 30 wt% in each nano silica concentration.

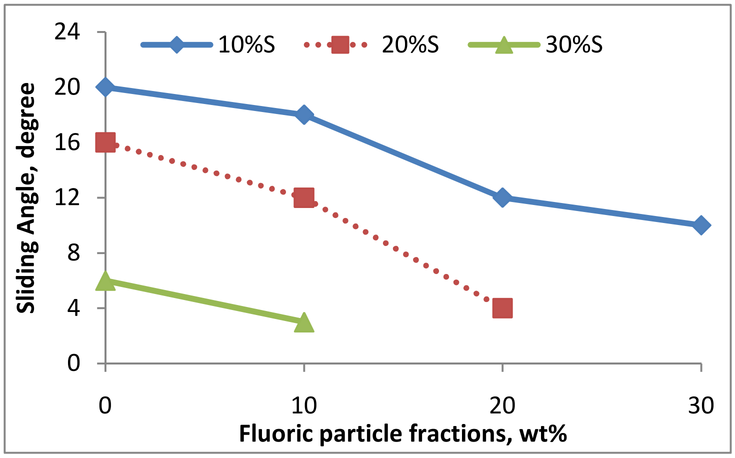


Figure 05-8: The sliding angles of fluoropolyurethane coatings with the combination of nano silica (S) and nano fluoric particle

The maximum sliding angle was attained at the point containing 30 wt% nano silica and 10 wt% fluoric particle. The lowest angle reached 3º. The highest fraction of nano silica and fluoric particle was 40 wt% and after this point, the dispersion of these materials in coatings were not possible.

Also, Figure 5-9 shows the sliding angles of fluoropolyurethane coatings were reduced when the fraction of nano silica and treated nano calcium carbonate (NC) combination were decreased. The concentrations of nano $CaCO_3$ were altered from 10 to 40 wt% while the nano silica fractions were varied from 10 to 30 wt% in each nano calcium carbonate fraction. The minimum sliding angle was 4º and the highest fraction of nano silica and nano calcium carbonate combination was achieved at 50 wt%.

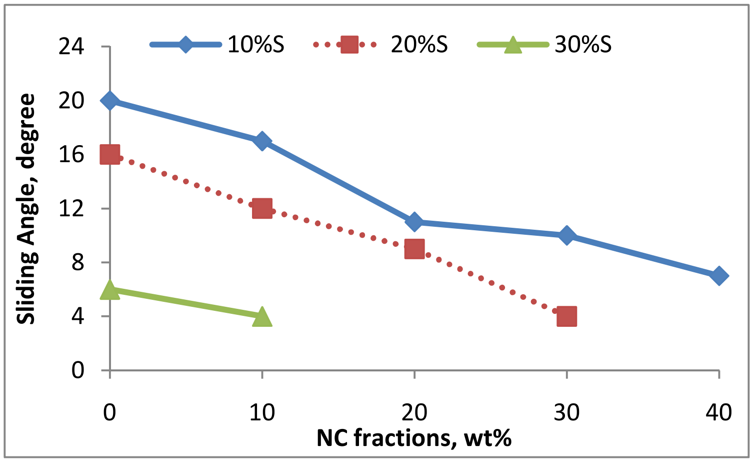


Figure 5-9: The sliding angles of fluoropolyurethane coatings with the combination of nano silica (S) and treated nano calcium carbonate (NC)

As it can be observed in Figure 5-10, the sliding angles of fluoropolyurethane coatings decreased when the concentration of nano silica and glass beads (G) combination were raised. The fractions of nano silica were varied from 10 to 30 wt% when the concentrations of treated glass bead were changed from 10 to 40 wt% in each nano silica fraction. The lowest sliding angle was 4° and the maximum fraction of nano silica and glass bead combination in fluoropolyurethane coatings was 50 wt%.

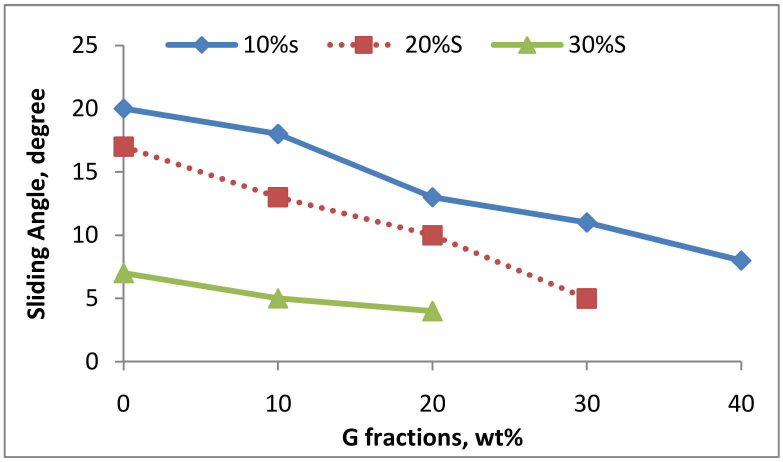


Figure 5-10: The sliding angles of fluoropolyurethane coatings including the combination of nano silica (S) and treated glass bead (G)

SEM pictures

The SEM pictures were utilized to evaluate the topography of coated surfaces. The Figure 5-11 showed the SEM picture of fluoropolyurethane coatings with 40 wt% nano silica.

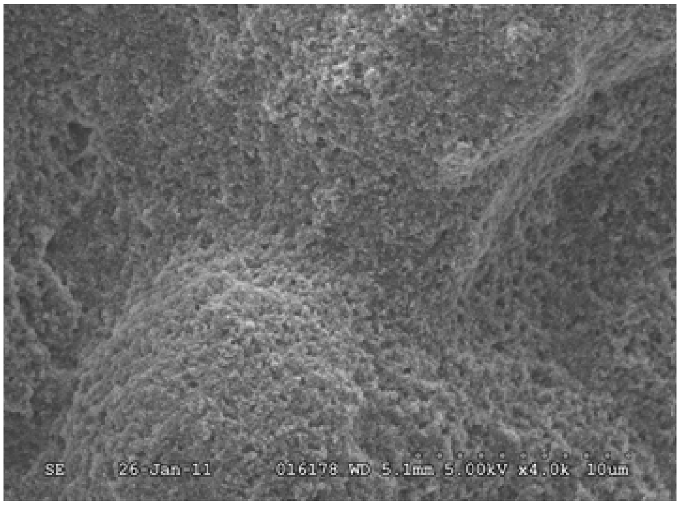


Figure 05-11: The SEM picture of superhydrophobic fluoropolyurethane coatings

Water immersion test

This test assesses the water durability of superhydrophobic coatings. The coated samples were immersed in water for 96 hours and then dried up in air to examine the durability of coatings with water immersion (Hillborg et al, 1999). The contact angles of fluoropolyurethane coatings before immersion in water were compared with contact angles after one day drying in lab air because the fluoropolyurethane can not recover hydrophobicity, so only the contact angle after one day drying was checked.

Figure 5-12 indicats the contact angle alterations of fluoropolyurethane coatings including hydrophobic additives before (B) and after (A) immersion in water. The concentrations of nano silica (S) or nano fluoric particles (F) were varied from 10 to 40 wt%. The results demonstrated that only fluoropolyurethane coatings including 40 wt% nano silica had a good durability after immersion in water and other formulations could not pass this test.

The fluoropolyurethane coatings including hydrophobic fillers (nano calcium carbonate or glass bead) were not superhydrophobic, so the durability of these coatings against water was not tested in this study.

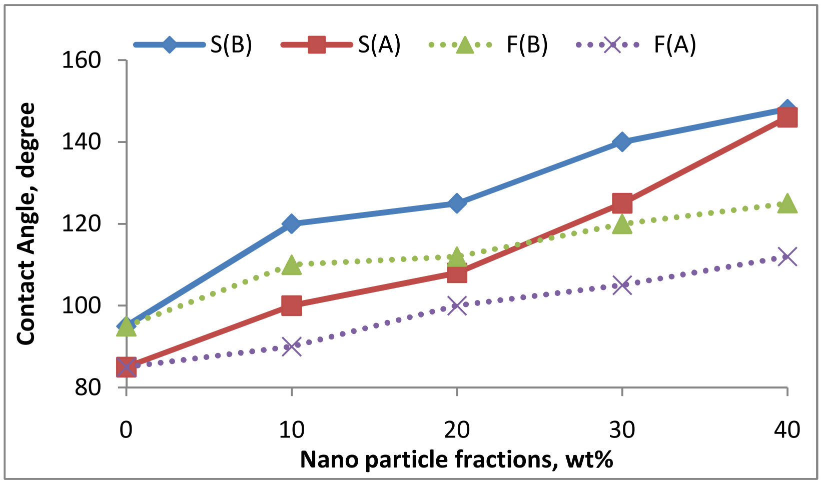


Figure 05-12: The contact angle changes of fluoropolyurethane coatings with hydrophobic additives after immersion in water

As it can be observed in Figure 5-13, the contact angles of fluoropolyurethane coatings with the combination of nano silica and fluoric particle change after immersion in water. The nano silica fraction was 20 wt% and fluoric particle concentration were varied from 10 to 20 wt%. The coatings containing 20 wt% nano silica and 20 wt% fluoric particle could pass this test.

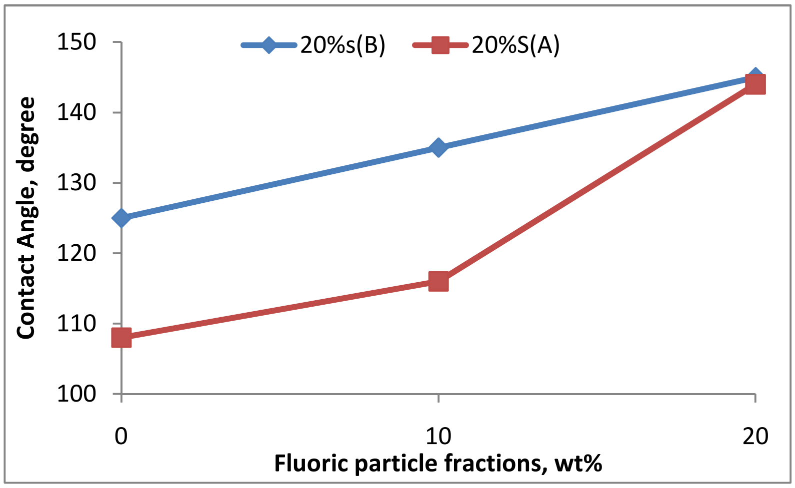


Figure 05-13: The contact angle changes of fluoropolyurethane coatings with 20 wt% nano silica and fluoric particle

Figure 5-14 illustrates the contact angle changes of fluoropolyurethane coatings containing the combination of nano silica and nano calcium carbonate (NC) before (B) and after (A) immersion in water. The fractions of nano silica were varied from 20 to 30 wt% while the concentrations of nano $CaCO_3$ were altered from 10 to 30 wt% in each nano silica concentration. The fluoropolyurethane coatings including the combination of nano silica and nano calcium carbonate could not pass the immersion test. The results of immersion tests for fluoropolyurethane coatings containing the combination of hydrophobic additive (nano silica or fluoric particle) and glass bead were similar to the results of coatings including the combination of hydrophobic additives and nano $CaCO_3$, so they have not repeated again here.

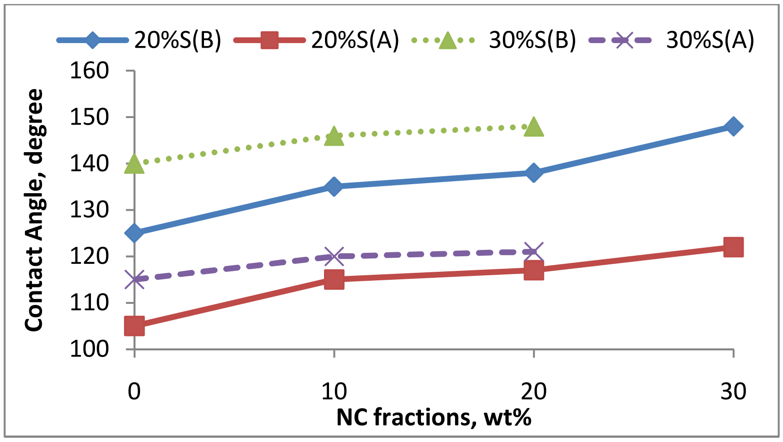


Figure 5-14: The contact angle changes of fluoropolyurethane coatings including the combination of nano silica and nano $CaCO_3$ (NC)

Adhesion

The adhesion of fluoropolyurethane coatings was measured in accordance with ASTM D3359 by using a cross hutch cutter. The adhesion results of fluoropolyurethane coatings will be indicated in the following:

Figure 5-15 demonstrates the adhesion changes of fluoropolyurethane coatings with hydrophobic additives (nano silica and ultrafine fluoric particle) on glass (G) and metal (M) substrates. The hydrophobic additives concentrations were changed from 10 to 40 wt%. The results showed that increasing hydrophobic additives fractions could reduce the adhesion of coatings. However, the reduction on metal was more considerable in glass surface and nano silica could reduce the coating adhesion more than fluoric particle.

The fluoropolyurethane coatings with hydrophobic fillers (nano calcium carbonate or glass bead) were not superhydrophobic. As a result, the adhesion of coatings including these fillers wered not measured in this project.

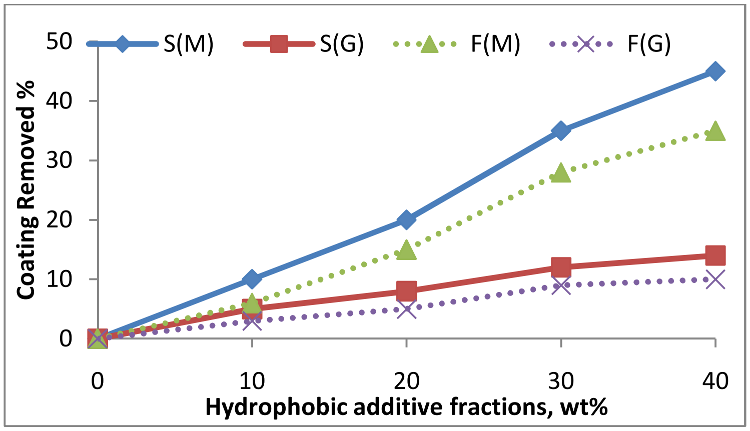


Figure 05-15: The adhesion of coatings including hydrophobic additives to metal (M) and glass (G) surfaces

As it can be found in Figure 5-16, the adhesion of coatings including the combination of nano silica and fluoric particle reduces with increasing the fraction of combination of these two additives. The fractions of nano silica were changed from 10 to 30 wt% while the fractions of fluoric particle were altered from 10 to 30 wt% in each nano silica concentration. However, the highest fraction of nano silica and fluoric particle was attained at 40 wt%. The point including 30 wt% nano silica and 10 wt% fluoric particle had the worst adhesion.

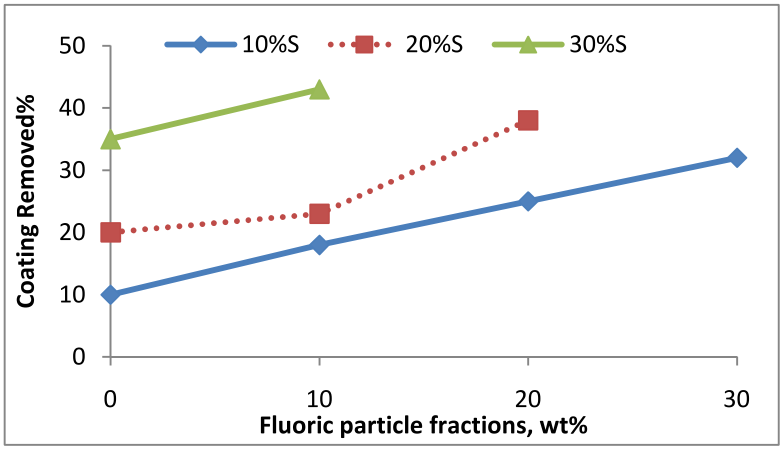


Figure 05-16: The adhesion of coatings including the combination of nano silica and fluoric particle

Figure 5-17 displays the adhesion changes of fluoropolyurethane coatings including the combination of nano silica and nano calcium carbonate (NC). The fractions of nano silica were changed from 10 to 30 wt% while the fractions of nano $CaCO_3$ were altered from 10 to 30 wt% in each nano silica concentration. The highest fraction of nano silica and nano calcium carbonate was achieved at 50 wt% and after this point, the dispersion of these materials in coatings were not possible.

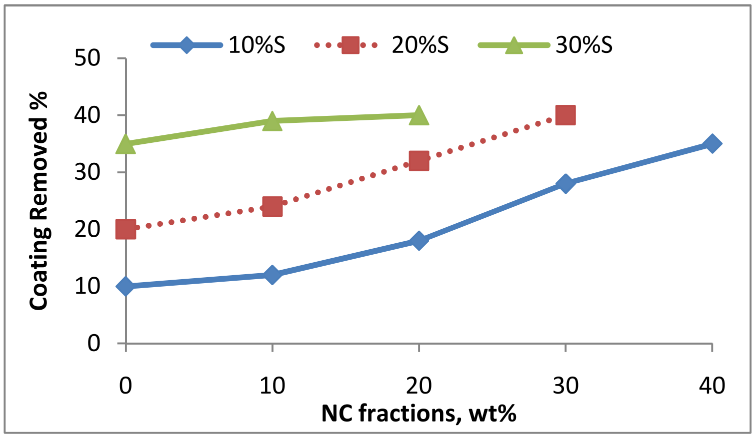


Figure 05-17: The adhesion of coatings including the combination of nano silica and nano calcium carbonate (NC)

The results of adhesion tests for fluoropolyurethane coatings containing the combination of hydrophobic additive (nano silica or fluoric particle) and glass bead were similar to the results of coatings including the combination of hydrophobic additives and nano $CaCO_3$, so they have not repeated again here.

UV durability

The UV durability test of superhydrophobic coatings was conducted with Q-Sun Xenon Test Chamber (Q-Lab Company, USA) in accordance with ASTM G-155. The total exposure time was 1000 hours; the contact and sliding angles of coatings were assessed every 100 hours to evaluate the effect of UV radiation on coatings.

Figures 5-18 and 5-19 indicate the contact and sliding angles changes against UV radiation for fluoropolyurethane coatings including 30 wt% and 40 wt% hydrophobic additives (nano silica (S) or fluoric particle (F)). The time zero was before starting UV test. The results showed that only fluoropolyurethane coatings with 40 wt% nano silica could pass the UV and weathering durability tests.

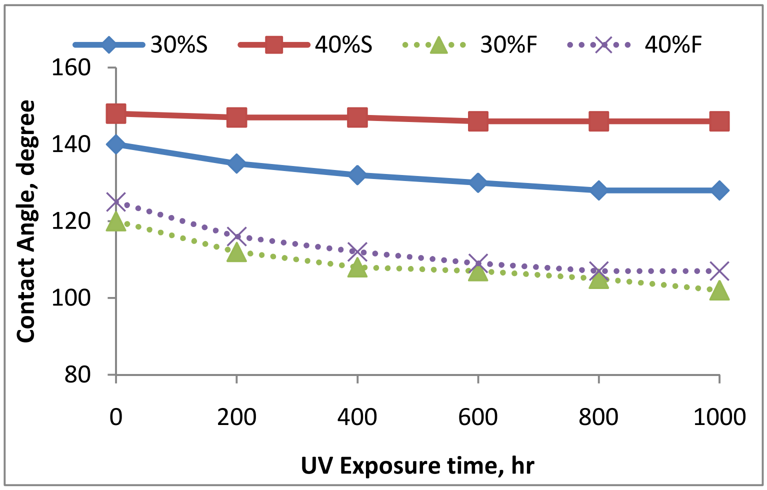


Figure 05-18: The contact angle changes of fluoropolyurethane coatings with hydrophobic additives against UV exposure time

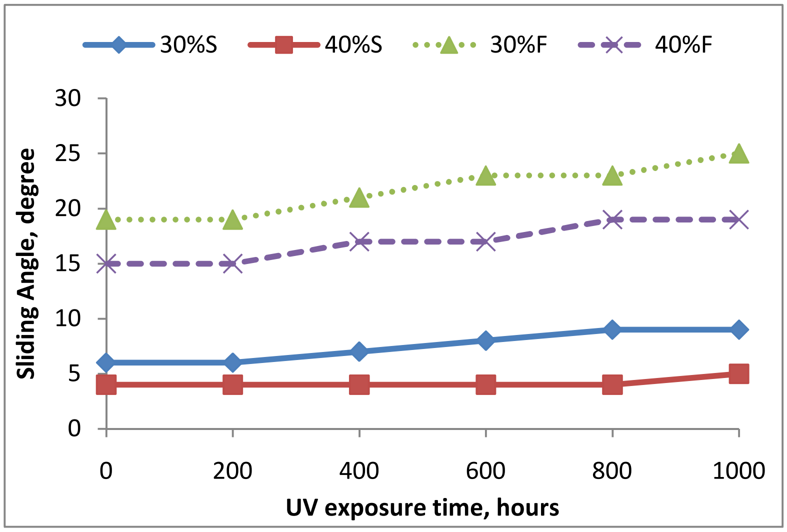


Figure 05-19: The sliding angle changes of fluoropolyurethane coatings with hydrophobic additives against UV exposure time

The results of fluoropolyurethane coatings with the combination of nano silica and fluoric particle or hydrophobic fillers (nano calcium carbonate and glass bead) showed that coatings including the combination of 20 wt% nano silica and 20 wt% fluoric particles could pass UV and weathering durability test.

Hardness

The test was done in accordance with ASTM D3363. Pencil test was utilized to assess the hardness of coatings. A set of calibrated wood pencils with different scale of hardness was used which the softest was 6B and the hardest was 6H.

Table 5-1 indicates the hardness of fluoropolyurethane coatings containing hydrophobic additives (nano silica or ultrafine fluoric particle) or hydrophobic fillers (nano calcium carbonate or glass bead). The fractions of hydrophobic additives or fillers were varied from 10 to 40 wt%. The results demonstrated that with increasing hydrophobic additives or fillers concentrations the coating hardness would raise.

Table 5-1: The hardness of fluoropolyurethane coatings with hydrophobic additives or hydrophobic fillers

Materials	**Hardness**				
	0 Wt%	**10 wt%**	**20 wt%**	**30 wt%**	**40 wt%**
Fluoric particle	3H	3H	3H	4H	5H
Nano silica	3H	3H	4H	5H	6H
Nano $CaCO_3$	3H	3H	3H	4H	4H
Glass bead	3H	3H	3H	3H	4H

The highest hardness (6H) was for fluoropolyurethane coatings with 40 wt% nano silica. The hardness of fluoropolyurethane coatings without additives or filler was 3H.

The data given in Table 5-2, demonstrates the hardness of fluoropolyurethane coatings containing the combination of nano silica (S) and fluoric particle. The fluoric particle fractions were altered from 10 to 30 wt% in each nano silica concentration. The nano silica fractions were changed from 10 to 30 wt%. The maximum hardness was attained at 30 wt% nano silica and 10% fluoric particle. The highest hardness was 5H and the maximum fraction of nano silica and fluoric particle was 40 wt% and after this point, the dispersion of these materials in polymers were not possible.

Table 05-2: The hardness of fluoropolyurethane coatings including the combination of nano silica and fluoric particle

Fluoric particle fractions wt%	**Hardness**		
	10 wt% S	**20 wt% S**	**30 wt% S**
0	3H	4H	5H
10	3H	4H	5H
20	4H	5H	
30	4H		

Table 5-3 demonstrates the hardness of fluoropolyurethane coatings containing the combination of nano silica (S) and treated nano calcium carbonate. The fractions of nano silica were varied from 10 to 30 wt% while the nano $CaCO_3$ concentrations were changed from 10 to 40 wt%. The maximum hardness (5H) was achieved at 30 wt% nano silica and 20 wt% nano calcium carbonate. The highest fraction of nano silica and nano $CaCO_3$ was 50 wt% and after this point, the dispersion of these materials in polymers were not possible. The hardness results of fluoropolyurethane coatings including the combination of nano silica and glass bead were similar to the results of nano silica and nano calcium carbonate, so they did not repeated again.

Table 05-3: The hardness of fluoropolyurethane coatings with the combination of nano silica and nano $CaCO_3$

Nano CaCO3 fractions	**Hardness**		
	10wt% S	**20WT% S**	**30WT%S**
0	3H	4H	5H
10	3H	4H	5H
20	3H	4H	5H
30	4H	5H	
40	4H		

Also, the fluoropolyurethane coatings containing the combination of fluoric particle and hydrophobic fillers (nano calcium carbonate and glass bead) did not indicate superhydrophobic properties, so the hardness of these coatings was not assessed in this work.

Rubbing resistance

The coating surfaces were rubbed by a 100% cotton cloth and by selfmade rubbing instrument. The fluoropolyurethane coatings including 40 wt% nano silica or the combination of 20 wt% nano silica and 20 wt% fluoric particles could pass 2500 rubs. Also the coatings including the combination of 30 wt% nano silica and 20 wt% nano calcium carbonate or glass bead could show rubbing durability too.

5-1-2 Discussion

The results of fluoropolyurethane coatings with hydrophobic additives and hydrophobic fillers showed that only nano silica could make coatings with contact angles higher than 130°. However, the ultrafine fluoric particle could increase contact angles more than hydrophobic fillers. The results of fluoropolyurethane coatings including the combination of nano silica and fluoric particle or hydrophobic additives indicated that the fluoropolyurethane coatings including at least 30 wt% of nano silica and aforementioned materials could have contact angles higher than 130°.

The fluoropolyurethane coatings including at least 30 wt% nano silica indicated sliding angles less than 7°. The coatings including fluoric particle or hydrophobic additives could not show sliding angles less than 11° and they were not superhydrophobic. Also, fluoropolyurethane coatings containing the combination of nano silica and fluoric particle or hydrophobic filler showed sliding angles less than 7° when the fraction of the combination were higher than 40 wt%. The coatings including the combination of nano silica and fluoric particle indicated less sliding angle compared with the coatings containing the combination of nano silica and hydrophobic filler. The contact angle hysteresis (CAH) of fluoropolyurethane coatings with sliding angles less than 7º were around 5º to 7º, so these coatings could show self cleaning properties due to low CAH.

The SEM picture confirmed the micro/or nano structure that is one of the important fact for superhydrophobic coatings.

The results of immersion water tests of fluoropolyurethane coatings with hydrophobic additives or the combination of nano silica and fluoric particle or hydrophobic fillers demonstrated that only the fluoropolyurethane coatings including 40 wt% nano silica or the combination of 20 wt% nano silica and 20 wt% fluoric particles could pass the water durability test. However, the fluoropolyurethane coatings containing the combination of 20 wt% nano silica and 30 wt% hydrophobic fillers were superhydrophobic, but they could not pass water durability test. This issue indicates that the polymer type is important in superhydrophobic coatings because RTV superhydrophobic silicone rubber coatings with the combination of nano silica and hydrophobic fillers could pass water immersion test.

The adhesion of fluoropolyurethane coatings including hydrophobic additives, hydrophobic fillers or the combination of these materials reduced when the concentration of additives or fillers increased. The coatings with highest contact angles showed the worst adhesion to the surface. However, the adhesion of coatings to the glass was better than metal surface.

The fluoropolyurethane coatings including 40 wt% nano silica or 20 wt% nano silica and 20 wt% fluoric particles could pass UV and weathering durability test and other formulations failed.

Fluoropolyurethane coatings including the hydrophobic additives, hydrophobic fillers or the combination of them indicated good hardness especially with increasing additive or fillers fractions. The highest hardness was with 6H at 40 wt% nano silica. The results showed that fluoropolyurethane coatings can be used in more wide range than RTV silicone coatings because they have a good hardness.

The rubbing resistance of fluoropolyurethane coatings with contact angles higher than 140º was about 2500 rubs, so they indicated good durability.

Coupling agents and superhydrophobic coatings

The coupling agent was mixed with superhydrophobic coatings containing 30 wt% hydrophobic additives (nano silica) to increase the adhesion of coatings to the substrate. The concentrations of coupling agents in samples were 2%, 4% and 6%. Figure 5-20 showed the effect of coupling agent fraction on fluoropolyurethane coatings. The results indicated that increasing the coupling agent fraction could increase the coating adhesion. The optimum point was between 4 to 6 wt%.

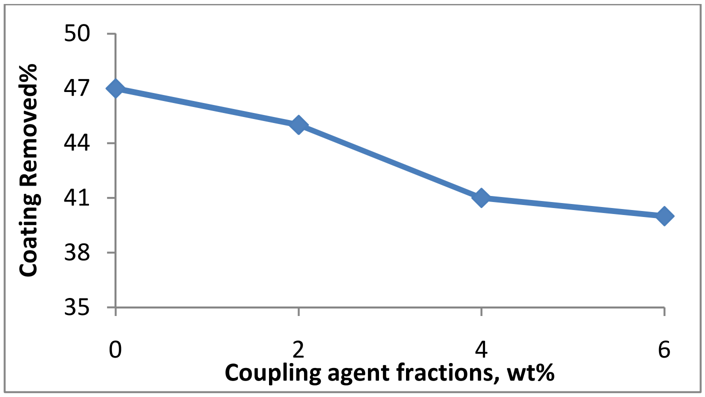


Figure 05-20: The effect of coupling agent fraction on superhydrophobic coatings including nano silica

Production method and solvent type

The production method can influence in the coatings property as it discussed before in superhydrophobic RTV coatings. The mixing of nano silica higher than 30 wt% in the usual method of coating production was not possible and only new methods could be used. Another factor that could affect the hydrophobicity of coatings was solvent type. For the mixing of nano silica in fluoropolyurethane coatings, aromatic solvents should not be used because they can affect the hydrophobicity of nano silica and reduce the contact angles of coatings. Also, solvents that evaporate very fast like acetone or methyl ethyl ketone should not be used in silicone rubber alone, because they can make crack on final coating films.

5-2 Icephobic Coatings

Ice and snow build-up on outdoor surfaces is a major problem for much outdoor equipment such as power transmission line, aircraft and boats. The ice can devastate the structures or defunctionalize the equipment. The instability of ships has been found in icing conditions for hundreds of years, but the ice prohibition was studied only after 1950s when the British trawlers Lorella and Roderigo were lost. The devastation results of ice are abundant. For example, many drivers have dangerous experiences with ice on highways and bridges. However, the most serious results are related to electrical grid. For instance, high voltage transmission towers collapsed because of freezing rainstorms. In Canada, 26 large towers collapsed because of ice storms between 1958 until 2002 and in the US, 205 towers collapsed during 1929 till 2000. Ice damage to transmission grid costs $10 million-$50 million for US annually (Petrie, 2009).

The control of ice can be done with different ways on static surfaces, so far the best way is to keep temperature of the surface above 0°C. For example, aircraft sometimes are stored in heated hangers. Some chemicals like glycol ethers can be used to de-ice aircraft, they can reduce the freezing point of water effectively.

An ideal and more economical de-icing method is to apply a material that prevents ice from building up rather than taking it off from the surface afterwards. For this work, the adhesion strength of ice should be less than shear stress that the ice applies to the surface. Generally adhesion can be chemically or physically binding of two substrates. Substrate that have reactive groups like OH or C=O groups in glass can make chemical attraction that have high adhesion strength, but substrates with limited or no available binding site make lower adhesion strength from van der waals forces. Ice phobic coatings that can reduce the ice adhesion can be a good candidate to prevent from ice building. The adhesion of ice to polymeric material is lower than metallic materials, because the interfacial strength usually is less than ice strength, so the failure happened at the interface. Hydrophobic surface has shown low ice adhesion and some researchers have found that super hydrophobic surfaces have the lowest ice adhesion and they can reduce the speed of ice forming. For practical ice phobic coating, contact angles should be higher than 90°. Fluorinated and polysiloxane coatings have the poorest wetting properties and are nominated as the best candidate for anti-ice coatings (Ryzhkin et al, 1997). There are some ice phobic coatings in the market and significant researches have been done to make coatings that have lower ice adhesion. We can divide them in two categories:

Superhydrophobic coatings

M. Farzaneh et al (2009) made superhydrophobic coatings with fluoropolymer and ZrO_2 powder or Ag nano particles and showed that superhydrophobicity with contact angle above 150° and CAH (Contact Angle Hysteresis) lower than 10° could reduce the adhesion of ice more than hydrophobic coatings. Wang et al (2007) indicated that superhydrophobic coatings could delay the forming of ice against usual coatings. They made some hydrophobic particles from Nano-calcium carbonate with FAS (fluoroalkyl silane), and then they blended these particles with acrylic resin and made superhydrophobic coatings. Also Cao et al (2009) made superhydrophobic coatings from the mixing of synthesized acrylic resin, silicone resin and organosilane-modified silica particles. The coatings were cured in 80°c for 2h. Their results demonstrated that only nano silica with particle sizes between 20-50nm can inhibit the ice formation.

Coatings containing materials that reduce ice adhesion or break ice

Dolan et al (2007) made erosion resistant anti-icing coatings. The coatings are formulated by fluoroelastomer or silicone rubbers and some filler like graphite are blended with these polymers to make a weak boundary layer on the surface of coating. Also, some fluorocarbon oils were added to the polymers. Final results showed that silicone coatings have lower ice adhesion and filler or oil can reduce the adhesion of ice. The shear strength of fluoroelastomer with oil and PTFE is around 150 KPa that is lower than Teflon which has shear strength of 238 KPa. Bhamidipati et al (2009) prepared ice phobic coatings with silicone phase change material. Phase change material (PCM) has a high fusion heat that melts and solidifies in a certain temperature. This material can store and release energy when material change from solid to liquid and vice versa. The coatings are formulated with silicone resin and PCM. When the temperature goes below 0°, the PCM makes volume changes and reduce the adhesion of ice.

The adhesion of ice to structures can make huge problems. Electrical transmission towers, bridge decks and transportation vehicles like aircrafts are some common facilities that can be affected severely by ice adhesion. The huge problem from ice adhesion to the substrates has motivated researchers to find some ways to prevent ice adhesion. Despite many works that have been done to make anti-ice coatings, the ice phobic coatings in the market can only reduce the adhesion of ice and cannot inhibit or break the ice; so these coatings needs more researches and works to respond the demand of their applications. This project focuses on anti-ice coatings that can break the ice on the coatings or reduce its adhesion considerably.

Results and discussion

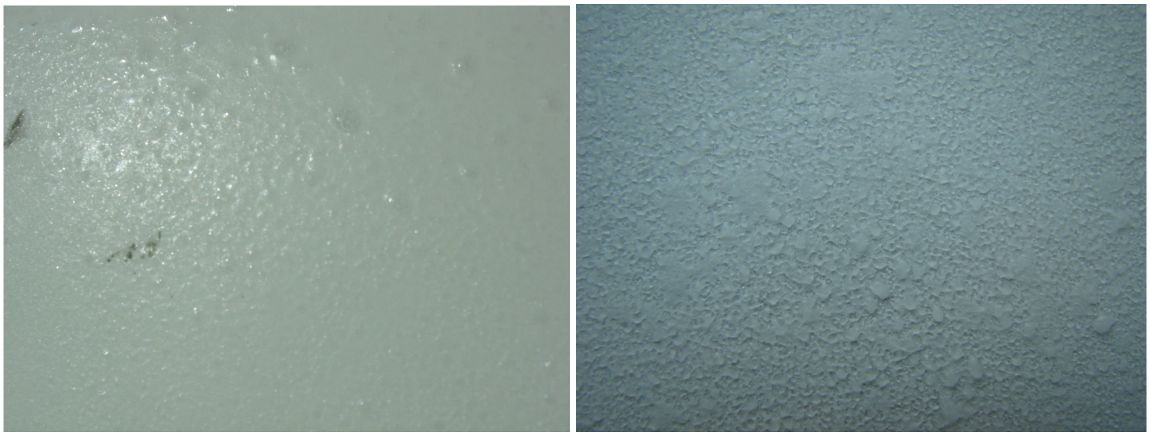
This part will discuss about the results of our icephobic coating researches. The samples coated by ice phobic coatings were held in the freezer and ice water (0 ºC) was sprayed on them (freezing rain test). The coated samples were compared with bared sample.

RTV silicone rubber or fluoropolyurethane coatings and hydrophobic nano silica

The ceramic tile was coated with RTV silicone rubber containing 30 wt% nano silica. Then coated sample and a bared ceramic tile were put outside in a snowy day. The both samples were compared with each other after one day (Snow test). The results demonstrated that there is not any adhesion of snow to superhydrophobic coating (Figure 5-21).

Figure 50-21: The snow test of coated and uncoated samples

The result of freezing rain test showed that RTV superhydrophobic coating could delay the forming of ice compared with uncoated sample and the droplets of ice on these coatings were small (Figure 5-22). Moreover, the RTV silicone coatings with 30% nano silica were compared with a commercial epoxy silicone icephobic coating (Micro Phase Company, USA). The commercial coating was not superhydrophobic and the adhesion of ice on uwo coating was less than commercial ones.



Uncoated Sample Coated Sample

Figure 5-22: The ice test of coated and uncoated samples

The results of snow and freezing rain tests of coated samples with fluoropolyurethane coatings with 30 wt% nanosilica were same as RTV silicone coatings with nano silica and were not displayed here.

RTV silicone rubber or fluoropolyurethane coatings including nano silica and graphite, deicers, PCM or oils (fluoro or silicone oils)

The results of freezing rain test showed that ice adhesion to the RTV silicone or fluorpolyurethane coatings would reduce with increasing graphite or oil fractions. The coatings including deicers could reduce the adhesion of ice better than graphite and oils, but the dispersion of these materials in coatings were not easy. Also, the results of 20% deicers were better than 5 wt%.

The results of freezing rain test demonstrated that silicone coatings with PCM could reduce the adhesion of ice like deicers. The droplets of water in some parts of ice in these coatings were seen after one hour from starting of tests. Also the result of 20 wt% PCM was better than 5 wt%. The final results of these coatings were worse than superhydrophobic coatings

RTV silicone rubber or fluoropolyurethane coatings and glass beads

The ceramic tiles were coated by RTV silicone rubber or fluoropolyurethane coatings with glass beads. The results of freezing rain tests showed that coatings could not break the ice on the surface. The final coatings were not superhydrophobic, so the adhesions of ice on them were stronger than superhydrophobic coatings.

Icephobic coatings with super absorbent polymers (SAP)

The result of freezing rain illustrated that the SAP could absorb water after forming the ice on the surface of coatings and this polymer performed volume change, but this volume change could not break the ice. Moreover, the coatings with SAP 30% could absorb more water than 20%. Also, the dispersion of this polymer in the coatings was not good and they tended to sediment.

Also the freezing test results of coated samples with one layer of fluoropolyurethnane coatings containing 20 or 30 wt% SAP and one layer of RTV silicone coatings exhibited that these coatings could not break the ice on the surface of coating. Generally, there was not any difference between one layer and two layers coatings and their results were not as well as superhydrophobic coatings.

CHAPTER 6

Conductive coatings

The electrostatic charge is attributed to attract the pieces of paper. Otto von Guericke in 1602 made the first electric generator that applied friction rubbing against a revolving ball of sulfur to produce static electricity. This electricity could be converted into attractive or repulsive forces by contact with the sulfur ball or contact with other bodies. The Franklin in 1706 proved that the nature of the spark is similar to that of lighting by his famous kite experiment. He described when a body has an excess of electric matter it is plus-electric while in case that body has too little electric matter it is minus-electric. Wilcke in 1757 made a triboelectric series for material that could be charged. The last material in a triboelectric series will become negatively charged when rubbed against any other material of the series that is positive. The time and intensity of the contact, the contact area, the rubbing intensity, and the grounding of the material can affect electrostatic charging (Dhogal, 1986). Though, some affinities are common. For instances, dry human skin, leather, fur or lead tend to stop electrons while amber, wood, gold, polyurethanes or PTFE be likely to become negatively charged. When wearing polyester cloths, the human body will tend to be charged positively. Dry hair will fly away when it is combed by a plastic comb. The attractive or repulsive forces will disappear with time due to instability of electrostatic charges. The material type, the humidity and environmental conditions can influence in discharging rate. The assumption that mechanical work generates electrical charge that is dissipated in friction makes triboelectric term. The electron capacity that is maximum possible quantity of charges on a body is a material parameter. The environment can affect the critical breakdown. The breakdown potential of dry air at atmospheric pressure is 30 KV/cm and when the voltage exceeds this point, the charge will be converted to electrical spark ((Pionteck et al, 2007).

The matter can be classified in accordance with its electric conductivity as insulator, semiconductor, conductor and superconductors. According to band theory, electrons exist in the valance bands, in the conductive band and at different energy levels. The electron-free band and completely filled bands have mean electron velocity equal to zero, so they can not contribute to conductivity. If the bands are partially filled, the conductivity will be achievable. The partially filled bands always make metallic conduction. In the insulator is not energy gap between the bands. There is a region of forbidden energy level which can not be occupied, so the conductivity is not possible since electrons can not switch between the completely filled valance band and the empty conductive band. However, in semiconductor the energy gap is small enough, so the electrons can jump by thermal activation from the valence band into the conductivity band. As a result, a certain degree of conductivity happens (Pionteck et al, 2007).

Electrostatic discharge causes fires and explosion in explosive industries. There are many accidents in petrochemical industries by static electricity. During the years between 1960 and 1975, 116 accidents of fire happened by electrostatic discharge in chemical industries of America. Oil tanks are the main part in petrochemical industries that can accumulate static charge, so antistatic coatings are applied on the inner wall of oil tanks to prevent the accumulation of static electricity in them. The amount of surface resistivity required to bleed off effectively this charge and prevent sparking, is between10^6 to$10^9\Omega/cm^2$ (Zhong et al, 2008).

Electromagnetic radiation is attributed to changes in electrical current or voltage levels. This radiation happens in discontinuous frequencies. Electromagnetic interference, EMI, happens when there is a source of electromagnetic energy or there is a receptor that is liable to a particular amplitude and frequency of transmitted source energy. Electromagnetic energy travels in all directions from the source and is produced in the form of spherical wave fronts. The wave includes an electric field and a magnetic field at any given point and they are perpendicular to each other and to the direction of propagation. EMI can be conducted when the source is connected to the receptor by power or signal cables. In this case, the interference is conducted from one unit to the other along the cables and it can be controlled by EMI filters. When a component emits energy that is transferred to a receptor through the atmosphere radiated EMI happens. Radiated interference can influence in any signal path within electronic equipment, so it is difficult to shield it. The sources of EMI are: natural like lighting or corona discharge;

electrical and electronic equipment like TV or cellular phones; industrial like arc welding or computers; commercial like cash registers or internal communication systems; and consumer goods like car ignition systems or remote controls. The performance of the very appliances is affected by all sources of electromagnetic interference. The usage of shielded enclosures and shielding materials can eliminate or reduce the radiated EMI. The second method for controlling EMI is to improve or reduce its weakness to interference from external EMI sources. The designing circuits and choosing components that are inherently less sensitive to interference can reduce or eliminate external EMI (Pionteck et al, 2007).

Generally EMI can be controlled by two methods that are: preventing emissions from appliances or acting in the transmission path (or shielding). The designing of circuits that do not emit EMI is difficult and expensive, so the shielding against EMI is more practical and desirable approach than first method since they are non-invasive to the circuitry. Electromagnetic shielding is the process of limiting the flow of electromagnetic fields between two locations, by separating them with a barrier made of conductive material. Typically it is applied to enclosures, separating electrical devices from the 'outside world', and to cables, separating wires from the environment that cable runs through. Electromagnetic shielding used to block radio frequency electromagnetic radiation known as RF shielding (Pionteck et al, 2007).

The amount of reduction is related to the material used, its thickness, the shielded volume size and the frequency of the electromagnetic field. Generally two methods are used for electromagnetic shielding that is conductive mesh and conductive coatings. The hole in the sheet or mesh should be considerably smaller than the wavelength of the radiation. Also conductive coatings make a continuous conductive layer that can be electrically connected to ground; so they can make effective shielding. Conductive coatings can be used for visible window applications, but for many such as microwave, liquid crystal displays (LCDs) or plasma displays (PDs) mesh coatings can make higher optical transmittance, lower effective sheet resistance, and higher electromagnetic shielding (Jacoby et al, 2009).

Electrically conductive coatings are required for a variety of applications such as static charge dissipation and electromagnetic/radio frequency interference (EMI/RFI) shielding. They are also used in the production of antistatic coatings, space heating, and in various electrical applications. The amount of conductivity required is dependent upon the specific application. Table 6-1 compares coatings in accordance with their resistivity and applications.

Table 6-1: The comparison of coatings according to their surface resistivity (Pionteck et al, 2007)

Application	**Surface Resistivity (Ω/sq)**
Usual coatings	$> 10^{13}$
Anti-static coatings	10^5-10^{13}
EMI Shielding	$<10^5$

Conceptually, there are three methods possible to design conductive coatings:

1) Utilize conductive polymers as the continuous matrix.
2) Incorporate conductive fillers as sufficient pigment volume concentration
3) Combination of both methods

While there have been many recent advances in conductive polymer technology, these materials have limited usage due to loss of conductivity upon environmental exposure (e.g. oxidation) and poor processability and solubility. Incorporating conductive fillers into a polymeric matrix that has desirable physical/chemical properties can produce most of conducting coatings. These fillers may include carbon black or graphite, metal oxides, conductively coated barium sulphate or potassium titanate, doped tin dioxide, doped zinc oxide (doped for example with aluminum, gallium, antimony, bismuth), or metallic fillers like silver, copper, silver nickel, etc (Syed Azim et al, 2006).

Percolation theory

The electrical conductivity of composites or coatings is related to filler volume fraction. The general idea is when we increase the amount of filler in composites; the particles contact to each other and a continuous way is established that electrons can pass this way.

This conductive network is formed in the base of percolation theory. “The beginnings of percolation theory are attributed to Hamersley and Broadbent in 1957.” They showed how the random properties of a medium can affect the diffusion of fluid on it. “Medium” and “fluid” can be used for different definitions like molecules penetrate through solid; fire expands form a frost and electrons flow an atomic lattice (McLachlan et al, 1990).

One example laid out by these two researchers was a system of channels. Each channel is converted to two new channels that there is a possibility of q for each new channel to be blocked. This random set of blocked channel will determine how a fluid can distribute through the channel network. This is a percolation process. An analysis similar to these channels can be used to explain electrical conductivity in composites. Electrons go through channels that are formed by conductive fillers like carbon fiber. Electron flows through carbon fibers freely, when they arrive to the end of fiber, they encounter with polymer matrix that works as a blocked channel for electrons. Once the amount of fillers were increased, the carbon fibers contact to each other’s and make a continuous way for electrons in the full volume of composite. Generally three regions control the conductivity of filled composites. In low volume fraction of filler, the conductivity of composite is similar to pure polymer. When increase the amount of filler, it reaches to the critical point or percolation threshold. At this point, fillers start to make a continuous network for travelling of electrons. After this point, there is not any increasing in conductivity, because the conductive network has been formed and the addition of filler volume fraction can not affect this network (Pionteck et al, 2007).

There are two ways to contact between the percolated fillers that are: only the contact resistance between the fillers or polymer chains maybe located between such contacts in such a low amount that they still allow electron hopping or tunneling. A conductive percolation pathway just at the surface of a part can prevent surface charges. Meanwhile, this type of part treatment could damage the surface network, so it is difficult in most cases to attain it. As a result, the whole material is filled with a conductive agent to make certain resistivity in part. Some factors can influence in the amount of conductive material to achieve percolation threshold. They are: shape of the conductive inorganic material; size of the conductive inorganic material; interaction between filler particles; semi-crystalline or amorphous nature of the polymer matrix. The percolation can be affected strongly by filler shape. For hard monodisperse spheres the volume percolation is 16% while the conductive fillers with extremely high or low aspect ratios cause to percolation at much lower volume concentration than spheres. The number of contacts between the filler particles in a given unit volume is mainly determined by the size and shape of the filler. When the size of filler is small, the contact area will increase. Each contact ends up in a contact resistance and these contacts can reduce the electron transport efficiency. The effective shape of the filler and the number of contacts between different filler units and polymer chains can be affected by the agglomeration behavior of fillers. For instance, the primary particles form primary aggregates in carbon black and these aggregates make fractal clusters with different spectral dimensions. The highly structured clusters cause lower percolation concentration than low structured carbon black clusters. The number of polymer contacts is lower as compared to lower structured cluster in these types of systems, so it leads to a lower combined contact resistance in a given volume. As a result, different percolation fraction is attributed to different carbon black types (Pionteck et al, 2007).

Another factor that can affect percolation is the interaction between conductive filler and polymer. Higher interaction between filler and polymer than between the filler particles leads to a better dispersion of conductive fillers. Moreover, it is possible that the filler is separated too much by the covering polymer chains when the wetting of the filler with polymer is too good. In this case an isolated and not percolated structure within the matrix is formed that is not satisfactory. For example, when carbon nanotubes are covered with reactive polymers before incorporating them into a matrix, the thick adhered polymer layer inhibits electrical percolation even with very good dispersion. The structure of polymer is another parameter that influences percolation. In amorphous materials like polycarbonate, the percolation is achieved in a small concentration range while in semi-crystalline polymers like polyamide, the percolation happens in a wider range. The context of filler-induced inhomogenous crystallization in which filler acts ac nuclei can explain the difference between polycarbonate and polyamide. When the coat is too thick the crystalline layers that are formed around the filler particles may prevent electrical percolation. The increasing filler particles leads to more nucleuses that can make crystalline layer finally thin and reach to percolation threshold. These effects are obvious especially when conductive nanofillers such as carbon nanotubes are utilized (Pionteck et al, 2007).

6-1 Background of conductive coatings

There are enormous researches about conductive coatings as antistatic coatings or electromagnetic shielding that some of them will be discussed in the following:

Anti static or dissipative coatings:

Antistatic coatings are used to bleed off electrostatic discharge and prevent sparkling. They usually have surface resistivity between10^6 to$10^9\Omega/cm^2$ (Zhong et al, 2008). Inexpensive conductive pigments like graphite or carbon black are usually used in these coatings. There are enourmous amount of researches about antistatic coatings that have been done by different researchers. Hashimoto et al (2007) studied the combination of polyphenylene ether and polyamide resins with electrically carbon black. They extruded resins with carbon black and concluded the samples have volume resistivity between 10^2 and 10^3 Ωm and percolation fraction was achieved at 40 wt%. Zhong et al (2008) mixed waterbase epoxy resins with conductive mica and conductive titanium dioxide at high speed stirring. The final coatings had volume resistivity about 10^6 Ωm and could be used for oil tanks and packaging materials. The percolation fraction was 30 wt%. Izawa et al (2005) made transparent antistatic coatings. They mixed Antimony Tin Oxide (ATO) with polyester resins. The final surface resistivity and percolation fraction were $6.3*10^6$ Ω/sq and 25 wt% respectively. Gottschling et al (2004) made conductive powder coatings from the mixing of epoxy and polyester resins with carbon black. The coatings were cured at 200 ºC for 10 min. The fraction of carbon black was 4 wt% and surface resistivity of final coating was $10^8\Omega$/sq. This coating could be used as anti static coating.

Glausch et al (1996) prepared anti static coatings from the mixing of acrylic resin, PVC (polyvinylchloride) and aluminum doped zinc oxide as conductive filler. The surface resistivity of coatings were equal to 10^6 Ω/sq and conductive filler fraction was 20 wt%. The final coatings were transparent too.

Conductive coatings for electromagnetic shielding

Continuous conductive coatings or mesh coatings can be utilized for electromagnetic shielding. These coatings should have surface resistivity less than 10^5 Ω/sq and are usually prepared from conductive pigments that show high conductivity like silver or nickel (Pionteck et al, 2007). Scientists have done various researches to improve conductive coatings for EMI shielding.

Continuous conductive coatings

Syed Azim et al (2006) made conductive coatings from the blending of epoxy resin with the combination of carbon black and graphite. The ratio of carbon black to graphite was 85/15 and the lowest surface resistivity was 50 Ω/sq. The final coating was cured at room temperature. Lee et al (2002) made conductive coatings with polyvinylidene fluoride (PVDF) and carbon nanofibers. Their results showed that coatings had volume resistivity about 33 Ωm and shielding effectiveness in frequencies between 0.4 and 1.6 GHz were about 8 to 12 dB. Also, they exhibited that conductivity and shielding effectiveness would rise with increasing the thickness of coatings. The percolation threshold was 40 wt%. Akiba et al (2006) prepared epoxy conductive coatings including 50 wt% silver powders. They concluded that the resistivity of final coatings is about 10^{-2} Ωm. Grunlan et al (2004) used single-walled carbon nanotube (SWNT) and polyvinyl acetate emulsion to make conductive composites. A high pressure carbon monoxide process was employed to make nanotubes, but synthesized SWNT were hydrophobic and mixed with a Gum Arabic to make a suspension. The suspension was blended with polyvinyl acetates and final composites were dried in room temperatures. The percolation threshold was 4 wt% and volume resistivity was 10 Ωcm. They indicated that after water evaporation, polymer particles would interdiffuse to form coherent film, so they would lock the SWNTs in a segregated network. Daewoo et al (2008) prepared conductive coatings from the mixing of silver-plated carbon nanotubes with melamine paste including silver powders. The high pressure carbon monoxide process was used to synthesize carbon nanotube. Electroless silver plating around nanotubes improved the interfacial contacts and an acid treatment (HNO_3) process of nanotubes made a homogeneous dispersion. The final coating was screen printed on glass slides and cured at 130ºC for 30min. The resistivity of final paste reduced too much compared with the paste including silver powder without nanotubes. The fraction of nanotubes was 2 wt% and the lowest resistivity achieved at $6*10^{-5}\Omega$cm. Also Bao et al (2007) used the nano and micro silver powder to make emulsion coatings. The acrylic copolymer or vinyl acetate latex was mixed with 60 nm and 4 µm silver powders. The final latex coatings were applied by Meyer bar on the glass slides and dried in room temperature. However, the cured film was not conductive. For making conductive films, dried samples annealed in air in convection ovens at 150ºC. The percolation threshold was attained at 3.6 vol% and resistivity was 10^{-4} Ωcm. Jiang et al (2002) made a nickel coated mica powder by electroless plating and mixed it with acrylic butadiene styrene resin. The final composite had a volume resistivity equal to 35 Ωcm and its percolation factor was 40 wt%. Zou et al (2008) made conductive composite coatings from the mixing of nickel coated graphite and methyl vinyl silicone rubber. The final coatings were cured at 112 ºC in 10 minutes. The percolation fraction was attained at 16 vol% and volume resistivity was 10 Ωcm. Also, this conductive filler could enhance the EMI shielding efficiency of coatings.

Conductive mesh coatings

Conductive mesh coatings are another type of electromagnetic shielding. Kim et al (2011) fabricated mesh filter film using the screen printing method. A screen mask with fine-line screen mesh with an ink composed of fine silver particles was used. A sheet-fed type of screen printer was utilized for the fabrication of the EMI shielding mesh on a polyethylene terephthalate (PET) film. The mesh coating was cured at 140 ºC for 10 min. The final surface resistivity was 0.5-0.7 Ω/sq and the mesh could show good electromagnetic efficiency. Lee et al (2006) formed a photodefined metal pattern with an enhanced life time in bilayer tin film structure of photoresponsive amorphous titanium dioxide (TiO_2) and hole-scavenger containing polyvinylalcohol (PVA). The whole processes included: spin coating and the curing of bilayer thin film of amorphous TiO_2 and PVA in oven at 100 ºC for 5 minutes; selective UV-irridiation through quartz photomask; washing the PVA layer with DI water; dipping to the Pd (palladium) catalyst solution; finally, washing the sample with DI water to remove the loosely bound Pd catalysts. The electroplating of nickel and copper was done respectively on the Pd sites to make pattern films. The final mesh pattern had a resistivity equal to 2.5 Ωcm. They demonstrated that mesh coatings with higher line thickness could improve the EMI shielding efficiency more. Kim et al (2006) made a conductive mesh layer from the photolithography process of a mesh metal layer of silver, copper and gold on the PET films. They indicated that this window mesh could be used as electromagnetic shielding in flat panel display devices.

Despite enormous researches about using nano fillers like carbon nanotube and nano silver, most of conductive coatings in the market that have high conductivity are made from metallic conductive fillers that are expensive and have to be compounded with polymers in high concentrations, so further researches needs to make conductive coatings with high conductivity and low cost. Also, mesh coatings that are used in the markets need a complex process and should undergo some different processing steps. This chapter discusses about conductive coatings and mesh coatings that are made from the following ways and have good conductivity and low prices for electromagnetic shielding:

1) Nano clay conductive coatings were made from the blending of polyurethane or epoxy resins that are used in the market for conductive coatings with nano clay. Feller et al (2004) used nano clay in the polyethylene composites including carbon black and demonstrated that nano clay could affect electrical and mechanical properties of composites.
2) The mesh coatings were made from three methods that included: the mixing of conductive coatings with polymer particles like Polypropylene pellets. These pellets were not mixed with coatings, so they could make hole (mesh) in coatings; conductive mesh coatings with hammer finishes additives that had different surface tensions and could make some small holes in the coatings; and emulsion

conductive inks that were prepared from the mixing of conductive ink with water and surfactant.

Conductive coatings

The surface resistivity of epoxy conductive coatings with different conductive fillers were measured to find the range of conductivity that filler can produce. The electrical and mechanical properties of nano clay polyurethane conductive coatings were compared with epoxy conductive coatings including nano clay. Also the effect of nano clay on polyurethane coatings with two different conductive pigments was evaluated. The effect of mixing time and resin to hardener ratio in nano clay polyurethane conductive coatings were examined too.

The conductive mesh coatings were made from the mixing of silver or graphite ink with polypropylene, hammer finishes additives or water (emulsion). Also, the effect of surfactant concentration, retarder concentration, solvent type and the effect of curing process in emulsion conductive mesh coatings were evaluated.

6-2 Results

The first part of following results is related to continuous conductive coatings and second part shows the results of conductive mesh coatings:

Contininuous conductive coatings

The surface resistivity, adhesion test, hardness, corrosion resistance or impact resistance were used to check the properties of coatings. The results are illustrated below:

Epoxy resins with conductive pigments

Different conductive pigments (fillers) were mixed with epoxy resin and surface resistivities of final coatings were measured. The electrical results of epoxy conductive coatings have shown in Table 6-2. The filler fractions in dry film were changed from 10 to 60 wt%. The objective of this experiment was to find the range of resistivity that different conductive filler could provid.

Table 6-2: The surface resistivity of epoxy conductive coatings

	Resistivity(Ω/sq)					
	10%	20%	30%	40%	50%	60 wt%
Carbon Black	Infinity	850	300	_	_	_
Graphite	120	110	50	_	_	_
Nickel Coated Carbon Fiber	Infinity	Infinity	Infinity	90	10	40
Nickel Coated Graphite	Infinity	Infinity	Infinity	140	60	50
Silver Coated Glass Bead	Infinity	Infinity	Infinity	55	1.5	0.9
Silver Coated Nickel	Infinity	Infinity	Infinity	120	10	60
Gold and Nickel Coated Carbon Fiber	Infinity	Infinity	80	1	0.35	0.55

The highest conductivity was attained by gold nickel carbon fiber. The highest fraction of carbon black and graphite was at 30 wt% and after this point the dispersion of powders in epoxy resin was not possible. The metal conductive filler except gold filler should be added at least in 40 wt% to show the conductivity in the pigments. The gold filler indicated conductivity in 30 wt%.

Nano clay conductive coatings

There are enourmous researches about the role of nanoclay in mechanical and electrical properties of conductive coatings, but there is not any research about the effect of nanoclay on conductive coatings. This study investigated the effect of nanoclay in electrical and mechanical properties of polyurethane conductive coatings with nickel coated carbon fiber. Furthermore, the role of resin to hardener ratio and mixing time in resistivity and mechanical properties of conductive coatings with nanocaly was studied. The effect of nano clay on two conductive coatings with two different conductive pigments (nickel coated carbon fiber or nickel coated graphite) was evaluated. Also, two different nano clay conductive coatings were compared together. They were: polyurethane conductive coatings and epoxy conductive coatings. The results are displayed in the following:

Polyurethane coatings and nickel coated carbon fiber

Initially, the electrical and mechanical properties of polyurethane coatings with nickel coated carbon fiber were investigated. The fraction of nickel coated carbon filler in polyurethane coating was varied from 10 to 60 wt% (dry fraction) to find the range of resistivity that conductive coatings could produce. Then, the effects of nano clay in properties of conductive coatings containing 35 wt% conductive pigments were assessed. Two different sizes of nano clay were utilized. The first one had a particle size of 5 µm and the second one had a size of 25 µm.

Figure 6-1 demonstrates the percolation threshold of polyurethane coatings with metal coated carbon fiber (the resistivity of coatings with 10 and 20% conductive filler were more than 1 KΩ/sq and were not shown in this figure). The percolation threshold was attained at 50 wt% of metal coated carbon fiber. As it can be seen, when the filler concentration reaches to 60 wt%, the resistivity increases again.

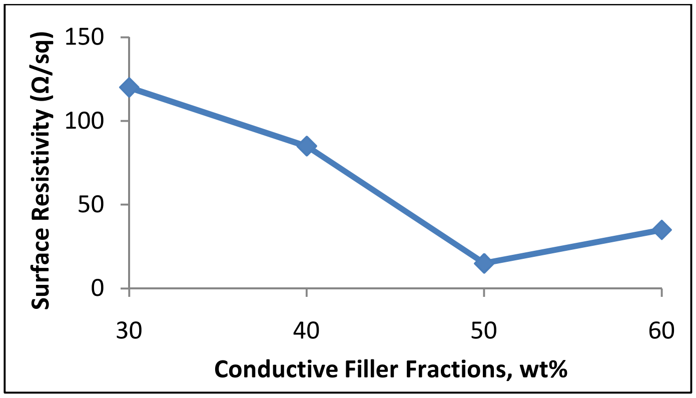


Figure 6-1: The effect of conductive filler fraction on the resistivity of polyurethane coating

Also, increasing filler fraction could affect the adhesion of coatings to the metallic substrate. Figure 6-2 compares the effect of filler fraction on conductive coating adhesion to the surface. The results indicated that with increasing conductive filler fraction, the coating adhesion would reduce.

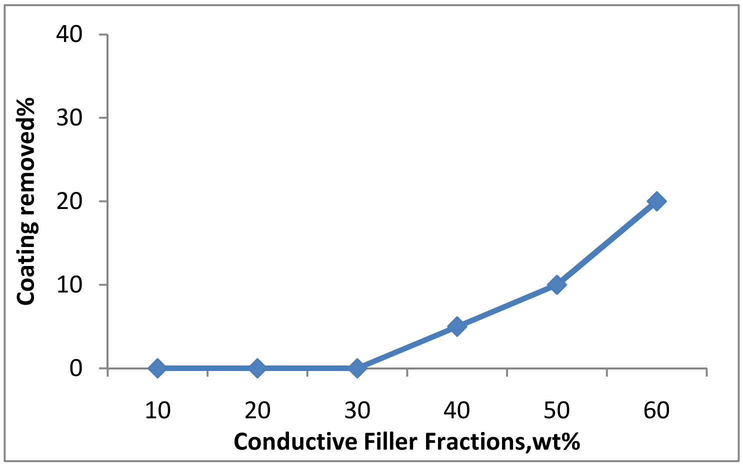


Figure 6-2: The effect of conductive filler fraction on coating adhesion

From the data given in Table 6-3, increasing conductive filler fraction can raise the hardness of conductive coatings. The highest hardness (5H) was achieved at point with 60 wt% nickel coated carbon fiber.

Table 6-3: The relationship of coating hardness with filler fractions

Filler Fractions **wt%**	**Hardness**
10	2H
20	2H
30	3H
40	4H
50	5H
60	5H

Polyurethane conductive coatings with nanoclay

Nanoclay in different concentrations from 2 to 8 wt% was added to polyurethane coatings with 35 wt% metal coated carbon fiber in dry film (this fraction was selected to find how nanoclay could reduce the resistivity). Figure 6-3 indicates the resistivity changes of conductive coatings with nanoclay fractions.

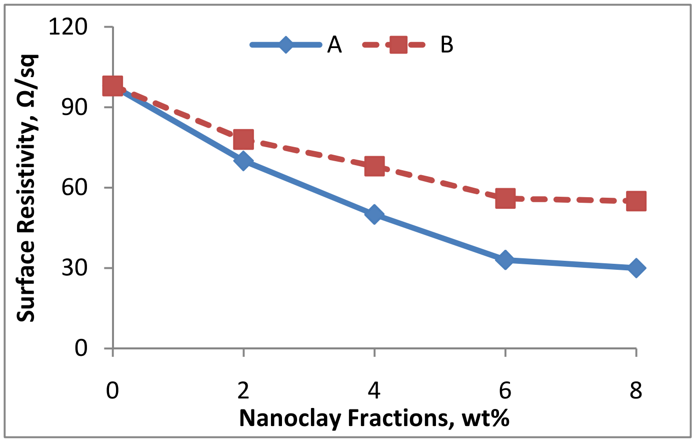


Figure 6-3: The effect of nanoclay fraction on the resistivity of conductive coating with nickel coated carbon fiber

The average particle size of nanoclay (A) is 25 µm and for (B) is 5 µm. As it can be seen in Figure 6-3, the nanoclay can reduce the resistivity of coatings and this reduction is more considerable with nanoclay (A) that has larger particle size than (B). The optimum concentration of nanoclay was got at 6 wt% and there was not considerable reduction in the resistivity after this point.

The nanoclay had high aspect ratio and could improve the hardness of coatings. As it can be found in Table 6-4, the conductive coatings hardness improves with nanoclay fraction increasing. The augmentation of hardness for both nanoclay (5 and 25µm) was same.

Table 06-4: The change of coating hardness with nanoclay fractions

Nanoclay Fraction wt%	**Hardness**
0	3H
2	3H
4	3H
6	4H
8	4H

Figure 6-4 illustrates the adhesion changes of polyurethane coatings with 35 wt% conductive filler against nanoclay fraction. The increase in nanoclay concentration could reduce the adhesion of conductive coatings to substrate slightly. The optimum point was achieved at 6 wt% nanoclay and there was not any change of coating adhesion after this point. The reduction in adhesion for both nanoclays was the same.

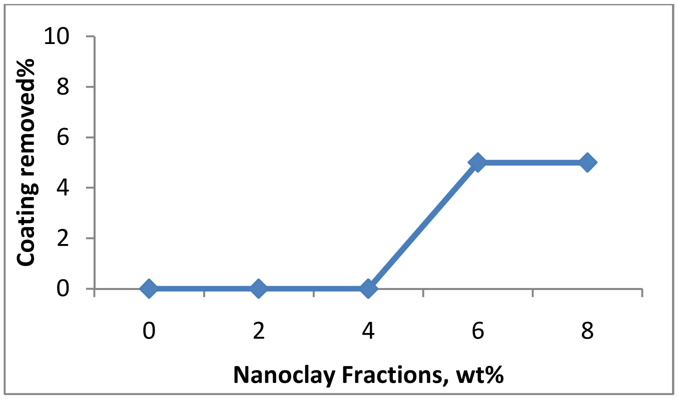


Figure 06-4: The effect of nanoclay fraction on coating adhesion

Figure 6-5 to 6-7 demonstrated the pictures of polyurethane conductive coating samples (including 35 wt% conductive filler) without nanoclay and with 6 wt% nanoclay after 500h salt spray test. The results indicated that nano clay could improve the corrosion resistant of conductive coatings.

Figure 06-5: The sample coated with polyurethane conductive coatings without nanoclay after 500 hours salt spray test

Figure 06-6: The sample coated with nano clay (25 µm) polyurethane conductive coatings after 500 hours salt spray test

Figure 06-7: The sample coated with nano clay (5 µm) polyurethane conductive coatings after 500 hours salt spray test

The resistivity tests were done on the samples of conductive coatings after salt spray test to evaluate the effect of salt spray test on electrical properties. As it can be seen in Figure 6-8, the resistivity of conductive polyurethane coatings increased after salt spray test. A was conductive coatings with 25µm nanoclay before salt spray and A_1 was after salt spray. The results indicated that the changes of surface resistivity decreased when the nano clay fraction rose.

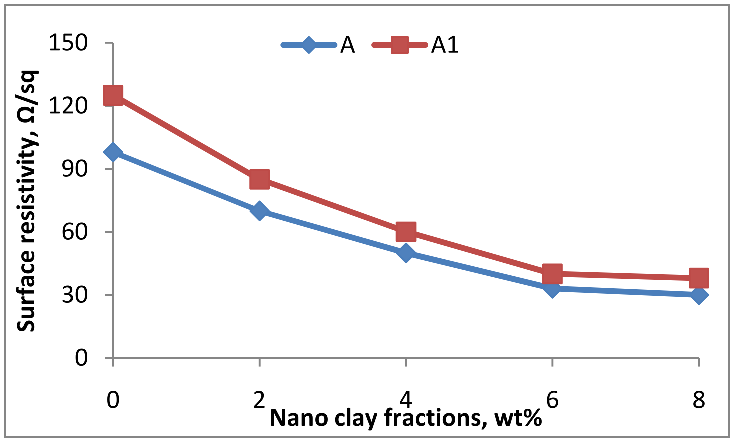


Figure 6-8: The effect of nanoclay fraction on the resistivity of conductive coating (including larger size nano clay) before and after salt spray test.

Also Figure 6-9 displays the changes in surface resistivity of nano clay conductive coatings. B was conductive coatings with 25µm nanoclay before salt spray and B_1 was after salt spray. The results demonstrated that the changes of surface resistivity decreased when the nano clay fraction increased. Also, the alteration in surface resistivity for conductive coatings including smaller size nano clay was less than coatings containing larger size.

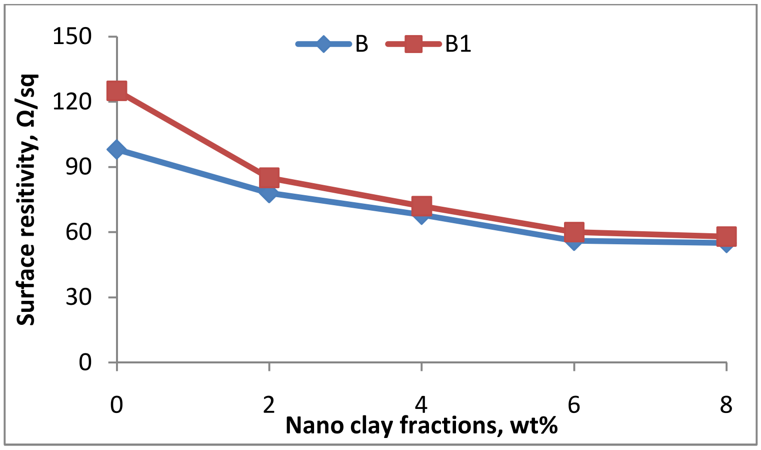


Figure 6-9: The effect of nanoclay fraction on the resistivity of conductive coating (including smaller size nano clay) before and after salt spray test

The effect of nanoclay conductive coating mixing time in coating properties

As it was mentioned before, conductive coatings of this project were dispersed in a ball mill. The time of mixing was changed from 1 to 5 hours to evaluate the effect of mixing time in conductive coating properties. The nanoclay concentration was 6 wt% (25 µm) and metal conductive filler fraction was 35 wt%. As it can be found in Figure 6-10, the resistivity of conductive coatings is reduced when the mixing time rises.

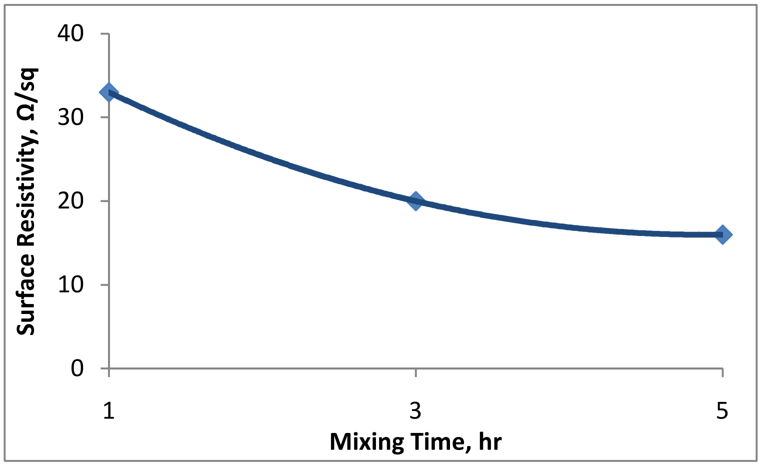


Figure 06-10: The surface resistivity of nanoclay conductive coating against mixing time

Furthermore, Table 6-5 demonstrates the hardness changes of conductive coatings with mixing time. The results verified that hardness will increase with mixing time. However, there was not any further change after 3 hours.

Table 06-5: The hardness changes of conductive coatings against mixing time

Mixing time, hours	**Hardness**
1	4H
3	5H
5	5H

Evaluate the role of resin to hardener ratio in conductive coating properties

The ratio of polyol resin to isocyanate hardener was varied from 3/1 to 5/1 in conductive coating with 35 wt% metal coated carbon fiber and 6 wt% nanoclay (25µm). Figure 6-11 indicates the alteration of resistivity with resin to hardener ratios. The surface resistivity increased with rising resin to hardener ratio.

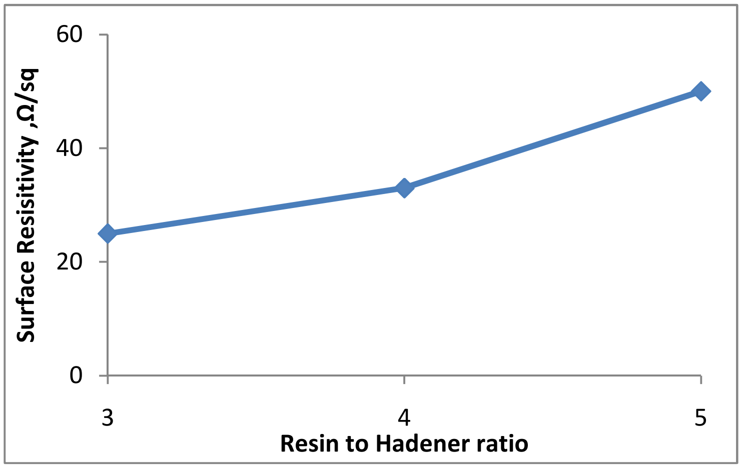


Figure 06-11: The surface resistivity of nano clay conductive coating against resin/hardener ratio

The comparison of conductive coatings hardness with nanoclay in different resin to hardener ratio determined that with raising the amount of hardener, the coating hardness would augment. Table 6-6 shows the hardness of conductive coatings with nanoclay in different hardener ratio.

Table 06-6: The hardness changes of conductive coatings in different resin/ hardener ratio

Resin/Hardener ratio	Hardness
3	5H
4	4H
5	3H

Figure 6-12 displays the change of conductive coating adhesions to resin/hardener ratio. The best adhesion was attained in 5/1 ratio and the worst one was in 3/1. The results indicated that increasing resin/hardener ration could reduce coating adhesions.

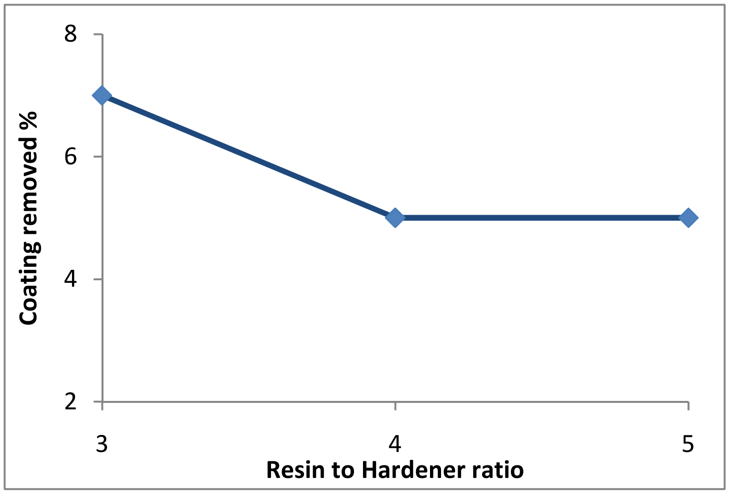


Figure 6-12: The effect of resin/hardener ratio in adhesion of nanoclay conductive coating

As it can be observed in Figure 6-13, raising the resin/hardener ratio can influence the impact resistance of conductive coating with nanoclay. The best impact resistance was achieved in 4/1 ratio that is the theoretically ratio of resin/hardener and the worst result was in 3/1 ratio.

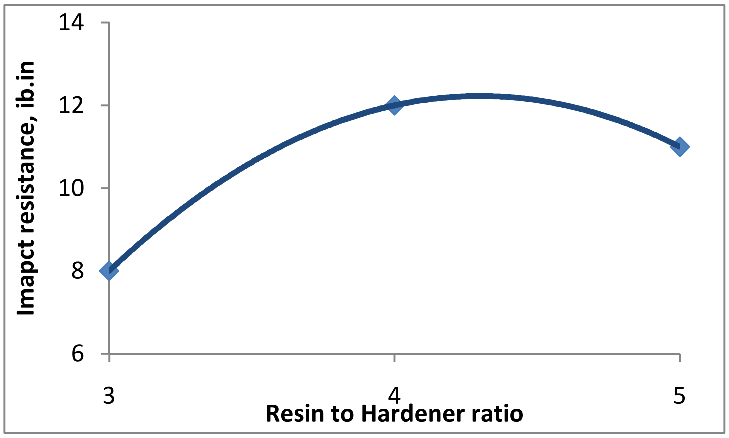


Figure 6-13: The effect of resin/hardener ratio in impact resistance of nanoclay conductive coating

The effect of conductive filler type in nanoclay conductive coating

Two different conductive filler were used here. The first type was metal coated carbon fiber and the second one was metal coated graphite. Polyurethane coating with 35 wt% conductive filler were used to evaluate the effect of nanoclay fraction in electrical and hardness properties of coatings. The nano clay fractions varied from 2 to 8 wt%. Figure 6-14 illustrates that the surface resistivity of both conductive coatings including metal coated carbon fiber and graphite reduced with increasing nanoclay fraction.

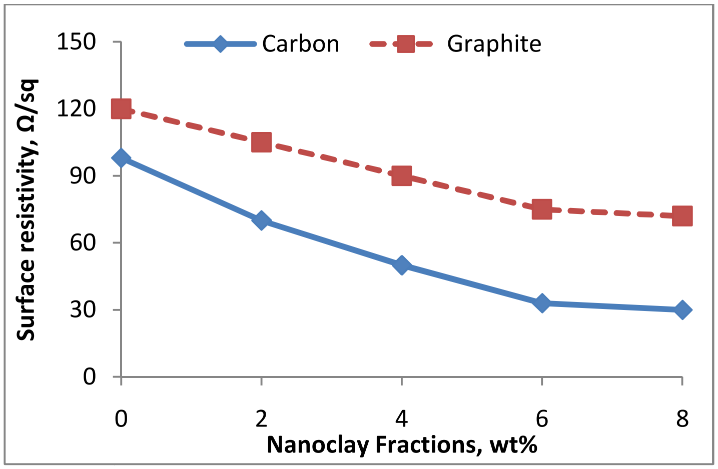
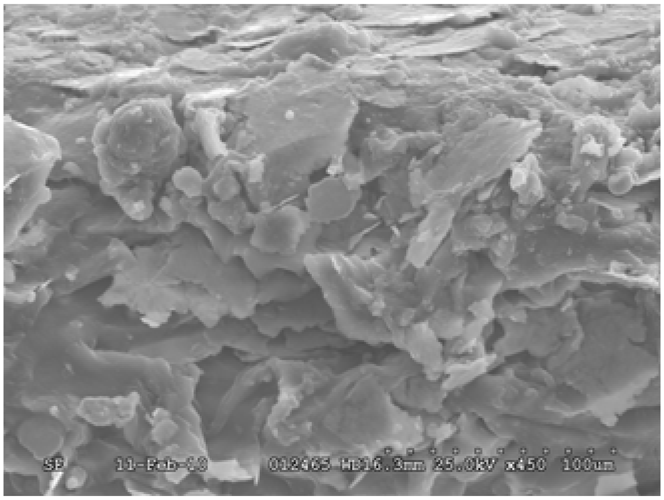
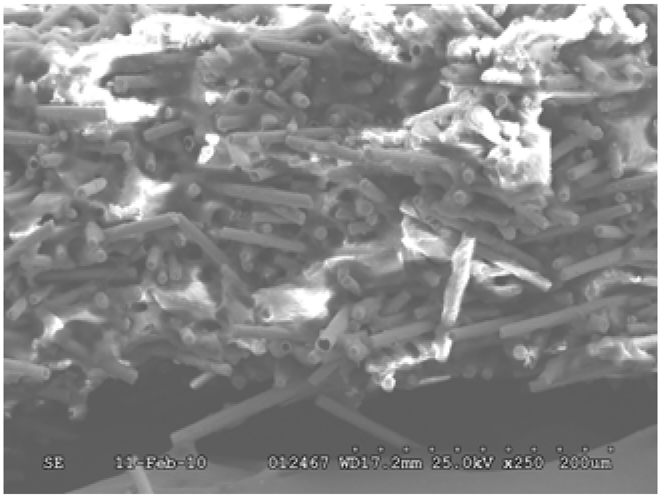


Figure 06-14: The changes of surface resistivity for two different conductive coatings against nanoclay fraction

The SEM picture was employed to investigate the effect of conductive filler type in surface resistivity of conductive coatings with nanoclay. The conductive filler fraction was 35 wt% and nanoclay concentration was 6 wt%. Figure 6-15 compares the SEM cross section pictures of conductive coatings including metal coated carbon fiber (C1) and metal coated graphite (G1).



C1: Conductive coating with metal coated graphite



G1. Conductive coating with metal coated carbon fiber

Figure 06-15: SEM pictures of two different conductive coatings including graphite (C1) or carbon fiber (G1)

The changes of conductive coating hardnesses with two different conductive filler in different nanoclay fractions are indicated in Table 6-7.

Table 06-7: The hardness changes of conductive coatings (Carbon fiber and graphite) against nanoclay fraction

Nanoclay Fractions wt%	Hardness	
	Carbon fiber	Graphite
0	3H	2H
2	3H	2H
4	3H	3H
6	4H	3H
8	4H	3H

The coating hardnesses of both coatings were increased with rising nanocaly fractions. However, the metal coated carbon fiber could increase hardness more than graphite.

The effect of resin type in nanoclay conductive coating

Two different resins were used here. The first type was polyurethane and the second one was epoxy resin. Two different conductive coatings (Polyurethane and epoxy) with 35 wt% metal coated carbon fiber were prepared to evaluate the effect of nanoclay fraction in electrical and mechanical properties of coatings. Figure 6-16 demonstrates that the surface resistivity of both polyurethane and epoxy conductive coating with metal coated carbon fiber reduces with increasing nanoclay fractions.

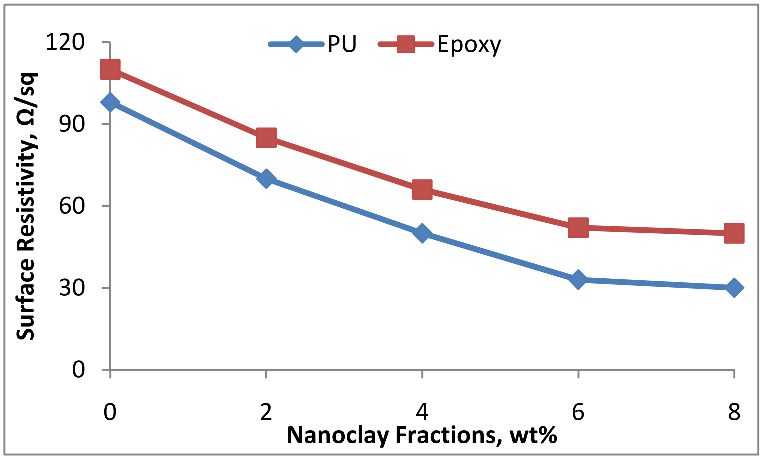


Figure 6-16: The effect of nanoclay fraction on the surface resistivity of polyurethane and epoxy conductive coating

As it can be observed in Table 6-8, the hardness of polyurethane (PU) conductive coating is higher than epoxy conductive coating. However, nanoclay could increase the hardness of both conductive coating (Epoxy and polyurethane) with metal coated carbon fiber. The optimum point for both coating was attained between 6 to 8 wt% nanoclay.

Table 6-8: The hardness changes of conductive coatings (PU and Epoxy) against nanoclay fraction

Nanoclay Fraction wt%	Hardness	
	PU	Epoxy
0	3H	2H
2	3H	2H
4	3H	3H
6	4H	3H
8	4H	3H

Moreover, Table 6-9 compares the adhesion changes of epoxy conductive coating with polyurethane conductive coating when nanoclay fraction varied from 0 to 8 wt%. The results indicated that epoxy conductive coating had better adhesion than polyurethane conductive coating against nanoclay fraction.

Table 06-9: The effect of nanoclay fraction on adhesion of polyurethane (PU) and epoxy conductive coating

Nanoclay Fraction wt%	Coating Removed%	
	PU	Epoxy
0	0	0
2	0	0
4	0	0
6	5	3
8	5	3

Generally, increasing nanoclay fractions could reduce the adhesion of both conductive coatings (epoxy or PU coatings).

Conductive mesh coatings

The conductive mesh coatings were made from the blending of plastic particles (polypropylene), hammer finishes additives or water (emulsion coatings) with conductive inks. The conductive mesh coatings have been prepared from different processes in literatures and have organized mesh holes while the fabricated condutice mesh coatings in this project are the first random mesh coatings that are prepared from a simple and inexpensive process. Conductive inks were used in this work since they have a fine particle size (less than 10 µm) and can be mixed with water better than usual conductive coatings that have particle sizes between 20 to 40µm. A high magnification microscope (5*10) was used to see the shape of mesh in coatings (The picture scales are 0.25 mm). Also, the surface resistivity of coatings was measured. The results will be illustrated below:

Conductive ink and polypropylene

The polypropylene was mixed with graphite ink or silver ink in two fractions: 20 and 25 wt%. The final coatings were applied on glass slides by Mayer bar and cured in 150 ºC at oven for 15 min. This temperature is the melting point of plastic. Polypropylene particles worked as mesh holes. Figure 6-17 displayed the picture of mesh coatings with polypropylene. The results showed that plastic particles were agglomerated in special parts of coatings and could not make a uniform mesh. The pictures of coatings in both fractions of polypropylene were similar and after 25 wt%, the dispersion of plastic in conductive ink was not possible.

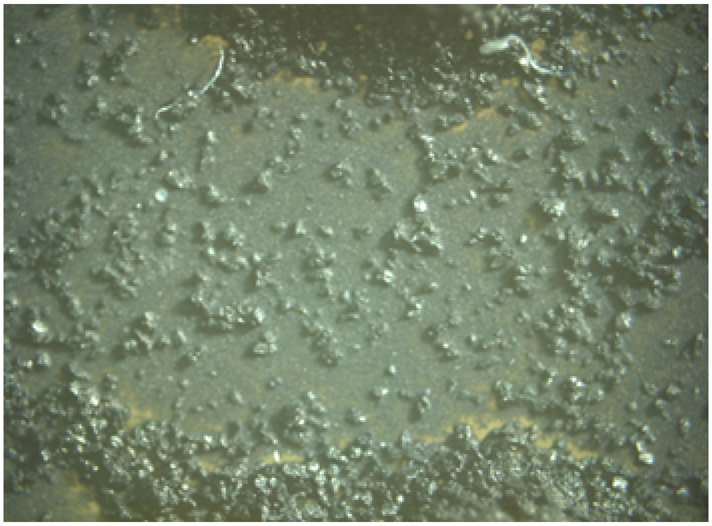


Figure 06-17: conductive mesh coatings including polypropylene

Also Table 6-10 indicates the changes of conductive mesh coating surface resistivity with plastic particles. As it can be seen, the surface resistivity reduces with increasing polypropylene fractions.

Table 06-10: The resistivity changes of conductive coatings with polypropylene

Polypropylene fractions, wt%	**Surface resistivity, Ω/sq**
0	0.6
20	15
25	23

Conductive ink with hammer finishe additives

The hammer additive was mixed with silver or graphite ink in 0.05 and 0.1 wt% fractions. The graphite ink can be used too. The final coatings were applied on the glass and cured at 100º at oven for 10 min. Figure 6-18 illustrated the picture of conductive mesh coatings with hammer finishes additive. The additive could make better meshes than plastic particles, but the number of meshes was not enough in both fractions.

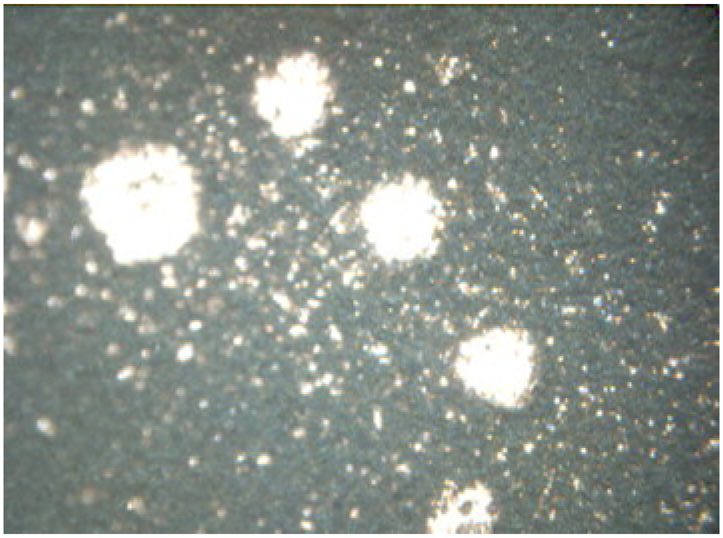


Figure 6-18: conductive silver ink with hammer finishe additive

Moreover, as it can be observed in Table 6-11, the surface resistivity of conductive mesh coatings were not altered by increasing additive concentrations. The results demonstrated that increasing additive fractions could not reduce surface resistivity.

Table 6-11: The resistivity changes of conductive coatings with hammer additive

Additive fraction, wt%	**Surface resistivity, Ω/sq**
0	0.6
0.05	1
0.1	1

Conductive ink with water (emulsion coatings)

Conductive emulsion coatings were made from the mixing of silver ink with surfactant and water. Figures 6-19, 6-20 and 6-21 displayed the picture of emulsion coatings with water volume% of 40, 45 and 50% respectively.

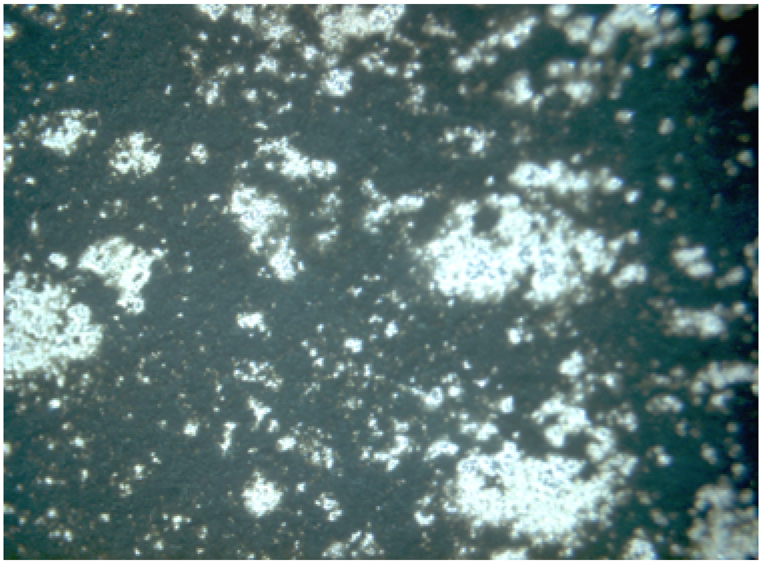


Figure 06-19: The conductive mesh coating including 40 vol% water

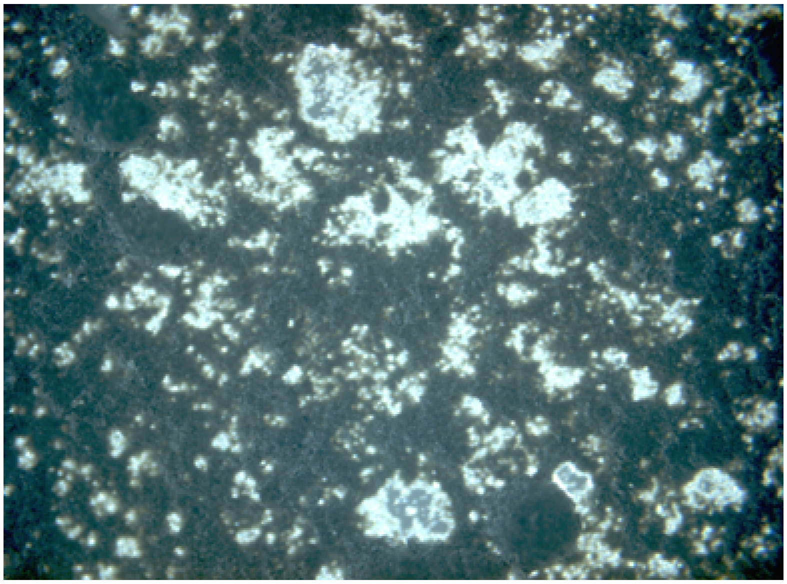


Figure 6-20: The conductive mesh coating including 45 vol% water

First silver ink was dissolved in acetone and surfactant was added to this mixture in the stirrer. Then water was added to dispersion drop wise in three steps. After adding water in each step, the emulsion was mixed in the stirrer. The water volume percent were altered from 40 to 50%. The results indicated that the best mesh coating was attained at 45 vol% of water. The graphite could not make an emulsion mesh coatings, so only silver ink were used here.

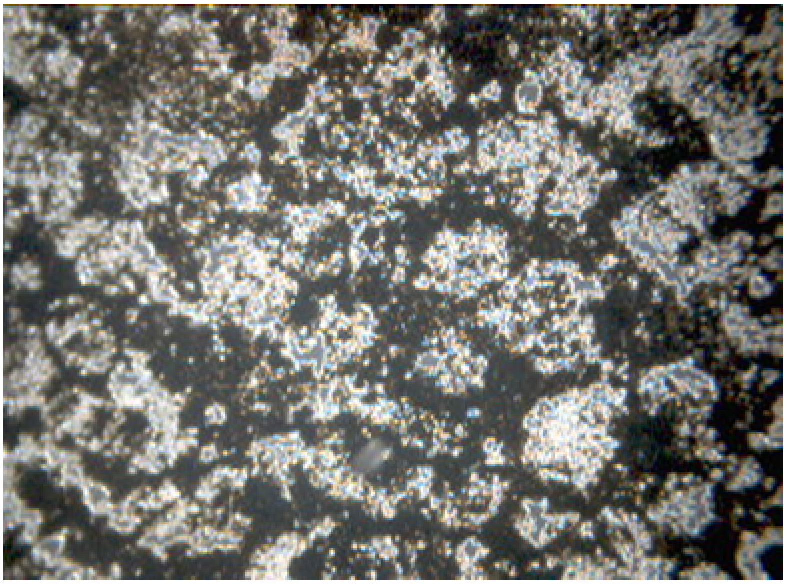


Figure 06-21: The conductive mesh coating including 50vol% water

The pictures illustrated that increasing water volume percent can raise the number of meshes in coatings. However, there were not any big changes in meshes when the water fraction increased to more than 50 vol%.

Also, the Table 6-12 demonstrates that increasing water volume can reduce the conductivity of final mesh coatings, so the point with 45 vol% of water can be the optimum point.

Table 06-12: The resistivity changes of mesh coatings with water fraction

Water concentration, Vol%	**Surface resistivity, Ω/sq**
0	0.6
40	1.3
45	1.5
50	2.4

Also the effect of surfactant fraction, solvent type, retarder fraction and curing process on the conductive mesh coatings were evaluated. The results were indicated in the following:

The effect of surfactant fraction

The concentration of surfactant in conductive mesh coatings including 45vol% water was increased from 5 to 10 wt%, but there were not any changes in mesh numbers or mesh shapes. Also, the surface resistivity of coatings did not alter.

The role of solvent

The solvent was changed from acetone to reducer E-25 in conductive mesh coatings containing 45vol% water. The results indicated that the new solvent made the size of mesh smaller, so the type of solvent can influence in mesh shapes (Figure 6-22). However, there was not any alteration in surface resistivity of coatings when the type of solvent was changed.

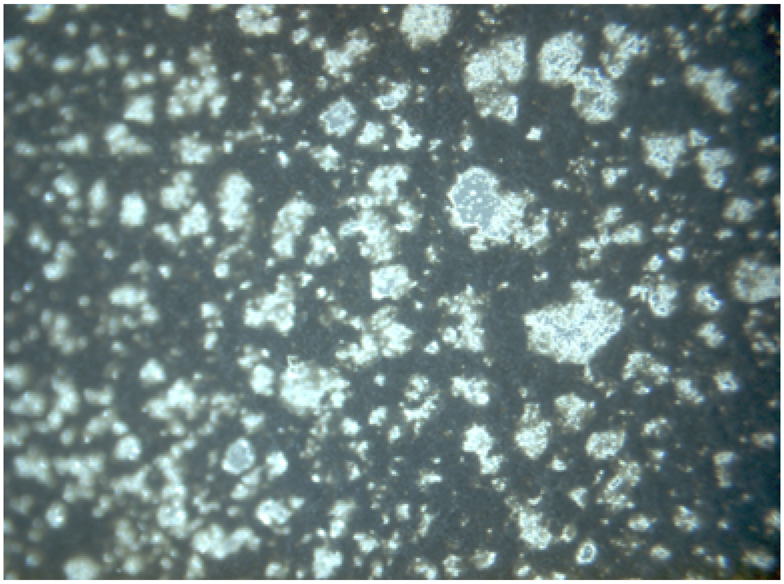


Figure 06-22: The effect of solvent type in conductive mesh coating

The effect of retarder

The fraction of retarder in conductive mesh coatings including 45 vol% water was varied from 2 to 4 wt%, but there was not any alteration in shape of meshes or in the surface resistivity of coatings.

The role of curing process

The effect of curing process in conductive mesh coatings with 45 vol% was evaluated. The mesh coatings were applied on glass slides and let the coated glass stay in lab air for 30 minutes before curing at oven in 100 ºC for 10 minutes. It helped coating to flow well on the substrate and solvents could evaporate uniformly compared with usual method that there is not enough flow time for samples before curing. Figure 6-23 showed the picture of conductive mesh coatings with this new curing process. The results indicated that coatings had larger mesh size.

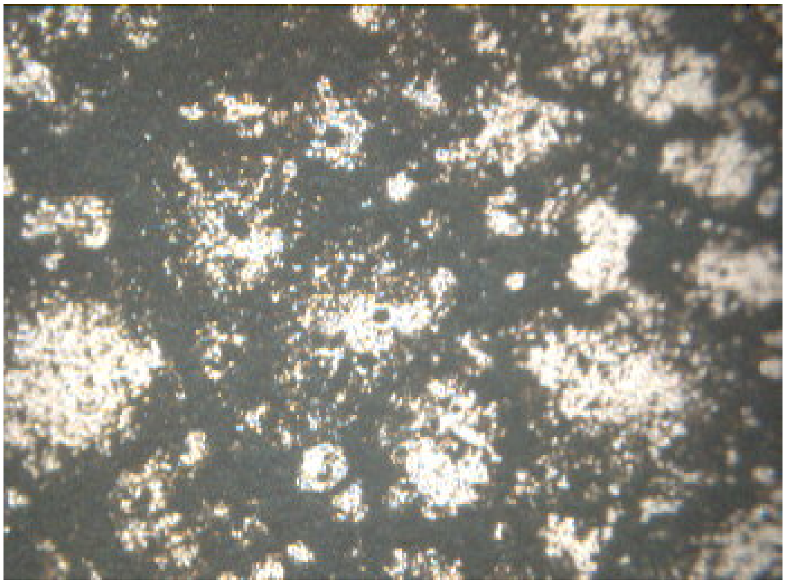


Figure 06-23: The role of curing process in conductive mesh coating

6-3 Discussion

Contininuous conductive coatings

The results of epoxy coatings with different conductive fillers showed that the highest conductivity was related to gold filler. Also the results demonstrated that for each of filler there was an optimum fraction that provides the highest conductivity and when the filler concentration was over this point, the conductivity decreased. This point was the percolation threshold. The results of metal coated carbon fiber indicated that the carbon fibers with high aspect ratio could improve the dispersion of filler in coatings better than other metallic powders like silver coated nickel or silver coated glass beads.

The results of polyurethane coatings including nickel coated carbon fiber indicated that after the percolation point, the increasing filler concentration could not improve electrical property and even reduce conductivity. Generally, when the nickel coated carbon fiber fraction in polyurethane coating increases, the resistivity and the adhesion of coatings reduces, but the hardness of coatings increases.

The nano clay could affect the resistivity of coatings in two ways. First it could improve the dispersion of conductive fillers in the coatings, but nano clay with smaller particle size was not dispersed as well as larger nano clay and it could not reduce the resistivity as well as later one. Second, the nano clay had some free ions in its structure that could develop the movement of ions in conductive coatings. Furthermore, nano clay could improve the corrosion resistance of coating because it had high aspect ratio that could reduce the diffusion of water to the bulk of coatings. The coatings with smaller size nano clay showed better corrosion resistance than larger size nano clay. Generally, nano clay could enhance the conductivity and hardness of polyurethane coatings containing nickel coated carbon fiber, but the adhesion of coatings reduced with rising nano clay concentration. However, this reduction in adhesion was not a big issue in industrial applications.

The smaller size nano clay could improve the corrosion resistance of conductive coatings more than larger size. However, the surface resistivity and hardness are more important than corrosion resistance in conductive coatings that are utilized in industry, so the larger size nano clay can work better than smaller size clay for conductive coatings. The mixing time could affect the properties of nano clay polyurethane conductive coatings. The electrical and mechanical properties of conductive coatings with nano clay improved, when the mixing time prolonged.

Another factor that could influence in properties of nano clay conductive coatings was the resin to hardener ratio. The results displayed that when this ratio in conductive coating increased, the resistivity reduced because the coating shrunk more and made the conductive filler closer to each other. This action could also augment conductivity. However, increasing resin to hardener ratio could reduce adhesion and impact resistance of coatings. Finally, it can be found from the results that the resin/hardener ratio can affect electrical and mechanical properties of conductive coating with nanoclay and there is an optimum ratio of resin/hardener ratio that the good mechanical and electrical property can be achieved. This point was in 4/1 ratio that had best adhesion and impact resistance. In addition, it demonstrated good surface resistivity and hardness. However, final application can affect the selection of hardener/resin ratio. For instance, in some applications the surface resistivity and hardness are more important than adhesion, so the 3/1 ratio can be used in this specific situation.

The comparison of nano clay polyurethane coatings with nickel coated carbon fiber or nickel coated graphite indicated that nano clay would decrease the resistivity of coatings with nickel coated carbon fiber more than that with nickel coated graphite. The results of SEM cross section of both coatings demonstrated that carbon fiber had a different structure than graphite. This structure could develop the conductivity of coatings better than graphite because the particles can contact with each other better. Also nano clay conductive coatings with nickel coated carbon fiber showed better hardness than nano clay coatings with nickel graphite because carbon fiber had high aspect ratio.

In addition, the type of resin in nano clay conductive coatings could influence final conductivity of coatings. The nano clay polyurethane conductive coatings illustrated lower surface resistivity than nano clay epoxy conductive coatings. It might be related to the hardness of polyurethane coating that was more than epoxy coating and could make a polymer network that particles were closer to each other in that. However, nano clay epoxy conductive coating had better adhesion than nano clay polyurethane coatings. The usage of each type of coating was related to its application. For instance, if only the surface resistivity and hardness were the key factors in final coating, the nano clay polyurethane conductive coating worked better than nano clay epoxy conductive coating.

Conductive mesh coatings

The results of mesh coatings with plastic particles indicated that increasing plastic particle could reduce the conductivity of coatings. Also the distribution of plastic particles in final mesh coatings was not uniform, so it is difficult to use polypropylene in mesh coatings before a better dispersion method is developed.

Also the hammer finishe additives together with conductive ink could make mesh coatings. The resistivity of mesh coatings did not change with increasing additive fractions. However, final coatings did not contain enough mesh to show good electromagnetic efficiency. There is a potential in this method if a way is developed that can disperse additives more uniformely in coatings.

The emulsion coatings that prepared from the mixing of conductive ink with surfactant and water made the best mesh coatings. The resistivity of mesh coatings increased with rising water volume fractions, so the optimum point was achieved at 45 vol% of water in coatings. The number of meshes in coatings was enlarged with increasing water volume fraction too. Also the increasing surfactant or retarder fraction could not affect the electrical property of coatings or the distribution of meshes in coatings. The replacing acetone with Reducer- E25 decreased the sizes of holes, but it did not affect surface resistivity. Also curing process could influence in mesh sizes in conductive emulsion coatings. The sample coated with mesh coatings stayed 30 minutes in lab air before curing at oven, so the sizes of final mesh became larger and they were distributed better in coatings. The solvents could evaporate uniformly in this way and this aided mesh holes to distribute better in conductive coatings. Finaly, emulsion coatings could provide the better random meshes than other methods and it is the first random mesh that is fabricated by simple coating method.

CHAPTER 7

Conclusions and recommendations

7-1 Conclusions

This study investigated two important functional coatings, superhydrophobic coatings and conductive coatings. Superhydrophobic coatings could be used in different applications such as marine, corrosion resistance, self-cleaning, ice-phobic coatings and high voltage insulators. There are a lot of researches about the fabrication of superhydrophobic coatings in the literature, but most of them are cured in high temperature and can not be used for work place or maintenance. This work focused on superhydrophobic coatings that were cured in room temperature and had good durability. Conductive coatings can be used as antistatic coatings, electromagnetic shielding or sensors. There are a lot of researches to make continuous conductive coatings or mesh coatings that have high conductivities and have been fabricated from nano or metallic fillers. However, these coatings have high cost or complex process and can not be used in industries. The objective of this project was to make conductive coatings or mesh coatings that had high conductivity, low cost and simple process.

The room temperature superhydrophobic coatings were made from the blending of RTV silicone rubber or fluoropolyurethane polymer with hydrophobic additives (nano silica or ultrafine fluoric particle), hydrophobic fillers (nano calcium carbonate or glass bead that were treated by fluoroalkylsilane) or the combination of hydrophobic additives and hydrophobic fillers. The results showed that superhydrophobic RTV silicone rubber coatings could prevent accumulation of dust and reduce ice adhesion for high voltage insulators. It could be found from the results of this study that the new RTV silicone rubber coatings could retain superhydrophobicity and passed erosion and track resistant that has been used in the industry for the evaluation of RTV silicone rubber coatings for high voltage insulators. Also, super hydrophobic RTV coatings showed good UV/water durability and sufficient adhesion to the ceramic surfaces. Furthermore, the finding determined that RTV silicone rubber with fluoric particle concentrations between 10-13 wt% and at least 35 wt% ATH can be a good candidate for superhydrophobic RTV insulator coatings. Moreover, the RTV coatings with hydrophobic fillers alone were not superhydrophobic, but hydrophobic fillers in combination with hydrophobic additives could make superhydrophobic coatings. Superhydrophobic coatings lost their durability when they immersed in water, but they could recover hydrophobicity. Superhydrophobic RTV coatings including the combination of hydrophobic additives and hydrophobic fillers (treated nano calcium carbonate or glass bead) could be used in some applications that the hardness of coatings was not importat like antifouling coatings.

Also the results of experiments showed that fluoropolyurethane coatings with nano silica could fabricate superhydrophobic coatings. The coatings including the combination of nano silica with nano fluoric particle or hydrophobic fillers (nano calcium carbonate or glass bead treated with FAS) could be superhydrophobic too. However, only fluoropolyurethane coatings with 40 wt% nano silica, the combination of 20% nano silica and 20 wt% nano fluoric particles or the combination of 30% nano silica and 10 wt% nano fluoric particle could pass water immersion test that shows the durability of superhydrophobic coatings. Also, coating including the nano silica only could pass UV test compared to other particles. The adhesion of coatings reduced with increasing nano particles fraction, but superhydrophobic coatings determined better adhesion to the glass compared with metal substrates. Moreover, the hardness of coatings increased with the rising nano particle fractions. Also the thickness of coatings, type of solvent and production method could affect the contact angles of superhydrophobic coatings. The coupling agent could enhance the adhesion of superhydrophobic coatings too.

The results of nano clay conductive coatings indicated that nanoclay could improve conductivity, hardness and the corrosion resistance of polyurethane conductive coatings including metal coated carbon fiber. The optimum fraction of nanoclay was achieved between 6 to 8 wt%. However, the nanoclay could reduce the coatings adhesion slightly. The mixing time and resin/hardener ratio could affect the electrical and mechanical properties of nanoclay conductive coatings. The best mixing time was 3 hours and the best resin/hardener ratio was attained at 4/1. The comparison of nanoclay conductive coatings including metal coated carbon fiber with metal coated graphite indicated that nanoclay could influence more in conductive coatings with carbon fiber. Also, nanoclay demonstrated better electrical properties and hardness with polyurethane coatings compared with epoxy coatings. To end with, nanoclay could decrease the cost of conductive coatings and improve the electrical property and hardness of them.

The results of mesh coatings demonstrated that conductive coatings that were made by emulsion method were a good candidate for electromagnetic shielding. This was the first random mesh coating that was prepared by a simple and inexpensive method. Also the type of solvent could affect the mesh sizes, but increasing surfactant or retarder fractions could not influence in mesh coatings. Moreover, the increasing water volume percent in emulsion conductive coatings could reduce the surface resistivity of coatings. As a result, the best emulsion coating was attained at 45vol% water. The extra flow of mesh coatings before curing could improve the mesh sizes in coatings too.

7-2 Recommendations

This study accomplished the objectives of two functional coatings that were defined before starting the work. However, there is more theoretical and experimental works that can further advance this research. The following recommendations should be considered as future work:

- Although the superhydrophobic RTV silicone rubber or fluoropolyurethane coatings were fabricated in this study, they did not show good adhesion performance to some substrates like metals. One of the methods that can improve the adhesion of coatings may be the use of primer coatings under superhydrophobic coatings. The effect of thickness on coating functionality should be studied theoretically and experimentally more because the high thickness coatings have shown smaller contact angles. The dispersion of nanomaterials in coating is another important factor that could influence contact angles of coatings and should be studied more to make uniform coating dispersion. The superhydrophobic coatings could reduce ice adhesion, but more work needs to make coatings that can inhibit ice adhesion considerably. The effect of superhydrophobic coatings in reducing ice adhesion should be studied theoretically and experimentally with more depth.

- While nano clay could improve the electrical and mechanical properties of conductive coatings, the mechanism of their actions in coatings are not clear and it should be studied in more depth. The nanoclay is a good candidate to reduce the price of conductive coatings, but it should be used with more different polymers and conductive fillers to evaluate its effectiveness in more details. The mesh coatings indicated a good choice for electromagnetic shielding, but their usefulness should be tested experimentally. The procedures that were used in this work have the potenitial to make inexpensive mesh coatings if the production methods are developed. The effect of productin methods like stirring time in emulsion coatings should be examined too. Also the stability of emulsion coating before application should be demonstrated.

Appendix I

Resins

Alkyd resins

The binders used in the production of alkyd paints. They are synthetic polyester resins that are modified with fatty acids and mainly are used in architectural coatings. Production of alkyd resins began in 1930 and they could replace stand oil in the architectural coatings because of their faster drying and curing rated accompany with better film hardness and gloss retention. They are synthetic polyester resins that are produced by esterification of polybasic carboxylic acids and polyhydric alcohols and always are modified with fatty acids. Alkyd resin can be made as solvent base or water base and are mainly used in the architectural coatings. The oil or fatty acids in this resin has a good flexibility that makes the application of coatings by brush or roller easier. The transesterifications is done on two stages that are: An excess amount of a glycerol is used to make the transesterification of a diester and a glycol; when the volatile alcohol usually ethanol has been exhausted the polycondensation will be occurred. Drying, semidrying and nondrying oils or their fatty acids are used for producing this type of resin. Also, the glycerol and pentaerytheritol are used as polyhydric alcohol. Phthalic acids are used as polybasic acids. Alkyd resins can be modified with some resins such as nitrocellulose or vinyl resins to improve their properties. For instance, alkyd nitrocellulose resins are used in high-grade furniture lacquers.

Cellulose-based resins

Nitrocellulose is a resin that displays fast solvent evaporation. The nitrocellulose are used mainly to make lacquers (clear paint without pigment) that are for coating wood, automotive repair, paper, foil, leather and in nail polish. The preparation of nitrocellulose varnish is simple and involves dissolution of resin in solvents and mixing. These lacquers can be applied by compressed air spray or airless technique. These resins can be blended with other resins such as alkyd, ketone, urea or acrylic resins. The price, color, influence on solvent release, gloss, hardness, sandability, yellowing and durability of the final coatings are important factors that could affect the selection criteria. Also the solvent mixture can influence on the quality of final coatings. All raw materials in the lacquer formulation should be solved in the solvents mixture. Acetate esters like butyl acetate and ketones like acetone are most important active solvents for nitrocellulose coatings.

Chlorinated rubber resins

This resin consists of 65% chlorine and is manufactured from degradation of natural rubber or polyethylene rubber by addition of radical formers and dissolving of this compound in carbon tetrachloride. This resin is used in underwater coatings on steel and concrete because of its high water resistance. The paints based on chlorinated rubber are stored in internally coated cans to get satisfactory storage stabilities. Also, the addition of 0.5% epychlorohydrin based on the weight of chlorinated rubber could stabilize both the coating in the liquid phase and reduce the cans rusting. Some solvents like ketone solvents can make gelation in this type of coatings and should not be used. These resins should be used with plasticizers to make a flexible film. The amount of plasticizer that is mixed with these coatings is important because it can influence in the final property of coatings. Also the type of plasticizer can be altered by application of coatings. For example, for chemical resistant coatings, nonsaponifiable plasticizers like chlorinated paraffins are used. This resin can be modified with other resins too. The coatings from this resin can be used as marine, traffic, fire-retardant and swimming-pool paints.

Acrylic resins

The coatings from this resin are now one of the largest product classes. Acrylic resins have copolymers of acrylate and methacrylate esters. The main properties of acrylics used in coatings are: bulk properties of acrylics like glass-transition temperature and mechanical properties; solution properties such as viscosity and solubility parameters. The methacrylates are stable to UV light and oxygen because of absence of tertiary hydrogen atoms. The flexibility of resin increases with rising chain length of the side group and usually acrylates are softer and more flexible than the methacrylates. Acrylic resins are divided to thermoplastic and thermosetting groups. The thermoplastic resins are cured in room temperature and are used in architecture and lacquers while the thermosetting resins are cured at elevated temperatures and are utilized in automotive enamels and appliances finishes. Acrylic coatings can be cured by solvent evaporation (organic solvent or water) or by cross linking with other resins like melamine or polyisocyanates (two pack resins). The largest application of acrylic resins is emulsion paint for ceiling, walls and building front. Moreover, two pack acrylic resins are used in automotive finishes and topcoats because of their high transparency, weather resistance, gloss retention and yellowing stability.

Polyester resins

Polyester resins are produced from the condensation of di- or polyfunctional monomers containing hydroxyl groups and carboxyl groups. The polyester resins are divided to two groups: unsaturated and saturated polyester resins that they have different curing mechanism. Unsaturated polyester resins are two pack systems and cured in room temperature from the reaction of unsaturated polyester resins and peroxide radicals (methyl ethyl ketone peroxide), these two components should be mixed only before application of coatings and the mixture of components is not storable. Unsaturated polyester coatings are mainly used in furniture coatings. Saturated polyesters are also two components systems and have hydroxyl groups in their polymer chains that can make a reaction with isocyanate or amino groups in room temperature or high temperatures. These polyester resins are used in coil coatings, can coatings and automotive finishes. The coatings are made from unsaturated polyesters contains monomers especially in coatings for UV curing. These coatings are cured in any thickness as the styrene acts as a solvent polymerises with the double bonds of the resin and is incorporated into the paint film. The peroxide radicals like cyclohexanone peroxide and methyl ethyl ketone peroxide are used to initiate the polymerization reaction. Unsaturated polyester resins also are utilized in stone putties and marble fillers.

Urea and melamine resins

Alkylated urea and melamine-formaldehyde resins are used for cross-linking of hydroxyl and carboxy-functional resins. These resins are produced from the condensation of urea or melamine with formaldehyde. The manufacturing process includes two reactions that are: the methylolation of an amino compound such as urea with formaldehyde that can be performed under basic or acidic conditions; the second reaction that is alkylation is carried out under acidic conditions. Urea resins can be used in acid curing coatings that cured in room temperature. These coatings are two pack systems and mainly are used for furniture. Melamine resins that have higher hardness are used in combination with polyester or acrylic resins in heat curing coatings like automotive industry and appliances. The nature of the functional groups, degree of polymerization and type of the alcohol used for alkylation can influence in the final properties of urea and melamine resins. The largest market for amino resins is in the automotive industries. Heat-cured automotive primers, primer surfaces, basecoats, and clear coats utilize melamine resins as cross-linking agents.

Phenolic resins

Phenolic resins are one of the oldest synthetic resins and produced from the condensation reaction of phenol and formaldehyde. If this reaction is catalyzed with acid, the name of phenolic resin is Novolac and if the reaction is catalyzed with bases, the phenolic resin is named Resol. The Resol are used in heat curing coatings for metal cans and containers; but the Novolac is only used in room temperature coatings for furniture polishes. The resols are of limited use as sole binders because of their brittleness and they are used in combination with plasticizing co-resins. The epoxy resins are blended with resol as a hardener. The novolacs have a well-defined melting point and are solid at normal temperature. They can be utilized in physically drying paints because they have largely inert behavior. The novolacs can be used as electrical insulation paints since they have a high dielectric constant. The phenolic resins can be modified with rosin and alkyd resins. This modified resin can be used in putties, priming coats, rust protection paints and colored topcoats. The novolac indicates minor importance as paint binder compared with phenolic resol resins. However, it is important as binder for basic dyes in printing inks.

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Curriculum Vitae

Name:	Seyed Amirhossein Seyedmehdi
Post-secondary Education and Degrees:	The University of Western Ontario London, Ontario, Canada 2007-2011 PhD
	Amir Kabir University Tehran, Iran 1999-2002 M.A.
	Amir Kabir University Tehran, Iran 1994-1999 B.A
Related Work Experience	Research and Teaching Assistant The University of Western Ontario 2007-2011
	Research Assistant Paint Factory, Iran 2000-2004

Publications:

S.A. Seyedmehdi, Hui Zhang, Jesse Zhu" Superhydrophobic RTV silicone rubber Insulator Coatings", *IEEE Transactions on Dielectrics and ElectricalInsulation,* submitted

S.A. Seyedmehdi, Hui Zhang, Jesse Zhu." The effect of nanoclay on conductive polymer coating containing metal coated carbon fiber", *Journal of Coatings Technology*, on submission

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