Development and Evaluation of Anti-Abrasion Polymer Coatings for Circulation Coins

By
Ayman Ibrahim

A thesis submitted to the Faculty of Graduate and Postdoctoral
Affairs in partial fulfillment of the requirements for the degree of

Master of Applied Science

In

Mechanical Engineering

Carleton University

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Abstract

The Royal Canadian Mint (RCM) has always been active in finding and supporting new and advanced coin production technologies. Most recently it revealed interest in polymer based coatings for its circulation coins. The motivation behind this development is to provide anti-abrasion, anti-corrosion and anti-bacterial abilities thus increasing the life span of coins in circulation. Polyurethane, polytetrafluoroethylene, advanced liquid glass, standard liquid glass and silicon R-2180 are selected and applied onto brass plated blank coins (loonies) and their wear resistance is investigated. Following coating application using a WS-650 spin coater, polyurethane, advanced liquid glass and silicon R-2180 showed satisfactory visual appearance in compliance with standards set by the Royal Canadian Mint. Pin-on-disc wear test is conducted on coated brass blanks; both advanced liquid glass and polyurethane exhibits superior results when compared to silicon R-2180. An additional abrasion test is carried out using a tumbling machine. Periodic tumbling is carried out in increments of 5 hr for 25 hr to assess the wear resistance of the three candidate materials. Over all, advanced liquid glass maintains 40% of the coating after 25 hr of tumbling compared to only 20% and 5% for polyurethane and silicon R-2180, respectively.

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Acronyms

ALG	Advanced Liquid Glass
CS	Cold Spraying
EDX	Energy Dispersive X-ray
EMS	Electro-Magnetic Signature
PTFE	Polytetrafluoroethylene
PS	Plasma Sprayin
PUR	Polyurethane
RCM	Royal Canadian Mint
RPM	Revolution Per Minute
SEM	Scanning Electron Micscope
SLG	Standard Liquid Glass

1 Chapter: Introduction

1.1 Research Background

The Royal Canadian Mint (RCM) is a commercial crown corporation producing circulation coins, numismatics and bullions for domestic and international markets. Additionally, the RCM operates full-service gold and silver refineries, storage facilities and precious metal exchange traded receipts. As a world class provider, the RCM is constantly improving and developing their products to meet both customer requirements and social/environmental regulations.

In general, circulation coins lose some elements of their surface features after being in circulation for a certain period of time. This change in surface appearance is attributed to wear resulting from coins interacting with one another and with other objects. This leads to the deterioration of the coins in circulation earlier than expected.

The subject of coinage wear has a long history and a number of studies published concerning wear rates and laboratory tests simulating the behaviour of coinage materials in service [1]. Due to the vast existence of different denominations of circulation coins around the world and the different environments to which coins are exposed, it is difficult to simulate real life wear loss of coinage materials. However, many methods and adequate wear test machines have been developed over the years to understand the relationship between laboratory and service data [2].

1.2 Research Objectives

This research in particular aims at producing coins for the RCM with anti-abrasion capabilities hence increasing the life span of coins in circulation. Polymer coatings with anti-abrasion capabilities were applied onto the coins using a spin coater hence a relationship

between spin coating parameters and coating thickness was determined to comply with the RCM coating thickness requirement. Moreover, different surface treatments were considered in an attempt to enhance the adhesion between the applied coatings and the coin's surfaces for long lasting effects. Finally, different test methods to investigate the wear resistance of the applied coatings were developed.

Brass plated coins (loonies) were primarily used in this research instead of other Canadian coin denominations since brass plated coins are expensive to produce compared to other Canadian coin denominations. Additionally, brass plated coins tends to lose the surface gloss after being in circulation for a short period of time. Loonies are manufactured using a multiply plating technique with an iron matrix plated with brass (70Cu-30Zn) to impart a golden finish. Although loonies were the primary focus of this research, the developed coatings may be used on other denominations of coins in circulation.

As for material selection, five polymers were initially selected in this research based on anti-abrasion ability, durability, availability: Polyurethane (PUR), Polytetrafluoroethylene (PTFE), advanced liquid glass (ALG), standard liquid glass (SLG) and silicon R-2180. All candidate materials are known for their anti-abrasion capabilities however, only ALG contains ethanol as an anti-bacterial agent.

1.3 Methodologies

After investigating state of the art coating applications, a spin coater was chosen to deposit the polymer coatings onto the surface of the coins as very thin coatings are required by RCM. The application process primarily consisted of three steps: pre-process (surface treatment), deposition process and curing. Once coating application was completed, all coated coins were visually examined for their optical properties and coating adhesion. Further analysis was

carried out on the acceptable coins to study the surface microstructure of the coatings and their performance in various tests. Although the wear ability of the candidate materials is solely investigated in this research, the anti-corrosion and anti-bacterial characteristics are also important coating features and have been investigated by Bingjie Xiao in a thesis paper titled “Development and Evaluation of Anti-corrosion and Anti-bacterial Polymer Coatings for Circulation Coins” [3]. The main tasks of the current research were as follows:

(1) All five candidate materials were applied using a spin coater. Spin coating parameters (spin speed) were altered for each material to achieve controllable thickness.

(2) Following the coating application process, all coins were visually examined to ensure compliance with the transparency requirement and good coating adhesion.

(3) Following visual examination, all accepted coins were analyzed using a Scanning Electron Microscope (SEM) to study the coating microstructure.

(4) The coating thickness requirement was assessed based on weight changes. Since each material differs in viscosity, a specific set of processing parameters accompanied each material to achieve the desired coating thickness.

(5) Two wear tests were employed in this research. Pin-on-disc test was first carried out which was then followed by tumbling. Weight loss analysis and SEM images were obtained after each test to further determine the anti-abrasion ability of each material.

1.4 Thesis Structure

This thesis consists of seven chapters in total. A summary of each chapter is presented below:

Chapter 1 introduces the background and the objectives of this research. Additionally, the methodology used in coating application and testing procedures is presented. Finally, a brief description of each chapter included in this research is summarized.

Chapter 2 is a literature review and it includes the history of circulation coins and minting techniques adopted by the US, Europe and Canadian mints. The chapter also briefly elaborates on Hertz contact stresses associated with pin-on-disk test as well as the materials properties influencing wearability. Additionally, Chapter 2 presents the coating requirements set by the RCM and current problems associated with coins in circulation. Finally, different coating application methods are discussed.

Chapter 3 introduces five candidate materials adopted in this research. Also, coin surface preparations along with coating fabrication are discussed.

Chapter 4 provides the details of experiments conducted to characterize the coated coins. Visual investigation, SEM images and relationship between coating thickness and spin speed are all examined.

Chapter 5 explains in details the two wear tests conducted in this research along with the outcomes for both pin-on-disc test and tumbling test.

Chapter 6 discusses the outcomes of the results acquired in Chapter 5. Coating thickness analysis and coating microstructure are also emphasized.

Chapter 7 concludes the work accomplished in this thesis paper by presenting the selected polymer coating based on abrasive tests of the three candidate materials. It also provides a summary of the results and outlines the main contributions made through this thesis. In addition, future work is also proposed.

2 Chapter: Literature Review

2.1 History of Metal Coins

A coin is a piece of money made of metal or an alloy of metals that conforms to a standard and represents a design. The chronology of coins first started in the Kingdom of Lydia (currently known as Turkey), where it is believed that the first coin was struck [4]. Lydia was well known for its natural sources of electrum (**Figure 2-1**), an alloy of gold and silver from which the first coin was made [5]. However, coinage can be interpreted as a Greek phenomenon since coins spread widely through the Greek world compared to elsewhere. Nevertheless, since Lydia was under the Greek influence at the time, it can be claimed that the invention of coinage occurred when the Lydian and Greek cultures interacted. However, the exact time when the first coin was struck has never been confirmed.

Coins found under the temple of Artemis at Ephesos were in the form of lumps of electrum where some coins were either marked, punched or even bared a design. The most famous coin is the Lydian lion, which was the world's first minted coin by King Alyattes around 600 BC in Sardis, Lydia [5] (**Figure 2-2**).

Figure 2-1: Electrum found in nature [6].

Figure 2-2: Lydian electrum trite, the world's first minted coin by King Alyattes [6].

From the limited information regarding the functionality of electrum coins, it was found that gold and coinage electrums were circulated widely and used for payments between states. Also, authorities behind issuing the earliest electrum coinages were unclear. It seems that the earliest coins were issued by individuals rather than states due to the large variety of ancient coinage types found. As a large number of coins varieties were found, scholars in the field believed that large number of mints existed. Many coins shared the same designs implying that they were produced at the same place [5].

The introduction of coins as accurate modes of payments and investments required highly precise minting techniques governed by a country's reining authorities. Minting techniques have evolved in two main areas of research over the years, one is the production of suitable blanks and exact weight, the other concerns the production of tools used for striking [7]. Such techniques are in use till today except that the methods have progressed and have been improved over the centuries. During the medieval times, coins were struck using two-coining dies prepared by engravers, a lower die to depict the coin in a negative form and an upper die (Figure 2-3). The blank coins were placed between the two dies and struck with a heavy hammer multiple times. This technique was not costly; however, it required skilled laborers.

Figure 2-3: Early coin striking method [8].

Around 1550, the screw press (Figure 2-4) was introduced by the German silversmith Marx Schwab as a coin striking technique [7]. The press consisted of two heavy iron screws that

were maneuvered by eight to twelve men in order to press the metal coins to a desired thickness.

Figure 2-4: Screw press used as a coin striking technique [8].

The screw press was in use for centuries until a German mechanic invented the coin press in the early 19th century (**Figure 2-5**). Also known as the toggle press, it performed in the same manner as the screw press except that it substituted the pressure from the screw of the screw press by a pressure exerted by a lever [8]. Such tool allowed several hundred of coins to be produced per minute. The toggle press was first driven using steam and then by electricity.

Figure 2-5: Toggle press introduced in the early 19th century [8].

2.2 Modern Coin Manufacturing Methods

2.2.1 United States Mint

Circulating coins represent ninety percent of the United States Mint production. Since 2004, 65 to 80 million coins have been minted every day [9]. The U.S. circulating coins are produced

in six different denominations: one cent (penny), five cents (nickel), ten cents (dime), twenty-five cents (quarter-dollar), fifty cents (half-dollar), and lastly one dollar [9].

In general, all denominations have the same manufacturing procedures except that the edges of dimes, quarters, half-dollars and dollars are marked with tiny ridges during the striking processes. This procedure is called reeding (**Figure 2-6**). Reeding functions as a preventive measure to avoid unlawful shaving or cutting of the precious metals [9].

Figure 2-6: Reeded coins (left) and smooth coins (right) [9].

The first step of the manufacturing processes is sketching a design to be struck on the coin. Once a drawing is selected, refined and approved, a US mint engraver would start the coin modeling process. There are two modeling processes [10]. First, the traditional methods where the relief is modeled in clay and refined using plaster (**Figure 2-7**), followed by scanning the resulting three-dimensional bas-relief sculpt. Plaster is poured over the clay model to display fine details. The engraver repeats the plaster process several times until the plaster model is perfect (**Figure 2-8**). Second, the digital methods where the designs are sculpted and refined using a wide range of software tools. Following both methods, the model is reviewed for defects and a digital database is created to confirm adherence to engineering guidelines. Once the modelling processes are completed, the model is released for manufacturing.

Figure 2-7: A clay model sculpted [10].

Figure 2-8: Plaster being created to display the design fine details [10].

During the manufacturing process, the U.S. coinages blanks are punched on a high speed automatic press corresponding in size to the coin to be minted; this process is known as planchets [9]. After the planchets are heated in an annealing furnace at 700°C to soften them, they are put in washing and drying processes which remove any oxides, tarnish, discoloration or contamination that remains after annealing [9]. Once the perfect blanks are dried, they run through an upsetting mill (**Figure 2-9**) to raise the rim around the blank edge which helps to protect the design from damages. The upsetting mill also allows the blanks to fit into the coining press collar.

Figure 2-9: Upsetting mill [9].

The upsetting process has two advantages. First, it hardens the edges and prevents the coins from eroding during usage. Second, it flattens the edge which would make it easier to automatically feed the coins into the high-speed coin press and help the staking process once they are ready for shipping. As soon as the coins are stamped with the design and inscriptions, they would become unique to the United States mint. Each row of stamping presses (**Figure 2-10**) runs the same coin denomination with the press setting adjusted to the strength of the metal. For example, the dollar golden coins require the utmost force, and pennies require the least [10].

Figure 2-10: Stamping presses [9].

Figure 2-11: An interior view of the stamping press [9].

Next, coins run through a quality control procedure to ensure the absence of defects and adherence to guidelines. If there are any defects, coins are scrapped and placed into destruction machines called wafflers (**Figure 2-12**) to be recycled for future use. [10].

Figure 2-12: Waffler for scrapped coins [9].

Coinages are then counted and bagged. Each bag is weighed before shipment to ensure that it contains the correct number of coins (**Figure 2-13**). Finally, the bags are shipped to the Federal Reserve Banks for distribution into the economy.

Figure 2-13: Bagging and weighting a coin bag [9].

2.2.2 Europe Mints

The euro coin series are produced in eight different denominations: 1 cent, 2 cents, 5 cents, 10 cents, 20 cents, 50 cents, €1 and €2 [12]. Each euro coin consists of two sides, a common side and a national side. The national side indicates the issuing country surrounded by twelve stars of the European Union [13]. The design implemented onto the national side must fit one of three themes, architectural and ornamental, aims and ideals of European Union, or European personalities. A total of nineteen countries in Europe are responsible for minting euro coins, however, the total value of coins enforced into circulation annually must be approved by the

European Central Bank [12]. Although the coins produced by each country would have a different motif, they can be used anywhere within the nineteen countries.

All eight euro denominations vary in size, weight, colour and metals. Such variations serve a number of practical considerations, for instance, variation in designs makes it easier for visually impaired to tell the coins apart. Also, the use of bimetal makes it difficult to counterfeit. All European mints follow the same manufacturing process in production [13].

The manufacturing process starts with a design process. The design process is carried out by an artist who develops scenes and impressions not only on a refined space and shape, but also with a three-dimensional aspect to enhance the design [13]. Once the design is finalized, dies and moulds are prepared to accommodate the design. The selected design is then transferred onto a plaster mould that is at least five times the size of the actual coin. This painstaking step allows the artist to perfect the design to the finest detail [14].

Once the plaster is established, it is then transferred onto a rubber resin mould where an epoxy resin mould is generated. This epoxy resin is placed inside a reducing machine called a pantograph (**Figure 2-14**). The pantograph traces the contour of the mould onto an engraved master die or matrix having the same diameter as the coin to be struck [14]. The master die (**Figure 2-15**) is used to prepare working dies for the striking process since the excessive pressure from striking will wear the die after multiple strikes.

Figure 2-14: Pantograph machine used to engrave a design onto a master die or matrix [13].

Figure 2-15: Matrix (left) and master die (right) generated by the pantograph [15].

Once the dies are ready, coining metal is prepared using large coiled strips of the required metal. The metal is scrubbed prior to any processing to establish a clean consistent surface [14]. The scrubbed metal is then placed inside a blanking press to produce the blank discs. The blank discs are annealed and rolled to an exact thickness required for each denomination of coins. Once the blanks are checked for defects, the striking process takes place using a press with a variable pressure that can reach over 2 MPa (Several hundreds of pounds per square inch)[13]. The pressure and duration vary depending on the coin surface characteristics, required finish and type of metal used. Once the pressed coins are checked, they are packaged, weighed and sealed prior to shipping for distribution through banks.

2.2.3 Canadian Mint

Canadian coins are produced nowadays in five different denominations: 5 cents, 10 cents, 25 cents, 1 dollar and 2 dollars [16]. Over 1 billion circulation coins are minted each year in the Canadian mint manufacturing plant located in Winnipeg. Each denomination follows a technical specification and design reflecting the diverse Canadian culture. In addition, the Royal Canadian Mint produces hand-crafted commemorative coins and medals. The Ottawa manufacturing facility produces on average 8,000 collector coins (numismatics) per eight hour shift where each coin is treated as an individual work of art. Both circulation coins and

numismatics go through different minting techniques, patented technologies and rigorous statistical sampling to ensure the highest quality standards [16].

The RCM produces all denominations following comparable procedures implemented by the US mint and Euro mints. However, the RCM owns several patented, cost reduction technologies and utilizes them in the manufacturing of circulation coins. To reduce costs modern circulation coins are made of non-ferrous or ferrous base alloys. In particular, plated steel circulation coins made their first appearance in the nineteen seventies; the mono-ply and bi-ply plating processes were introduced to produce plated steel circulation coins with acceptable surface corrosion and wear resistance. A mono-ply process consisted of plating a single layer of metal (e.g. plating copper using a cyanide process or plating nickel using nickel sulphate) onto steel [17]. This process deteriorated the coining die life due to the abrasive columnar microstructure resulting from plating the metal layer. The bi-plating process consisted of plating two layers of metal onto steel. For instance, the steel core was coated with copper followed by a layer of nickel. Again there was an environmental concern with this process [17].

After extensive research, the RCM invented the multi-ply plating process (**Figure 2-16**) that achieves more than two layers of metals onto a steel core. For example, a steel core can be plated with nickel, copper and then more nickel. The multi-ply process overcame the shortcomings of die deterioration in the mono-ply and the environmental concerns associated with bi-ply plating processes.

Figure 2-16: Multi-ply plating process adopted by the RCM [18].

However, several others problems such as blistering and sever mechanical deformation during minting are associated particularly with multi-ply plating. For instance, micropores may occur due to defects in the previously plated metal or on the surface of the steel core. Such micropores cause bridging during the subsequent electroplating procedures and as a result, the entrapped air may blow causing blisters when exposed to pressure from coining applications [19]. RCM further improved the plating process by controlling the current used in electroplating the metal coating. For instance, the metal plate was initially electroplated at a low current density followed by full current density [19]. This minimized bridging of micropores and ensured full coating coverage. **Figure 2-17** presents a cross section view of a steel core followed by nickel strike and finally copper plating deposited at low (1.2 to 1.5

amps) and high (6 to 7 amps) current density while electroplating. It can be observed that using low current for copper as in **Figure 2-17 (a)** prevents copper bridging as compared to high currents used in **Figures 2-17 (b) and (c)**.

Figure 2-17: Cross sectional views of depositing of molecular layer of copper: (a) at low currents, (b) and (c) at high currents [19].

Additionally, the RCM introduced a plating process to remove plating stresses associated with multilayer deposition, hence, increasing the coin's surface hardness. The plating process comprised heating the metal or alloy blanks at or above a recrystallization temperature sufficient to soften the metal or alloy for minting [17]. Once plating was applied, the metal or alloy blanks were heated to eliminate plating stresses at a temperature below the recrystallization temperature of the outermost plating layer. For example, if nickel plating was applied, the blanks were heated between 425°C and 550°C but for copper plating, the heating temperatures were between 225°C and 275°C for about 2 hrs. The total deposited plating thickness is approximately 25 microns and it increases surface hardness and resistance to wear and corrosion over the desired 20 year circulation life of coins [17].

Finally, the multi-ply plating invention also overcame the issues associated with calibrating vending machines. Coins are used on a daily basis as means of payments in vending machines. If the machines cannot distinguish between different coins made of the same alloy or similar size, this can result in fraud. For instance, using the mono-ply plating process, only a single layer is plated over a steel core and as a result, the coin cannot be distinguished from other single plated steel coins due to their vast existence around the world. This issue was a potential cause for fraud in vending machines. However, the multi-ply plating process provides means to overcome such difficulties by defining the thickness of the deposited metal layers hence providing each coin with a unique electromagnetic signature (EMS) that can be identified through proprietary algorithms in vending machines [18]. EMS is unitless and represented by a unique frequency figure affected by the diameter, edge thickness, weigh and alloy composition of the coins.

2.2.4 Problems Associated with Circulation Coins

Metals such as copper, aluminum and zinc have a vast range of mechanical properties and are widely used in coin manufacturing industries. However, due to the extreme environments the coins are exposed to, material loss or surface discoloration often occurs. Two main factors are responsible for the early deterioration of the coins in circulation: abrasion and corrosion. Abrasion results from constant interactions with other solid bodies or even fabrics causing the coin's surface to lose some or all elements of the design on the coin. Corrosion on coins results from the direct contact with human sweat causing the coins to lose original color and gloss. Finally, coins in circulation carry contaminants and bacteria when passed from one person to another which presents a significant health risk to the public. Therefore coatings are considered an option to increase the life span of the minted coins (resistance to wear and corrosion).

Polymer-based coating in particular became the focus of this study due to their light weight, transparent nature and low cost.

2.3 Polymer Coatings on Metals

Polymers are substances that are composed of long chains of repeating molecules. The process of making long chain polymer molecules is called polymerization [20]. Polymerization is achieved by causing identical monomers to attach to each other or through condensation reaction that involves combining a number of chemicals. Molecules with high molecular weight greater than 10^5 amu are called macromolecules. The long molecular chains are usually bonded together with weak electrostatic forces called van der Waals bonds. However, the changes that occur in polymers during degradation are manifested differently depending on which degradation processes are involved. **Figure 2-18** presents the basic types of polymers based on characteristics and origins. Although polymer coatings have been in use for over 40 years, information on their degradation modes is largely empirical in nature [21].

Figure 2-18: Classification of polymeric materials and important thermoplastic and thermosetting plastics [20].

Polymer degradation is most frequently classified based on factors responsible for degradation; these being thermal, mechanical, chemical, biological and even hydrolytic in nature [22].

2.3.1 Thermal Degradation of Polymer Coatings

Thermal degradation of polymer coating on metal surfaces is a result of exposure to elevated temperatures either during processing or use. High temperatures exposure results in chemical changes without the involvement of other compounds [23]. All polymers can be degraded chemically by heat; however, when heated to the extent of bond rupture, polymers will follow three major pathways: side group elimination, random scission and depolymerisation.

2.3.2 Mechanical Degradation of Polymer Coatings

Mechanical degradation of polymer coatings occurs due to the application of physical forces in tension or shear. It includes all kinds of mechanically-induced breakdown of the materials such as plastic deformation, cracking, crazing and fatigue.

Abrasive wear is a major cause of polymer coating mechanical degradation on metal caused by displacement of material from a surface in relative motion due to the presence of hard protuberances or hard particles present or embedded in a surface [24]. Based on the definition, two types of abrasions exist (**Figure 2-19**). The first type is the two-body abrasion. Such abrasion occurs when polymers slide against a rough surface causing deterioration of the polymer. Second type of abrasion corresponds to the three-body abrasion. Three body abrasions occur when abrasive particles are introduced in a sliding system either as environmental contaminations or as products of corrosion or even as a result of two body abrasion [24].

Figure 2-19: Demonstration of two and three body abrasive wear [25].

Given the two types of abrasive wear, fracture toughness K_{Ic} and hardness H play an important role in the wear rate of materials. In a study conducted by Sevim and Eryurek on assessing the abrasive wear of materials using pin-on-disk abrasion test, it was found that the abrasive wear is dependent on the abrasive size particle and the fracture toughness of the wear

surface [26]. Additionally, they concluded that the wear rate of materials with small fracture toughness and high hardness is high. In general, the pressure p used for abrasive wear test is a function of fracture toughness and hardness as shown below [26]:

$$p \propto \frac{K_{Ic}}{H} \quad [2.1]$$

Since the major cause of coin deterioration is related to coins in contact with one another and other objects, such contact can be typified using Hertz contact theory. The stresses resulting from contact are known as the Hertzian contact stresses. In general, Hertz contact theory applies to two non-conforming bodies with the following assumption: (1) the surfaces are under normal load, (2) the area of contact is finite and significantly smaller than the bodies, (3) the contact is purely elastic and finally (4) no friction upon contact [27]. Although the stresses may not be significant, but will impact the surface features over time. Hertz theory generally applies to arbitrary elastic geometry surfaces in contact, however, only pin on disc Hertz contact theory will be discussed in this research due to the wide range of different elastic bodies in contact with coins.

Figure 2-20: Pin on disc Hertz contact [28].

Figure 2-20 presents a sphere and a flat plate in contact under an applied normal load, representing the elastic deformation during pin-on-disc wear test. The rectangular area is the area due to the deformation of both bodies. The maximum pressure resulting from the applied normal load can be computed using Equation (2.2) where P_o is the maximum pressure, P is the

total load specified, r is the radius of the sphere, E^* is the effective modulus of elasticity and a is the contact area radius formed [29].

$$P_o = \frac{3P}{2\pi a^2} = \left(\frac{6rE^{*2}}{\pi^3 r^2}\right)^{1/3} \quad [2.2]$$

Alternatively, the area formed and total compression can be evaluated using the following two equations where δ is the total compression, z is the depth of penetration and E_1, E_2 are the elastic modulus and ν_1, ν_2 are the Poisson ratio associated with each body. The dashed lines in **Figure 2-20** corresponds to the overlap of the two surfaces if deformation did not occur [29].

$$\frac{1}{E^*} = \frac{1-\nu_1^2}{E_1} + \frac{1-\nu_2^2}{E_2} \quad [2.3]$$

$$a = \left(\frac{3Pr}{4E^*}\right)^{1/3} \quad [2.4]$$

$$a = \sqrt{rz} \quad (\text{Valid for } z=\delta) \quad [2.5]$$

$$\delta = \frac{a^2}{r} \quad [2.6]$$

Using the aforementioned equations in computing for the maximum pressure at a point, contact radius and the depth of penetration, the principle stresses in the materials can be calculated yielding the maximum shear stress as shown below [30]:

$$\sigma_x = \sigma_y = -P_o \left[\left(1 - \frac{z}{a} \tan^{-1} \frac{1}{z/a}\right)(1 + \nu) - \frac{1}{2(1 + \frac{z^2}{a^2})} \right] \quad [2.7]$$

$$\sigma_z = \frac{-P_o}{1 - \frac{z^2}{a^2}} \quad [2.8]$$

$$\tau_{max} = \frac{\sigma_x - \sigma_z}{2} = \frac{\sigma_y - \sigma_z}{2} = 0.31 P_o \quad [2.9]$$

Figure 2-21 presents a comparison between stress distribution on a circular area of radius “ a ” caused by uniform pressure (left) and Hertz pressure distribution (right). At the surface, the stresses caused by Hertz pressure are 1.5 times the stresses caused by uniform pressure

distribution. It can also be observed that the Hertz stresses varies along the circular radius area “ a ” which provides an accurate measure of stress distribution compared to the uniform pressure distribution assumption which is consistent throughout the circular area formed. Moreover, investigating the maximum shear occurring below the surface along the z axis, it can be observed that the maximum shear ($0.31P_0$) based on Hertz pressure distribution occurs at a depth of $0.48a$. This maximum shear is higher and occurs earlier compared to the maximum shear evaluated based on the uniform pressure distribution along the axis of symmetry.

Figure 2-21: Stress distributions above and below the surface caused by (left) uniform pressure distribution and (right) Hertz pressure distribution acting on a circular area of radius "a" [29].

2.3.3 Chemical Degradation of Polymer Coatings

Chemical degradation of polymer coatings is a process that affects all plastics used in daily life. It mainly concerns with corrosive chemicals, gases or liquids that will attack and degrade most polymers through chain scission or oxidization [30]. As a result of chemical degradation, the chemical structure of polymers changes including bond scissions and formation of functional groups [31].

2.3.4 Biological Degradation of Polymer Coatings

Biological degradation of polymer coatings occurs on a few types of polymer such as plastics [32]. The process of biological degradation takes place when organic substances such as bacteria, fungi, yeast or enzymes degrade the polymer through an attack of certain functional groups. However, factors such as polymer characteristics and type of organism govern the level of biodegradation. The following four steps are required for polymer biodegradation to occur [33]:

1. Attachment of microorganisms to the surface of the polymer
2. Growth of microorganism resulting from the use of polymer as a carbon source
3. Primary polymer degradation
4. Ultimate degradation

Also, the following characteristics are used to detect biodegradation of polymers:

1. Level of hydrophobicity
2. Polymer size, molecular weight and density
3. Amount of amorphous and crystalline regions
4. Structural complexity
5. Presence of brittle bonds

6. Molecular composition

2.3.5 Hydrolytic Degradation of Polymer Coatings

Hydrolytic degradation usually occurs on polymers with functional groups that are sensitive to water [31]. Such degradation occurs due to the presence of moist or acidic conditions in the environment of the polymer causing chain scission as a result of hydrolysis of the main chain.

2.3.6 Polymer Coatings Degradations Apposite to Coin's Deterioration

Since coins are used in a vast number of environments through which coin deterioration occurs, only a few of the polymer degradations aforementioned relates to the current thesis paper. Starting with the thermal degradation of polymers, such phenomena do not apply in this research since elevated temperatures are required to cause deterioration (usually 100°C or above depending on the type of polymer used) [23]. As for the mechanical degradation of polymers, it is the primary focus in this research since the coatings applied onto the coins are of polymeric base and the mechanical properties of the coatings were assessed based on durability. Mechanical degradation of coins occurs as a result of continuous interactions between coins or even with other objects. Two and three body abrasions were presented along with Hertz contact theory in attempt to understand the nature of the mechanical degradation occurring in coins. Chemical degradation of polymers is also relevant to the deterioration of coins since human sweat plays a major role in the corrosion of coins resulting in the loss of elements of the surface features of the coins. As for biological degradation, it does not apply to the current study due to the nature of the polymers applied in this research. Bacterial infections transmitted through coins presents potential health risk, therefore an anti-bacterial polymer coating was considered (ALG). Another team member has taken into consideration the corrosion degradation and bacterial infections caused by coins in her thesis paper

referenced in Chapter 1. Finally, since the selected five candidate materials are of hydrophobic nature, the hydrolytic degradation of polymers do not apply to selected polymers. Hydrolytic degradation mainly affects polymers with hydrophilic characteristics.

2.4 Coating Fabrication Techniques

For centuries, coatings have been used for decorative or protective purposes. Coating selection and deposition technique are primarily governed by the required characteristics of the coated film. Over the years, coatings have been traditionally applied using a number of different techniques, including, brushing, dipping, spraying, electrodeposition, plasma spray, Cold Spray (CS) and spin coating. Each of these techniques has their own advantages and disadvantages associated with film thickness, durability and material compatibility. Only those suitable for polymer deposition will be discussed in the following sections.

2.4.1 Dip Coating

Dip coating is the most widely used deposition technique because of its vast range of applications especially industrial and laboratory applications. Dipping is the process that uses a tank of a specified material into which the substrate is immersed and then retracted at a specified rate [34]. In general, the dip coating technique takes several steps as demonstrated in **Figure 2-22**.

Figure 2-22: Fundamental stages of sol-gel dip coating [35].

Starting with the immersion of the substrate, a coherent film is entrained on the substrate upon withdrawal, which then is followed by drying. In order to achieve a final coating, usually a curing or sintering step is involved [35]. The coating thickness is determined based on the competition between viscous forces, surface tension and gravity. The final coating thickness uniformity is dependent on fluid (procured polymer) properties, substrate surface features and ambient conditions [36].

The advantages of this coating technique are no excessive material loss, inexpensive and rapid coating application, however, it lacks precision in coating thickness due to the difficulty in controlling all factors involved in the coating process. Additionally, areas not to be coated must be masked prior to coating and de-masked after coating, which requires labour and time [34]. These disadvantages prevented the use of dip coating for the current research since the entire surface of the coin had to be coated to allow for mechanical testing. Moreover, it would not allow for controlling the coating thickness which was a primary requirement set by the RCM.

2.4.2 Brush Coating

Brushing is a coating technique that requires the least amount of investment. However, it is the least repeatable process since it is completely operator-dependent. A good quality synthetic fibre brush, compatible with the product being applied, should always be used. Extreme care should always be exercised while using the brushing technique to prevent bubbling, inconsistent coverage or brush fibre contamination. Generally, this technique is often used for the application of strip coating and for coating complex areas where the use of other coating methods would lead to considerable losses. Disadvantages of brush coatings are similar to dip coating including inconsistent coating thickness, quality and it is more adequate to use for low volume prototype runs [34]. Although brush coating is inexpensive and allows for coating complex areas, it limits the control of the coating thickness applied and for that reason it was not considered in the present research.

2.4.3 Spray Coating

Spray painting is a method used almost everywhere paint is applied due to its versatility and the economy in the use of paint. There are five major spray systems, airless, conventional, hot spraying, cold spraying and plasma spraying techniques [37].

2.4.3.1 Conventional Spray Coating

The conventional air spraying system atomizes and transports the paint by the flow of compressed air. This provides sufficient velocity to propel the particles onto the work piece [38]. Spray coating applications are common in manufacturing environments such as auto and furniture industries where a few coating layers are applied to achieve a uniform coverage. High pressure is used in depositing the material onto the work piece so only a small amount is

deposited onto the surface and the rest is wasted [39]. **Figure 2-23** demonstrates the losses of material as a result of using conventional air spray.

Figure2-23: Material wasted as a result of using conventional air spray technique [39].

Since the film thickness deposited using this technique is usually less than 0.0254 mm (0.001 in), several coating application may be required. Additional disadvantages includes excessive overspray, poor efficiency, low production rate and high maintenance cost [39]. Two primary concerns associated with coating thickness and material over spray limited the use of spray coating in this research.

2.4.3.2 Airless Spray Coating

In the airless spray systems, the material is atomized without the use of compressed air, however, the material is pumped under high pressure 3-31 MPa (500-4500 psi) through a spray tip where it is atomized and directed to the part [40]. The resulting coating is uniform and requires lower number of applications compared to the conventional spray system leading to high demand in manufacturing industries. The primary advantage of airless spray system is associated with its ease of use and simplicity consisting of only a pump, filter and airless gun (**Figure 2-24**). The pump siphons material from the container and propels it under high pressure through a filter and into the airless gun.

Figure2-24: Conventional airless spray system [39].

The excessive pressure utilized in the airless spray technique can produce unstable spray hence affecting the uniformity of the coatings applied. Also, the high pressure tends to wear the spray nozzle faster than expected which would add unnecessary costs to the project considering the large number of coins coated.

2.4.3.3 Hot Spray Coating

Hot spraying is a method used for applying viscous or hard to spray coatings. Special solvents are used which reduces the viscosity of the material when heated. Upon atomization, the faster evaporation solvent is removed and the drop in temperature produces more viscous, run resistant material that can be applied in thick layers [40]. **Figure 2-25** illustrates a hot spraying system. It is similar to the conventional airless spray system but with the addition of a heater placed between the pump and the filter. The advantages and disadvantages of hot spray coating is similar to that of airless spray technique however, it is primarily utilized for highly viscous materials.

Figure2-25: Hot spray system [39].

Although some of the five candidate materials applied in this research have high viscosity which makes hot spray technique desirable, the deposited layers are thick which may prevent achieving a coating thickness in the microns level.

2.4.3.4 Cold Spray Coating

Cold Spray (CS) coating is a process of spraying solid state particles via supersonic impact at temperatures much lower than that of hot spray [41]. CS coating falls into the larger family of hot spray coating. There are two types of CS coating system, the high pressure cold spray (**Figure 2-26**) and the low pressure cold spray (**Figure 2-27**).

Figure 2-26: Operating principles of low pressure cold spray [42].

Figure 2-27: Operating principles of high pressure cold spray [42].

Pressure differences and direction of spray are the two primary differences between the two CS systems. As shown in **Figure 2-26** and **2-27**, the powder is fed perpendicularly in low pressure CS compared to feeding the powder inline as in the high pressure CS. CS coating is not intended to replace any of the well-established thermal plasma spray techniques, however, it is expected to supplement and expand the range of applications of thermal spray as an environment friendly coating method. The major advantage of the CS method is the low temperature involved which makes it possible to coat polymer materials at lower temperatures. Additionally, the low heat input requirement helps in depositing a coating free from oxides and the overspray raw material can be collected and reused [41]. All the five candidate materials used in this research were provided in liquid form therefore, CS coating was neglected.

2.4.3.5 Plasma Spray Coating

Plasma Spray (PS) coating is a process that involves heating a material near or above its melting point and propelling the resulting molten matter at high speeds onto a clean substrate where it cools and forms a coating [43]. Any materials, such as metals, ceramics, and cermet, in the form of powder, can be deposited using PS coating technique. **Figure 2-28** presents a schematic diagram of a plasma spray process to form a coating. The final coating thickness can vary between 0.03 to 1 mm [44].

Figure 2-28: A schematic of plasma spray coating process [44].

The advantages associated with using PS coating include the flexibility of the material choice and simple substrate surface preparation. However, a major disadvantage of this technique, similar to most aerosol techniques, is the limitation in coating small or deep cavities due to the inaccessibility of the spray gun [43]. Similar to the CS spray technique, Plasma spray can only be used for powder coatings which prevented the utilization of this coating technique in the current research.

2.4.4 Electrodeposition

Electrodeposition or electrocoating is the application of metallic coatings to metallic or other conductive surfaces by electrochemical processes [45]. Advantages of electroplating includes meeting high production requirements, lower applied costs and it improves the physical properties of the end product [46]. The material particles employed in this process are suspended in an aqueous solution and are given an electrostatic charge through applying a DC voltage. As soon as the conductive work piece enters and passes through the tank, the material particles are attracted and deposited onto the surface creating a uniform coating that is more than 90% resin and pigments [45]. Once the desired thickness is achieved, the work piece is rinsed in water and baked at a time and temperature depending on the type of material deposited. A major disadvantage associated with electroplating is that both the coating material

and the substrate must be conductive to electricity. Since polymers are nonconductive and all the selected candidate materials are of polymeric nature, the electrodeposition technique was not applicable.

2.4.5 Spin Coating

Spin coating is a predominant technique that has been used to produce uniform, thin films, with thickness in the order of micrometers and even nanometers. The process consists of spreading a thin axisymmetric film on a planar substrate rotating at a constant speed [47]. The overall physics involved in spin coating can be divided into four stages as illustrated in **Figure 2-29**.

Figure 2-29: Key processes of spin coating [48].

Two common dispensing methods can be used in spin coating, static and dynamic dispensing. Static dispensing is used for small substrates coated with fluids having low viscosity and liquid coating is applied when the substrates are at rest. Dynamic dispense on the other hand is used when the coating material is highly viscous and the coating material is applied while the substrate is rotating at a low speed.

The deposited coating properties are affected by factors such as spin speed, acceleration, spin time and the atmosphere in the enclosure (affects contact angle of the fluid on the solid and evaporation rate). However, spin speed is considered to be the most important factor. The speed defines the degree of centrifugal forces applied to the liquid coating resin as well as the velocity and turbulence of air immediately above the substrate [49]. In general, higher speeds and longer spin times would lead to a thinner film.

Advantages of spin coating include low cost, fast operating, less parameters to control compared to other coating methods and the most important, the ability for the thin film to progressively get more uniform as it thins [50]. However, such method is limited to small sized substrates since large substrates cannot be spun at a sufficiently high speed to allow the film to spread evenly over the large surface.

Spin coating technique was preferred over the eight aforementioned coating techniques because it allows for coating thickness control especially at the micron level. Regardless of the viscosity of the material being applied, the spin speed can be controlled to allow for the even spread of the coating over the entire surface of the substrate. Moreover, this technique minimizes excessive material loss since a fixed amount is dispensed over the substrate's surface. Furthermore, only one coating run is required rather than multiple runs as in most spray coating techniques to achieve a uniform and even coating.

3 Chapter: Materials and Coating Fabrication

3.1 Material Selection and Specifications

After extensive research on commercially available polymers known for their transparency and anti-abrasion ability, five candidate materials were considered for potential use on circulation coins. **Table 3-1** presents the basic characteristics of the five chosen candidate materials. Additionally, each of these coatings is discussed in detail below.

Table 3-1: Characteristics of the five chosen candidate materials.

Material	Supplier	Cost (CAD)/Liter	Curing Method	Density (g/cm^3)	Viscosity $g/cm.s$
PUR	MINWAX	18.27	Room Temperature	0.8	38.00
PTFE	Dupont	278.00	Oven Curing	1.1	13.00
ALG	Liquid Glass Shield	1857.26	Oven Curing	0.2	0.04
SLG	Liquid Glass Shield	341.07	Oven Curing	0.2	0.04
Silicon R-2180	Nusil Technology	60.50	Oven Curing	0.9	32.00

3.1.1 Polyurethane

Polyurethane (PUR) is a polymer consisting of organic units joined by urethane links. PUR is formed through the poly addition reaction of di-isocyanate or polymeric isocyanate with a polyol in the presence of suitable catalysts and additives [51]. Different grades of PUR can be produced depending on the types of isocyanates and polyols used. As a result, various types of PUR with different chain lengths, cross-links and extenders can be established [52]. However, the main constituent of PUR is the urethane links, which can be chemically expressed as

PUR is an exceptional material that associates the elasticity of rubber with the toughness and durability of metal, providing it with good physical, thermal and chemical resistance, as well as high tensile strength and abrasion resistant advantages [53]. Due to the aforementioned attributes, PUR is used in a wide range of applications ranging from clothing and furniture finishing to high performance industrial coatings. However, there are two limiting factors that are associated with PUR, hence restricting its wider applications: (1) instability at temperatures above 90°C; and (2) flammability [54]. Based on the advantages of PUR, it was chosen in attempt to provide the coins with a transparent and abrasion resistance surfaces. In this research, PUR was provided by MINWAX, US. The polymer assumes a beige color in its liquid form (**Figure 3-1**).

Figure 3-1: Polyurethane.

3.1.2 Polytetrafluoroethylene

Polytetrafluoroethylene (PTFE) is a synthetic fluoropolymer with a functional group of tetrafluoroethylene. PTFE has a unique structure in the form of rigid cylindrical rod with a smooth surface due to the presence of fluorine atoms running helically along the surface [55]. Therefore, PTFE is well known for its low coefficient of friction (0.05 to 0.01) and high temperature resistance (up to 260°C). It has a wide range of applications ranging from food and medical industries to aerospace and computer industries [56]. Often, PTFE is used as a lubricant because of its excellent physical and chemical properties, especially chemical inertness [57]. PTFE can chemically be expressed as

A study carried out by Khedkar, J revealed that the wear rate of PTFE was influenced by the width of molecular bands rather than the crystallinity of the polymer [58]. Additionally, the wear rate can be further reduced through quenching PTFE into ice cold water from a melting state, rather than slow cooling [58]. In this research, PTFE was purchased from Dupont. The product is in a liquid form and has a milky color (**Figure 3-2**).

Figure 3-2: Polytetrafluoroethylene.

3.1.3 Liquid Glass

Liquid glass is a transparent and non-toxic polymer known for its wide range of usage to protect surfaces against a variety of environmental degradations. Two types of liquid glass materials composed of silicon dioxide were chosen for this research. Both standard (SLG) and advanced (ALG) liquid glass materials were purchased from Liquid Glass Shield, Europe. These materials have great potential to provide anti-abrasion and anti-corrosion. In addition, ALG also has anti-bacterial capability. Based on the Material Safety Data Sheet (MSDS) provided by the vendor, ALG contains siloxane as the active agent with an anti-microbial compound associated with ethanol. **Figure 3-3 (a)** and **(b)** show SLG and ALG respectively.

Figure 3-3: Liquid glass materials: (a) standard liquid glass, and (b) advanced liquid glass.

3.1.4 Silicon R-2180

Silicon R-2180 is silicon-based polymer produced by Nusil Technology, US. This coating material is formulated with high tear strength elastomers, tailored for low surface friction [59].

Figure 3-4 presents the chemical structure of silicon R-2180, where the R groups represent the functional organic constituents such as methyl, phenyl or trifluoropropyl.

Figure 3-4: Silicon R-2180 chemical structure [59].

Silicon R-2180 was supplied in two parts, part A contains the silicone base and part B contains the catalyst. The two parts are mixed at a ratio of 1:1 prior to application. The reason for having two parts is primarily to prevent the hardening of the mixture at room temperature. Silica acts as the reinforcing filler in the silicon base through enhancing the van der Waals forces once cured. **Figure 3-5** presents both parts of silicon R-2180 along with the final mixture.

Figure 3-5: Silicon R-2180.

3.2 Experimental Preparation

This section will discuss the standard steps used in preparing substrate samples prior to coating application. Additionally, several different surface treatments are also detailed here with the purpose to enhance the coating and substrate adhesion.

3.2.1 Specimen Preparation

Proper cleaning and preparation of coins surfaces prior to film coating application is a critical step to the success of coating application. All substrate surfaces should be considered contaminated in the as-received state. Even freshly coated or recently cleaned surfaces will collect dust and dirt quickly when being left in the ambient environment, hence should be cleaned immediately before film application. One major issue with coating application is finger print marks on the coin surface. This should be avoided by adhering to a strict rule of never touching coins with bare hand. Clean tweezers should be used at all times. The following cleaning process was employed prior to coating application.

An ultrasonic cleaner was first filled with water as the working fluid. Using tweezers, three coins, at a time, were placed into a clean 600 ml beaker filled with 400 ml of water along with a few drops of liquid soap. The beaker was then placed into the ultrasonic cleaner and it ran

for 20 min. After that, the beaker was placed under running water to ensure the coins were soap-free. After 10 min of rinsing, the water was drained carefully out of the beaker and it was filled with acetone up to 300 ml. Additionally, a pair of tweezers were also placed in the acetone beaker for cleaning before being used to handle the coins. The acetone filled beaker was then placed into the ultrasonic bath and ran for 15 min. Shortly after, the beaker was removed from the ultrasonic cleaner. Using the cleaned tweezers, the coins were picked one by one and placed 1 cm away from a hot stream for 1 min each. The coins were then wrapped in a clean paper and taken immediately to the spin coater for film application.

3.2.2 Alternative Surface Treatments

Due to the poor adhesion of PTFE to coin substrates, several alternative surface treatments were applied on the substrates in an attempt to enhance adhesion (only for PTFE material).

3.2.2.1 Acid Etching Treatment

A phosphoric acid solution (85% H_3PO_4) provided by Fisher Scientific was used to etch the coins into a porous, rough surface. A mixture containing 50 ml of phosphoric acid and 350 ml of water was prepared to etch the coins. The coins were etched for approximately 20 min or until slight color change occurred. Following the etching process, each coin was placed under running water for 5 min and in acetone in an ultrasonic bath for another 5 min before drying.

3.2.2.2 Grit Blasting Treatment

Sand blasting is another technique that was used in effort to enhance the adhesion of PTFE. Several coins were sandblasted at 0.2 MPa (35 Psi) for approximately 1 min while maintaining the nozzle at 90 degrees to the coin surface. All coins were cleaned using the aforementioned cleaning process after the sandblasting process. **Figure 36** illustrates a comparison between a freshly cleaned coin and a sandblasted coin.

Figure 3-6: Sandblasting: (a) sandblasting chamber, (b) cleaned bare coin, and (c) sandblasted coin.

3.2.2.3 Polishing Treatment

Manual polishing was also used to enhance the adhesion of PTFE on to the coins. A few coins were polished using 600 grit SiC sandpaper followed by standard cleaning procedure.

Figure 3-7 shows the polisher used in the polishing process along with a comparison between a cleaned coin and a polished coin.

Figure 3-7: 600 grit polishing treatment: (a) polishing machine, (b) cleaned bare coin, and (c) 600 grit polished coin.

3.2.3 Coatings Application

A spin coater WS-650 (**Figure 3-8**) provided by Laurel Technologies was used to apply several coatings onto the coins in this research. A spin coater was preferred over other application methods for two major reasons: (1) to obtain a uniform coating, and (2) a fast and cost effective method compared to other application methods. Since the coating thickness requirement established by the Royal Canadian Mint is within the range of 10 microns, the thickness and the uniformity of coatings were of great importance.

Figure 3-8: Coating application equipment: (a) WS-650 spin coater, (b) high pressure gas valve, and (c) balls-eye water level.

The auxiliaries to the spin coater consist of a nitrogen cylinder, high pressure gas valve, Teflon tubing, drain container, a balls-eye water level to ensure the flatness of the vacuum chuck, a vacuum and RPM controller. Vacuum suction was used to hold the coins in place during spinning and the nitrogen gas (controlled at 0.41 to 0.48 MPa) was used to purge the excessive coating materials from entering the mechanical part of the spin coater. Additionally, the balls-eye water level was used to ensure the flatness of the coin hence ensuring a uniform coating. Finally, the RPM controller allowed the spinning speed to be adjusted for the different viscosity values of the candidate material being applied.

3.3 Coating Fabrication

Since each of the candidate materials has its own viscosity, different spin coating process parameters were employed to achieve the desired coating thickness and uniformity. The following sections describe the spin coating process and the parameters selected for each coating material.

3.3.1 Spin Coating Process

Two types of coating techniques are associated with the WS-650 spin coater, static and dynamic. In the static method, the liquid coating is dispensed onto the specimen when it is at rest and then it is rotated at a desired RPM (revolutions per minute) to allow the coating to

spread evenly throughout the specimen surface. This coating process is repeated at different intervals and at different RPMs. As for the dynamic method, the coating material is deposited while the specimen is spinning at a set speed and for a set amount of time to achieve the desired coating thickness.

In this research, the static method was selected for applying all candidate coating materials due to the small specimen size and the ease to control the coating thickness. Once a fixed amount of the liquid coating was dispensed onto the specimen, it ran at 500 RPM for 5 sec to ensure the even spread of the coating material, followed by 25 sec at a set RPM ranging from 100-8000RPM depending on the thickness requirement. The spin speeds were selected based on the trial and error methodology. For each of the five candidate materials, approximately 50 coins were coated while varying the RPMs and coating durations. Each coated coin was analyzed until the desired coating thickness for each candidate material was achieved.

3.3.2 Coating Process Parameters

The coating process parameters are different for each coating material. The reason for this is due to the different viscosity associated with each coating. Each coating material was tested under a range of RPMs during the second step of the coating process under the static mode until the thickness requirement was met. This RPM value would be used for the remaining coating application. Further information and coating thickness vs. RPM graphs will be provided in the following sections.

3.3.3 Curing Process

A Vulcan 3-550 benchtop furnace provided by Ney Tech Company was used for curing the coatings in this research. Once the coating was applied, all coated coins were placed onto a stainless steel tray and placed inside the oven to start curing.

Based on coating vendor's specifications, each coating material was cured at a certain temperature to enhance the adhesion and coating hardness. For PUR, the curing temperature was room temperature and the duration was a minimum of 24 hr. However, all other coatings required curing at elevated temperatures. For PTFE, the curing process was carried out in two steps: (1) drying the coating with a hot air stream for 1 min and (2) baking in a furnace at 385°C for 30 min. As for liquid glass coatings, both ALG and SLG followed the same curing process: 250°C for 1 hr. Finally, silicon R-2180 was cured in three steps: (1) ambient temperature for at least 45 min, (2) baking in a furnace at 75°C for 45 min and finally (3) 150°C for 135 min. All cured specimens were left to cool in air once the curing process was completed.

3.4 Coating Fabrication Impediments

Although the spin coater used in this research is quite simple and efficient, producing high quality coatings with controlled thickness through varying spin speed and duration is challenging. The spin coater only allows coating to be applied on one surface of the coins as a high vacuum was used to hold the coin in place during spinning. Coating the other side after curing the first side was not viable as curing process inevitably caused discoloration/contamination on the bare surface. For this reason, all the experimental work presented in this thesis is based on coins coated on one side.

4 Chapter: Coating Characterization

Coatings were usually evaluated by visual inspection as soon as they were cured. Following visual inspection, weight measurements would be taken to calculate the coating thickness. Microstructure and composition of both bare and coated coin were investigated using Scanning Electron Microscope/Energy Dispersive X-ray (SEM/EDX). SEM analyses were carried out using Tescan Vega- II XMU SEM equipped with an Oxford EDX spectroscopy system for quantitative elemental analysis. In order to enable the samples to be conductive, all sample surfaces were coated with a gold film. When viewing a SEM image, the bright areas represent thinner coating or bare coin (more electron signals from underlying metallic substrate). Additionally, each coin was analyzed using the EDX system to provide the chemical composition of specified areas of interest. However, the EDX system is unable to accurately quantify the light elements whose atomic number is below eight, such as carbon and oxygen.

4.1 Microstructure of As-Received Circulation Coin

A Canadian loony weighs 6.27 ± 0.25 grams with a diameter and edge thickness of 26.5 mm and 1.95 mm respectively. A cross section of a \$1 coin blank (loonie) was prepared by cutting and polishing. Since the RCM uses a multi-ply plating technology to produce all loonies, the cross section could be divided into three sections (based on color variation), each being analyzed by SEM/EDX to detect the exact composition (**Figure 4-1**).

Figure 4-1: SEM image of bare coin cross section (Section 1 is the brass surface of the coin).

Based on the SEM/EDX results, loonies are composed of an iron core plated with nickel then brass respectively. Section 1 illustrates a higher concentration of Zn (14.7 wt%) and Cu (34.7 wt%), indicating a brass plating at the surface of the coins. Moving on to Section 2, the Zn and Cu concentrations gradually decrease and an increase in Ni (27 wt%) is observed. This indicates a layer of Ni plating underneath the brass coating. Finally, Section 3 shows a significant decrease in Cu, Zn and Ni. However, the Fe content increases to 87.3 wt% representing an iron core. **Table 4-1** summarizes the compositions in three sections shown in **Figure 4-1**. It is to be noted that Al, Si and Ca are present in minor quantities in some areas. This was assumed to be impurities in the system.

Table 4-1: EDX results for the cross section of bare coin.

wt%	Fe	Ni	Cu	Zn	O	Al	Si	Ca	Total
Section 1	37.57	3.10	34.75	14.79	7.09	0.78	1.22	0.70	100.00
Section 2	49.92	27.02	11.43	4.75	5.00	0.62	0.90	0.36	100.00
Section 3	87.30	3.00	5.98	2.43	0.44	0.85	0.81		100.00

4.2 Coating Evaluation

Once the coatings were successfully applied onto the coins, each candidate material went through several tests to examine the compliance of each coating with the standards set by the Royal Canadian Mint. The following sections present the tests.

4.2.1 Visual Examination

First the appearance of the coating on coins was assessed. The criterion is that the coatings must not change the surface characteristics of the coins such as color and reflectivity. Hence, the applied coating must be transparent. For visual examination, all coins were photographed using a Canon 5D Mark III camera before and after the coating application process. The parameters of the cameras were set up as follows at all time: focal length = 35 mm, exposure time = 0.005 seconds and ISO (sensitivity to light) = 100.

From the visual examination of the coated coins, only PUR, ALG, silicon R-2180 were found to be transparent. As for PTFE and SLG, they were found to have an impact on the transparency of the coins. **Figure 4-2** shows a comparison between a bare coin and the three qualified candidate coatings.

Figure 4-2: Bare and qualified coated coins: (a) bare coin, (b) PUR-coated coin, (c) Silicon-coated coin, and (d) ALG-coated coin

Additionally, a slight color change was observed on the silicon- and ALG-coated coins. This was attributed to the tendency of brass to oxidize during the curing process. To confirm such phenomenon, an uncoated coin was cured at the same temperatures respective to that of

silicon- and ALG-coated coins. **Figure 4-3** illustrates a comparison between an uncoated coin and an uncoated heat-treated coin at 250°C for 1 hr.

Figure 4-3: Comparison of color change between (a) heat-treated coin at 250°C for 1 hr. and (b) non-heat treated coin.

Furthermore, SEM/EDX analyses were conducted on the heat-treated bare coin shown in Figure 4-4 (a) and a noticeable amount of oxygen content was found. **Table 4-2** lists the Zn, Cu and O contents of a heat-treated and non-heat-treated coins.

Table 4-2: Comparison of EDX results between heat-treated and non-heat treated coins.

wt %	Cu	Zn	O	Total
Non-heat-treated	69.70	30.30	2.19	100.00
Heat-treated	69.53	28.29		100.00

For SLG, a blue tint was observed on the surface of the coin once the coating was applied and cured. **Figure 4-4** presents a comparison between a bare coin and a SLG-coated coin.

Figure 4-4: Comparison between (a) bare coin and (b) SLG-coated coin.

As for PTFE, in addition to its non-transparent nature (milky), it exhibited poor adhesion to the coin substrate characterized by poor surface coverage and easily scraped off using finger nails (**Figure 4-5**). Although three alternative surface treatments (etching, grit blasting and SiC sand paper polishing) were used in attempt to enhance the adhesion of PTFE to the coin's surface, the adhesion was nevertheless very poor **Figure 4-6** presents a comparison of PTFE coated coins coated under different RPMs and surface treatment methods.

Figure 4-5: PTFE coating peeled off by nail.

Figure 4-6: PTFE-coated coins under different treatments.

4.2.2 Coating Thickness Analysis

In order to fulfill the thickness requirement of 8-12 μm set by the RCM, coins were coated using the spin coater at different RPMs and their thickness values were measured. Only PUR, ALG and silicon R-2180 were tested in this study since PTFE and SLG did not meet the transparency requirement. Fifty coins were coated for each of the three candidate materials. All the coins were cleaned and weighed four times prior to coating application and weighed another four times after coating application. A weigh balance provided by Acculab with a precision of ± 0.5 mg was used to weigh the coins. Using the weigh difference, coin surface area and cured coating density, the coating thickness was evaluated using **Equation 4.1**.

$$t = \frac{V}{A} = \frac{Wc}{\rho A} \quad [4.1]$$

where t is the film thickness, V is the coating volume, Wc is the weigh difference before and after coating, ρ is the density of the coating and finally, A is the surface area of the coin.

Figure 4-7 illustrates the coating thickness as a function of spin speed (RPM) for PUR, ALG and silicon R-2180 coatings on brass plated coin blanks. Since ALG is the least dense coating material, lower RPMs were selected for this material. As for higher density materials such as PUR and ALG, higher spin speeds were used. Based on the graphs in **Figure 4-8**, the optimal spin speed required for PUR, ALG and silicon R-2180 to meet the set standards are 6000, 500 and 4000 RPM respectively. Thus these speeds were used to apply the coatings for further tests.

Figure 4-7: Variations of coating thickness as a function of the rotational speed (RPM) (The standard deviation of $\pm 4 \mu\text{m}$ is based on weighing each coin four times before and after coating application).

4.3 Microstructural Analysis of the Coatings

SEM analyses were performed on the coated coins to investigate the uniformity of the coatings and presence of defects. The SEM images were obtained for the coins only meeting the thickness requirement of 8-12 μm . Three coins conforming to the thickness requirement were analyzed and SEM images were obtained at the center and the edge of each coin. All SEM images acquired for each material were similar in the sense of uniformity and impurity. **Figure 4-8** and **Figure 4-9** provide a comparison between PUR, ALG and silicon R-2180 at 80X and 1000X, respectively. From these figures, PUR is observed to be quite uniform, however, some bright spots are observed indicating impurities/contamination. Impurities such as Na, Cl and K are present on these spots. This is likely caused from dust collected during the curing process under ambient condition. As for ALG and silicon R-2180, they are not as uniform as PUR based on comparing SEM images, however, no impurities were detected in the coatings even at high magnifications.

Figure 4-8: SEM images (80X) of the microstructure of the coated materials at the centre of the coins: (a) PUR (white dots indicating impurities), (b) ALG (white shadow indicating non-uniform coating), and (c) silicon R-2180 (white shadow indicating non-uniform coating).

Figure 4-9: SEM images (1kX) of the microstructure of the coatings at the center of the coins: (a) PUR, (b) ALG, and (c) silicon R-2180.

In addition to the SEM images acquired at the center of the coins, additional SEM images were captured at the edges of the coins to better understand the coatability of selected polymer on the corners. **Figure 4-10** presents a comparison of PUR, ALG and silicon R-2180 coatings at the edges of the coins at 80X and **Figure 4-11** at 1KX. It is obvious that the coating at the edge is less uniform than that at the center. For PUR, an increased number of bright spots are found at the edge of the coin in addition to the presence of cracks. No obvious cracks were detected in the ALG or silicon R-2180 coatings.

Figure 4-10: SEM images (80X) of the microstructure of the coatings at the edge of the coins: (a) PUR, (b) ALG (bright spots indicating uneven coverage of the coating), and (c) silicon R-2180 (bright spots indicating uneven coverage of the coating).

Figure 4-11: SEM images (1KX) of the microstructure of the coatings at the edge of the coins: (a) PUR, (b) ALG, and (c) silicon R-2180 (bright spots indicating uneven coverage/impurities in the coating).

5 Chapter: Wear Tests

Circulation coins are used on a daily basis for a variety of purposes such as paying for a bus ticket, making a call from a public telephone or even purchasing a bottle of water from a vending machine. During these practices, the coins are subjected to surface abrasive by various objects and wear takes place over time. Wear of a material can be caused by various mechanisms such as adhesive wear, surface fatigue, fretting wear and erosive wear [60]. However in this research, the primary focus was on abrasive wear mode, which more closely simulates the wear condition of the coins in use. Abrasive wear is defined as the resulting wear when a hard surface slides across another surface that is relatively softer [61]. Two different test methods were employed to evaluate the abrasive wear resistance of the polymeric coatings on the coins. The first test method is a standard wear test known as a pin-on-disc tribometer. The second test method involves a tumbling machine. Both methodologies and test procedures are explained in details below.

5.1 Pin-on-disc Tribometer Test

In general, this test utilizes a flat lower specimen (coins in this case) and a ball shaped upper specimen that slides against the flat lower specimen. The upper specimen moves relative to the lower surface in a liner motion under a prescribed set of conditions [62]. Two approaches are used to evaluate the extent of wear a material is subjected to during pin-on-disc test: (1) the material loss from a surface using weight loss, and (2) the material loss evaluated using volume loss. In this research, weight loss was used to evaluate the deterioration of the materials after wear test due to the very small thickness of the coatings.

5.1.1 Test Apparatus

The multi-purpose wear test system used in this research is model No: NEO-TRIBO MPW110 provided by NEOPLUS. Wear tests were performed in dry sliding condition, according to ASTM G99 - 05(2010). This apparatus uses a rotating pin pressed under a normal force of 2.45 N against a static disk (coin). The pin used was a ball having a radius of 2.5 mm and was made of Teflon. During the test the specimen in disc form was placed horizontally with its center at a distance of 5 mm away from the vertical axis of the pin shaft. The pin (ball) was spinning at a constant speed of 100 RPM. As the result of friction/wear, a 10 mm diameter circular wear track was generated on the specimen surface, which represents the wear loss of the specimen material.

A circular sample holding fixture was used to hold the coins, as shown in during the test. It is of great importance to ensure that the coins were flat once mounted into the circular fixture to obtain meaningful results. A torpedo level was utilized to confirm the flatness of the surface after installation.

Moreover, due the limited height of the coins, they have to be mounted into a bakelite resin to increase the height. However, since the candidate materials used in this research are of polymeric in nature, they could not withstand the pressure and heat during mounting. An alternative approach was developed using cured bakelite puck with coins glued onto it (**Figure 5-1**). Care was taken to ensure that the glue does not contaminate the coated surface and the coins remain flat, relative to the holding fixture.

Figure 5-1: A mounted coin on a premade bakelite.

5.1.2 Wear Test Parameters

Table 5-1 summarizes the wear test parameters used for all three candidate coatings, PUR, ALG and silicon R-2180. The aforementioned parameters were used every time the test was carried out, however, the test durations varied. All materials were initially tested for 2 min. and based on the abrasion resistance of the sample tested; the wear test duration for the following sample was determined.

Table 5-1: Pin-on-disc hardness test parameters utilized in wear testing of the coins.

Parameters	Value
Test Radius (mm)	5.00
Rotation Speed (RPM)	100.00
Applied Load (g)	250
Applied Force (N)	2.45
Ball Bearing Material	nylon

A 5 mm diameter nylon ball with an Elastic modulus of 1.2 GPa and Poisson's ratio of 0.4 instead of commonly used steel balls, was employed in this research. This was done due to the soft nature of polymer coatings. The Teflon ball was replaced after each test to ensure a good contact between the ball and the coated surface. The Teflon ball is mounted in the head where a 5 mm is indicated, as shown in **Figure 5-2**.

Figure 5-2: The 5 mm wear head utilized in the pin-on-disc test.

5.1.3 Wear Test of Polyurethane Coating

Five brass coins were coated using PUR. The coating thickness was controlled within the range of 8-17 μm obtained by varying the coating RPM as illustrated in **Table 5-2**. As no prior information was available in the literature regarding the wear behaviour of PUR coating in pin-on-disc wear test, the test durations were initially chosen arbitrarily based on thickness and wear track marks observed after testing. The test was initiated using the thinnest coating (Coin 5) and ran for 2 min. Based on the visual appearance of Coin 5 after testing, the wear test duration for the next tested coin was determined.

Table 5-2: PUR coated coins used in pin-on-disc test.

Coin	Coating Rotational Speed (RPM)	Thickness (μm) ± 2 μm	Wear Test Duration (min)
1	3500	17	10
2	4000	15	8
3	5000	13	5
4	6000	10	3
5	7000	8	2

Figure 5-3: Five PUR coated coins subjected to pin-on-disc wear test (samples 1-5 from left to right).

SEM images were acquired to validate the worn PUR coating, i.e., substrate metal exposure. Observing the SEM images of PUR coated coins subjected to the wear test, only minimal wear tracks can be detected on the worn surfaces of the coins.

Figure 5-4: SEM images of coins 1-5 after wear test: (a) coin 1, (b) coin 2, (c) coin 3, (d) coin 4 tested for 3 min, and (e) coin 5 tested for 2 min.

5.1.4 Wear Test Results of Advanced Liquid Glass Coating

To better understand the wear/abrasion behaviour of the ALG coating, five brass coins were coated with ALG of different thicknesses, comparable to those of PUR. **Table 5-3** details the thickness of five coins and the coating RPM utilized.

Table 5-3: ALG coated coins used in pin-on-disc test.

Coin	Coating Rotational Speed (RPM)	Thickness (μm) ± 2 μm	Wear Test Duration (min)
1	100	17	10
2	200	15	8
3	300	13	5
4	500	10	3
5	800	6	2

The wear test procedures were similar to that of PUR tested coins. **Table 5-3** also presents the test durations for each ALG coated coin until first sign of wear track was observed. From **Figure 5-5**, no wear tracks were observed on the ALG tested coins hence the wear test durations were increased. Wear test durations were similar to that of PUR tested coins to allow for comparability.

Figure 5-5 shows all five coins after wear test. It can be observed that no wear tracks are visually visible on any of the coins.

Figure 5-5: Brass coins coated with ALG after pin-on-disc wear test (sample 1 to 5 from left to right).

SEM images were obtained to validate the ALG coating for its wear resistance based on pin-on-disc test. **Figures 5-6** presents the SEM images for the coins. **Figure 5-6** shows that sample 1 has non-uniform coating thickness and also lack of coating on the side of the coin, as illustrated by the bright contrast of the location near the lower left side of the coin. There are

also numbers of irregularities on the coating surface due to the variation of rotational speed used in applying the coating. However, all ALG coated coins demonstrated minimal losses as a result of pin-on-disc wear test. As the bright contrast of wear track is the result of metallic substrate exposed to the surface, the wear results here suggest that a thicker coating require longer wear test duration in order to expose the metal surface.

Figure 5-6: SEM images of coins 1, 2, 3, 4 and 5 after pin-on-disc test (arrows indicating wear tracks): (a) Coin 1 tested for 10 min, (b) coin 2 tested for 8 min, and (c) coin 3 tested for 5 min, (d) coin 4 tested for 3 min, and (e) coin 5 tested for 2 min.

5.1.5 Wear Test of Silicon R-2180 Coating

Finally, five coins coated with silicon R-2180 were also subjected to pin-on-disc wear test. The five coins consisted of a silicon coating with thicknesses similar to that of the ALG and PUR coatings previously subjected to wear. However, the RPM varied in order to achieve the desired thicknesses ranging from 6-17 μm . **Table 5-4** presents the thicknesses of all coins coated with silicon along with the coating fabrication RPM used.

Table 5-4: Silicon R-2180 coated coins used in Pin-on-disc test.

Coin	Coating Rotational Speed (RPM)	Thickness (μm) ± 2	Wear Test Duration (min)
1	2500	17	6
2	3000	15	4
3	3500	13	4
4	4000	10	3
5	5000	6	2

The wear test procedures were similar to that of PUR and ALG coated coins, an initial 2 min test was adopted on the thinnest silicon coated coin (Coin 5 in this case). The test durations were varied depending on the coating thickness and when visible wear tracks were observed. **Table 5-4** illustrates the wear test durations for each silicon coated coin. As seen in **Figure 5-7**, all coins have visible wear track marks after equal or shorter test durations.

Figure 5-7: Five silicon R-2180 coated coins subjected to pin-on-disc wear test (samples 1-5 from left to right).

SEM analysis was carried out to confirm the complete deterioration of silicon R-2180 coating from the coin's metal substrate. From SEM images shown in **Figure 5-8**, metal

exposure on all coated coins is clear and the wear tracks are much more apparent than that observed on the PUR and ALG coated coins after wear test, for much longer durations.

Figure 5-8: SEM images coins with wear tracks generated (bright circles are an indication of the wear tracks): (a) coin 1 tested for 6 min, (b) coin 2 tested for 4 min, and (c) coin 3 tested for 4 min, d) coin 4 tested for 3 min, and (e) coin 5 tested for 2 min

5.1.6 Pin-on-disc Wear Test Summary

Based on the SEM images of the worn surfaces following the pin-on-disc wear test, ALG and PUR coatings yielded minimal wear tracks after similar durations when compared to silicon R-2180 coating. The ALG coating with a thickness of 17 μm (produced at 100 RPM) was found to be less uniform than all the other ALG coatings; the non-uniformity became more obvious by observing the wear tracks. This is because of the low RPM utilized in applying the coating which prevented the coating from spreading evenly over the entire surface of the coin. Even though the ALG coating was non uniform, it was able to withstand the 10 min pin-on-disc wear test with only minimal wear. Additionally, PUR coating with thicknesses ranging from 8 - 17 μm endured wear test for similar durations to that for ALG and had the same wear track characteristics when examined under SEM. Finally, five coins were coated using silicon R-2180, all coated coins were uniform in surface appearance. A 17 μm silicon coating was tested for 6 min and the results were unacceptable. The coating was completely worn out and led to the exposure of the brass plating underneath the silicon coating.

Overall, PUR and ALG performed best in the pin-on-disc wear test. No visible wear tracks were observed on either ALG or PUR coated surfaces after testing at a fixed duration. As for silicon R-2180, the coating was completely removed after 2 min test (for the thinner coating). All silicon R-2180 coins showed wear tracks that was visible by bare eyes and SEM images were obtained to confirm metal exposure.

Furthermore, the maximum shear stress experienced on the coating surface was theoretically evaluated using Hertz contact theory equations presented in Chapter 2. The maximum shear stress was evaluated for each of the three materials based on the parameters used in pin-on-disc wear test and mechanical properties of the three coatings. The modulus of

elasticity, Poisson ratio and shear yield strength for PUR are found in literature [63] and presented in **Table 5-5**. For ALG, since the exact composition was proprietary, the mechanical properties of silicon dioxide were adopted for ALG since it is a main ingredient in ALG. Finally, the shear yield strength of R-2180 was calculated using the tensile yield strength (6.57 MPa) and Von Mises principle where yield strength = $0.557 \times$ tensile yield strength, applicable to ductile materials. **Table 5.5** also presents the maximum pressure concentrated at a point evaluated using Hertz contact theory and max shear stress as a result of contact between the coating and the nylon ball during pin-on-disc wear test.

Table 5-5: Mechanical properties, maximum shear stress and pressure evaluated using Hertz contact theory.

Material	Poisson Ratio	Modulus of Elasticity (GPa)	Shear Yield Strength (GPa)	Maximum Shear stress (GPa)	Maximum Pressure (GPa)
PUR	0.5000	0.6900	0.0086	0.0088	0.0287
ALG	0.1700	73.0000	31.0000	0.0164	0.053
Silicon-R2180	0.3700	1.0000	0.0065	0.0097	0.0314

5.2 Tumbling Test

To further investigate the resistance to abrasion in a different mode, tumbling test was carried out on the coated coins. Tumbling is a method used in determining mass loss by abrasion and impact of other solid surfaces [63]. Such test resembles the wear loss as a result of repeated interactions between coins and other objects, although the results may not exactly simulate the real life scenarios since the weights and types of coins/objects vary widely.

Tumbling, therefore, was mainly conducted in this study to determine which of the three candidate materials can withstand tumbling wear better under similar test conditions.

5.2.1 Test Apparatus

A C20 rotary tumbler designed by Lortone, Inc. was used in this research. The tumbler consisted of a 1/6 HP motor, bearings, drive belt, guard belt, pulleys, shafts and a barrel. The barrel contains the substrates to be tested (coins plus other medium if necessary). It has a capacity of 9 Kg (20 lb) and the internal hexagonal walls are made of rubber. The six flat sides help the substrates turn and allow continuous cascading impact effect.

5.2.2 Tumbling Test Analysis

Initially, PUR, ALG and silicon R-2180 were tumbled for a 24 hr period at a rotational speed of 30 RPM to investigate the durability of each coating. The 30 RPM tumbling speed was chosen based on the RCM tumbling procedures, additionally; all coins were coated based on the RCM thickness specification of $10 \pm 2 \mu\text{m}$. Each material was tumbled alone under a specified load of 100 g consisting of 5 coated coins and 10 bare coins inside the barrel. Once the tumbling test was completed, all coins were weighed four times to examine the weight loss due to the tumbling wear. Additionally, SEM images on all 5 coated coins were captured for the evaluation of coating damage. Weight loss was calculated using **Equation [5.1]**:

$$\% \text{ of weight loss} = \frac{W_{ci} - W_{ct}}{W_c} \quad [5.1]$$

where W_{ci} is the mass of coated coin before tumbling, W_{ct} is the mass of the coated coin after tumbling while W_c is the coating mass determined during coating application.

Figure 5-9: Coated coins after 25 hr tumbling test: (a) ALG, (b) PUR, and (c) silicon R-2180.

Figure 5-10: SEM images of the coated coins surfaces after 24 hr tumbling test: (a) ALG, (b) PUR, and (c) silicon R-2180.

Table 5-6: Coating loss by weigh due to tumbling.

	Wci (g) ± 0.4 mg	Wct (g) ± 0.4 mg	Wc (g) ± 0.4 mg	% Weigh Loss ± 5%
PUR	6.2976	6.2956	0.0025	80%
ALG	6.3248	6.3229	0.0032	60%
Silicon	6.3232	6.3168	0.0068	95%

Initially, the 10 bare coins were analyzed for wear loss. It was found that bare coins had very minimal losses due to tumbling ranging between 0.004-0.006 % of original weigh. As for the coated coins, based on the SEM images, ALG was considered superior compared to PUR and silicon R-2180 coatings as there were still patches of coating remaining on the ALG surface, represented by the darker areas. Also, according to the weight loss analysis, **Equation [5.1]**, ALG, PUR and silicon R-2180 lost approximately 60, 80 and 95% of the coating respectively after the 24 hr tumbling test.

5.2.3 Periodic Tumbling

To further assess the wear resistance of each coating during tumbling, another 24 hr test was carried out on the three candidate materials, but each coin was inspected after 5 hr increments by weighing before and after the test. **Figure 5-11** presents the wear losses for all three coating materials based on percentage of weight loss during tumbling (all five coins were analyzed and each coin was weighed four times). In this periodic tumbling test, bare coins analysis were omitted since only minimal losses were observed as indicated in the continuous 24 hr tumbling test. SEM images of the ALG coated coins after the tumbling test are presented in **Figure 5-12**. As shown in these images, the ALG coating, represented by the dark constituent, was gradually removed during tumbling test. Tumbling test results show that ALG has better abrasion resistance than the other coatings under the test conditions used in this study.

Figure 5-11: Wear losses due to tumbling for ALG, PUR and silicon R-2180 coated coins (The standard deviation is ± 5 %based on weighing each coin four times before and after tumbling).

Figure 5-12: SEM images of the ALG coated coins after periodic tumbling: (a) 5 hr test, (b) 10 hr test, (c) ALG 15 hr test, (d) 20 hr test, and (e) 24 hr test.

5.2.4 Tumbling Wear Test Summary

All five coated coins were weighed before and after tumbling to measure the deterioration of the coatings based on percentage of weight loss due to abrasion wear. In the first test, all

materials were subjected to a continuous 24 hr tumbling test. Bare coins yielded very minimal losses due to wear as for ALG, PUR, and silicon R-2180 they lost approximately 60, 80 and 95 % of the coating respectively after 24 hr. All three materials showed various extent of metal exposure, but ALG coating was less damaged, compared to PUR and silicon R-2180. Based on the SEM images (captured on all five coins after tumbling), ALG coated coins still maintained a good coating coverage at the center of the coins while only 20 and 5 % of PUR and silicon coating were left respectively.

Furthermore, to understand the progression of abrasive wear behaviour of each candidate material during tumbling, periodic weight measurement was carried out on the coated coins at an interval of five hours. The test was terminated after 24 hours, at which point there was no silicon coating remaining on the coin surface.

As shown in the **Figure 5-11**, silicon R-2180 coated coins lost approximately 50% of the coating in the first 5 hours. The deterioration rate of the silicon coating became less after 15 hrs of tumbling. This is because most of the remaining coating was mainly concentrated around the edge of the coins which made its removal more difficult. As for PUR and ALG, they both had similar trends of coating loss, but ALG coating performed better towards the end of the 24 hr tumbling by approximately 20%. SEM images were further obtained to confirm the results in **Figure 5-11**, illustrating the losses of coating on the coin surfaces. Note that the darker areas represent the coating and the brighter spots indicate metal exposure, hence coating loss.

(a)

(b)

(c)

Figure 5-13: SEM images after 5 hr tumbling: (a) PUR, (b) ALG, and (c) silicon R-2180.

Figure 5-14: SEM images after 10 hr tumbling: (a) PUR, (b) ALG, and (c) silicon R-2180.

Figure 5-15: SEM images after 15 hr tumbling: (a) PUR, (b) ALG, and (c) silicon R-2180.

Figure 5-16: SEM images after 20 hr tumbling: (a) PUR, (b) ALG, and (c) silicon R-2180.

Figure 5-17: SEM images after 24 hr tumbling: (a) PUR, (b) ALG, and (c) silicon R-2180.

6 Chapter: Discussion

6.1 Coating Materials and Coating Application

This research began with five candidate coating materials known to have abrasion resistance and meet the initial transparency requirement: PUR, PTFE, ALG, SLG and silicon R-2180. All five materials were applied on the coins using a spin coater while varying the RPM based on coating's viscosity. The spin coater was able to achieve a thin uniform coating for the coin coating application. However, the spin coater limited the deposition of the materials to only one surface of the coins. This was attributed to the high vacuum used in holding the coin while spinning which made it difficult to coat all three surfaces (top, bottom and edge).

Both PTFE and SLG were excluded from further evaluation due to the lack of transparency after the curing process, while PUR, ALG and silicon R-2180 were selected for further tests. SLG coating had a blue tint after curing at 250°C while PTFE exhibited milky color and did not adhere well to the surface of the coins treated with etching, sandblasting and polishing. Although PUR influenced the reflectivity of the brass coins under bright light and ALG coating was slightly darker than bare brass coins after oven curing process, these differences were hardly noticeable to the untrained eye. As for silicon R-2180, no differences were observed between a silicon coated coin and a bare coin. This is attributed to the low curing temperature of 150°C for silicon compared to that of 250°C for ALG. Transparency and reflectivity of the coatings were assessed visually at this stage. However, to better evaluate the physical appearance of the coating after deposition and curing, a standardized examination should be utilized. For instance, a colorimeter can be used to measure the absorbance of particular wavelengths of light on each coated surface hence providing an accurate measure of coating

transparency. Also, a reflectivity meter allows for assessment of the transparency of each coating providing a solid comparison between the chosen candidate materials.

6.2 Coating Thickness Analysis

Further coating deposition was carried out with PUR, ALG and silicon R-2180 to determine the optimal RPM to achieve the required thickness of 8 - 12 μm . Since each material differs in viscosity, a wide range of RPMs (100 - 8000 RPM) was tested until the desired coating thickness was achieved; fifty coins were coated and analyzed. The coating thickness was evaluated by weighing the coins four times prior to coating and four times after coating and curing process to allow for repeatability. Based on this analysis, a standard deviation was acquired and presented in **Figure 4-7**.

Since ALG coating has the least viscosity, the desired coating thickness was achieved under lower RPMs as observed in **Figure 4-7**. Additionally, ALG shows a liner trend between RPM and coating thickness. As for PUR, its viscosity is similar to that of silicon R-2180 and as a result, they have a similar dependence of coating thickness on RPM, as observed in **Figure 4-8**. Both PUR and silicon coating thicknesses stabilized when the rotational speed approaches 2000 RPM. The high viscosity of both PUR and silicon prevented the spread of these two coating materials at rotational speeds lower than 2000 RPM. However, once the rotational speed exceeded 2000 RPM, the coatings evenly spread throughout the coin's surface and it was a matter of increasing the RPMs to achieve a thinner and uniform coating.

6.3 Coating Microstructure Analysis

To investigate the quality and uniformity of each coating on the coin, SEM images were acquired on the coated coins with required thickness. Based on microstructure analysis results, PUR and silicon R-2180 coatings were quite uniform but some bright spots were detected on

the PUR surface as a result of curing at room temperature which allowed dust to collect on the surface. However, no cracks were found. As for ALG coating, it was not as uniform as the PUR coating but there was no dust or cracks observed. Overall, PUR, ALG and silicon R-2180 all had good surface coverage on the coins and no exposed metal was observed on the coated coins.

6.4 Wear Tests

Once the coating thickness and microstructure analysis were completed, PUR, ALG and silicon R-180 were put through two different types of abrasive wear tests. The first type was pin-on-disc wear test. The test specimens included a total of 15 brass plated coins, 5 coins coated with PUR, another 5 with ALG and the last 5 with silicon R-2180. All coins were coated at different coating RPMs to achieve a coating thickness near the range of 8-12 μm . The wear test durations were selected based on indication of visible wear tracks on the surface of the coins. The pin rotational speeds were selected to be in the range of 30-150 RPM to allow sufficient data collection. Silicon R-2180 yielded the highest wear rate; a 17 μm coating was completely worn after 2 minutes of wear test and SEM analysis confirms the results. As for PUR and ALG coated coins, both coatings had minimal coating losses as a result of pin-on-disc test at all five test durations. No wear tracks were visible on any of the PUR and ALG coated coins after testing, however, based on SEM images ALG coating was slightly superior compared to PUR tested under the same parameters. The SEM analysis conducted in this test was qualitative. Image processing software should be used to quantify the worn out areas and perhaps provide more qualitative outcomes. Additionally, weighing the coins before and after carrying out the pin-on-disc test did not result in meaningful data as the pin pushed the coatings to the side rather than removing it.

Theoretical calculations were carried out to understand the effects of pin-on-disc wear test. The maximum shear stress was theoretically evaluated based on Hertz pressure distribution and compared to the shear yield strength for each material. For silicon R-2180, the maximum shear stress was 9.7 MPa which exceeded the material's shear yield strength of 6.5 MPa. This result was consistent with the observation of complete removal of the silicon coating as observed in Chapter 5. As for PUR, the shear stress also exceeded the material's shear yield strength, however, the difference was much smaller compared to silicon R-2180 (**Table 5-5**). This did not result in the complete deterioration of the coating as that in silicon R-2180, however, minimal wear tracks were observed which indicates that the material started to displace. Finally, for the ALG coating material, the material's shear yield strength was much higher than the computed shear stress (**Table 5-5**). This implies the superiority of ALG over both PUR and silicon R-2180. However, the mechanical properties of the ALG material were based on silicon dioxide which may have resulted in deviation from the actual shear yield strength value. The results evaluated based on Hertz pressure distribution are in line with the wear results from the pin-on-disc wear test, although Hertz theory does not take into consideration the friction between surfaces, depth of coating material and assumes no plastic deformation.

The pin-on-disc test was only carried out using unstamped brass coins, meaning the coins did not have a relief. Since a spin coater was used to apply the coating materials onto the coins, the relief was believed to prevent the even spread of the coatings resulting in a non-uniform coated surface. Keeping in mind that the spin coating technique is not feasible for mass production and it was only used in this research for the purpose of validating the selected

candidate coatings. Additionally, the relief free brass coins were selected since pin-on-disc requires a flat surface to give accurate measures of wear.

The second wear test used in this research was tumbling test. Tumbling test was carried out to simulate the wear rate of coins in contact with one another under set values of parameters. Initially, the tumbling test was conducted on PUR, ALG and silicon R-2180 coated coins for a continuous 24 hr period. Each time any of the three materials were tested, the tumbler contained a 100 g consisting of 5 coated coins and 10 bare coins. Each coating material was left to tumble for a full day at 30 RPM based on the RCM tumbling test procedures. Based on analysis for the coins before and after tumbling, bare coins yielded the lowest wear rate of 0.004% compared to 80, 60 and 95 % for PUR, ALG and silicon R-2180 respectively. Although bare coins yielded the lowest wear rate, , the purpose of this study was to compare the performance of different coatings in which ALG coated coins yielded superior results to both PUR and silicon R-2180. Based on SEM images after tumbling, the wear of all three materials after 24 hr can be easily observed on the surface of the tumbled coins. Moreover, periodic tumbling was carried out to investigate the deterioration of the coated coins within 5 hr increments for 24 hr period. The results are presented in **Figure 5-11**. It can be observed that silicon R-2180 coated coins lost approximately 50% of the coating within the first 5 hr of tumbling, ALG maintained 40% of the coating compared to only 20% for PUR after 24 hr tumbling.

The results obtained from both pin-on-disc wear test and tumbling test deviate somewhat from real life coin deterioration due to the vast number of factors affecting the coin. For instance, the tumbling test is designed to simulate coins deterioration in one's pocket or wallet etc. However, the exact amount and types of coins interacting with one another are arbitrary.

Therefore, tests carried out in this research only provide ranking of the five candidate materials under a set value of parameters.

Although only brass plated coins were used in this research, the observations are applicable to other coins. Application of coatings can follow the same procedures as that used to coat brass coins with a spin coater, however, since brass and nickel have different surface friction, different coating RPMs have to be used . Lastly, coatings must be applied after the relief has been stamped to prevent damage to the polymer coatings.

7 Chapter: Conclusions and Future Work

According to the conditions of circulation coins in use, abrasion, corrosion and bacteria resistance are important characteristics for these coins. In this research, five candidate coating materials were initially chosen. All coating materials were applied onto the coin blanks using spin coating technique. Based on preliminary evaluations of coating adhesion and color change as a result of the curing process, three candidates, polyurethane (PUR), advanced liquid glass (ALG) and silicon R-2180, were selected for further testing. Based on pin-on-disc and tumbling tests, ALG material yielded superior abrasion resistance results when compared to both PUR and silicon R-2180. The following conclusions can be derived based on the experimental work conducted in this research:

- (1) Based on visual examination, PUR, ALG and silicon R-2180 were found to have minimal effect on the color or the reflectivity of the brass coins.
- (2) The required coating thickness in the range of 8 - 12 μm was achieved for the three coatings under different rotational speeds. The spin speeds used for PUR, ALG and silicon R-2180 to achieve the desired coating thickness were 6000, 500 and 4000 RPM, respectively.
- (3) Based on pin-on-disk test results, PUR and ALG showed better wear resistance when compared to silicon R-2180, and the wear rate of PUR and ALG, in terms of the duration prior to the first sign of wear track, were similar.
- (4) Tumbling test was conducted to simulate the abrasive wear of the three candidate coatings. The coating weight loss due to abrasion was the greatest for silicon coating, losing 50% after the first 5 hr of tumbling. ALG and PUR had similar weight loss trends; however, ALG was slightly more resistant to abrasive damage. ALG had 40% of the coating remaining after 25 hr tumbling compared to only 20% that of PUR.

The following contributions were made through this thesis work:

- (1) A Relationship between spin coating process parameter and resulting coating thickness was established.
- (2) A method was developed and used to evaluate thin, transparent coating's wear progression based on the first sign of wear track.
- (3) An abrasive wear resistance test using tumbler and preparation of test protocols, including standard number of coins in the barrel, separation of each coating, and periodical stoppage for mass loss evaluation, was developed.
- (4) Recommendation was made to RCM with regard to the use ALG coating for circulation coins.

The following future tasks are suggested:

- (1) Development of an industrial coating process for applying coating to all sides of the coins. Methods such as fluidized bed and electro-deposition should be investigated.
- (2) Conduct field tests of coated coins where coins are put into controlled circulation.
- (3) Finally, the EMS of the coins should be investigated after coating application to prevent vending machines fraud.

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