SYNTHESIS, CHARACTERIZATION AND FOULING EVALUATION ON SUPERHYDROPHOBIC COATING MODIFIED USING CARBON SOOT.

MUHAMAD SYAFIK BIN MOHD HANAPI

UNIVERSITI SAINS MALAYSIA

2021

SYNTHESIS, CHARACTERIZATION AND FOULING EVALUATION ON SUPERHYDROPHOBIC COATING MODIFIED USING CARBON SOOT.

by

MUHAMAD SYAFIK BIN MOHD HANAPI

Project proposal submitted in partial fulfilment of the requirements for the degree of Bachelor of Chemical Engineering

2021

ACKNOWLEDGEMENT

First and foremost, I'd like to offer my heartfelt gratitude and special appreciation to my project supervisor, Assoc. Prof. Ir. Dr. Leo Choe Peng, who possesses the content of a genius: she always supported and guided me to be more professional. Without her assistance and active participation in every level of the process, this paper would never have been completed.

I would like to express my heartfelt appreciation to all postgraduate students for their gracious collaboration. They are not only eager to share their thoughts, valuable information, and abilities, but also their time to lend me a helping hand.

Furthermore, the physical and technical contributions of all academic and administrative employees at Universiti Sains Malaysia's School of Chemical Engineering, laboratory technicians, and especially Mrs. Yusnadia Mohd. Yusof, are greatly acknowledged. This project would not have been possible without their financing and assistance.

Apart from that, I'd like to express my gratitude for my parents' love and support, Mohd Hanapi Bin Mamat and Rositah Binti Kasmudi, as well as my siblings. Additionally, I would want to express my heartfelt appreciation to my classmates and course instructors, particularly Ismat Muhsin Bin Baharuddin. They kept me pushing forward, and this task would not have been feasible without their assistance.

Once again, it is whole-heartedly appreciated to you all for the tremendous positive feedbacks given along with the continous support received.

Muhamad Syafik Bin Mohd Hanapi

July 2021

TABLE OF CONTENTS

LIST OF TABLES

Page

LIST OF FIGURES

Page

LIST OF SYMBOLS

Symbol	Description
θ_w	Contact angles of rough surfaces
θ	Contact angles of smooth surfaces
γ_{sg}	Surface tensions of solid-gas
γ_{sl}	Surface tensions of solid-liquid
γ_{lg}	Surface tensions of liquid-gas
r	roughness ratio
f_1	Area fraction of solid on the surface
F_2	Area fraction of gas on the surface

LIST OF ABBREVIATIONS

CS	Carbon soot
PVDF	Polyvinylidene Fluoride
W/D	Withdrawal/Drawing
FTIR	Fourier Transform Infrared Spectroscope
SEM	Scanning Electron Microscope
CA	Contact Angle
CAGR	Compound Annual Growth Rate
PFC	Perfluorinated compounds
PDMS	Polydimethylsiloxane
PVA	Polyvynil Alcohol
PMMA	Poly(methyl methacrylate)
SEBS	silica nanoparticles and polystyrene-b-poly(ethylene-co-butylene)-b-polystyrene
LFS	Liquid Fire Spraying
WCA	Water Contact Angle

LIST OF APPENDICES

SINTESIS, PENCIRIAN DAN PENILAIAN PENUH PADA SALUTAN SUPERHIDROPHOBIK DIUBAH MENGGUNAKAN JELAGA KARBON

ABSTRAK

Lapisan superhidrofobik adalah satu idea yang meniru alam sekitar, yang mempunyai kelebihan terbesar dalam pencegahan kakisan pada logam. Ini kerana permukaan sentuhan dan cecair dapat diminimumkan sehingga dapat memberikan ketahanan yang besar terhadap kelembapan di sekitarnya. Tesis ini adalah untuk mengetahui bahawa superhidrofobik dapat dicapai di permukaan jelaga karbon dari api lilin. Sampel kemudian dicelupkan ke dalam campuran PVDF/Aseton untuk meningkatkan hubungan superhidrofobik.Jelaga karbon (CS) yang melapisi slaid kaca yang diperoleh sebagai keadaan hidrofobik. Ia dikumpulkan dari lilin penggunaan umum untuk membuktikan tingkah laku hidrofobik dari jelaga karbon yang dikumpulkan. Mikropipet digunakan untuk menjatuhkan beberapa tetesan di permukaan untuk memeriksa sudut kontak yang terjadi pada permukaan jelaga karbon. Polimer yang digunakan ialah 0.8g Polyvinylidene Fluoride (PVDF) dicampurkan dengan betul dan berterusan sehingga mencapai pencairan sempurna dalam 80ml berasaskan Aseton. Proses mencelupkan adalah dalam Pengeluaran / Pengambilan berterusan (W / D) pada 40 mm / s dan mengambil masa pada 4 minit. Proses pengeringan dilakukan sepanjang hari pada suhu bilik. Sudut kontak pada permukaan kedua-dua sampel dapat diperoleh melalui lensa Mikroskopik. Sebagai kesimpulan, jelaga karbon dari lilin dapat mencapai hidrofobik dan dapat mencapai superhidrofobik dengan campuran PVDF / Aseton dalam keadaan tertentu.

ABSTRACT

Superhydrophobic coating is an idea that imitate the surrounding nature, whichn has the biggest advantage in corrosion prevention on metals. This is because the surface of contact and liquid can be minimized so it can offer great resistance to humid surrounding. This thesis are to know the superhydrophobic can be achieve surface on the carbon soot from candle flames. The samples later are being dipped into PVDF/Acetone mixture to improve superhydrophobic contact. Carbon Soot(CS) that coating the glass slides which are obtained as hydrophobic state. It is collected from general uses candles to prove the hydrophobic behaviour from the carbon soot collected. Micropipette are being used to drop a few of droplets on the surface to check the contact angle occurred on the surface of carbon soot. The polymer used are 0.8g of Polyvinylidene Fluoride (PVDF) are mixture properly and continuously until it achieved perfect dilute in 80ml of Acetone based. The dip-coating process are in the constant Withdrawal/Drawing (W/D) at 40 mm/s and taking at 4 mins. The drying process are done in whole day time at room temperature. The contact angle on the both surfaces of samples can be obtained through Microscopic lens. As conclusion, carbon soot from candles can achieve hydrophobic and can achieve superhydrophobic with mixture of PVDF/Acetone in certain conditions.

CHAPTER 1
INTRODUCTION

Chapter 1 discusses the overview of this research and the importance of coating in various equipment and its performances. Generally, this chapter summarizes the significance of coating using candle soot with PVDF, the problem statement and the research objectives of this research.

1.1 Background

Coating is necessary to extend the lifespan of metals and maintain their properties for different functionalities. For instance, aluminium alloys which are widely used in the power system and electrical transmission require coating, especially in the coastal areas. Aluminium alloys are widely used due to their low cost, low density, high strength, excellent electrical and thermal conductivity (Naderizadeh et al., 2020). They corrosion resistance reduce in coastal area which have high humidity, high salt content and high average annual temperature (Naderizadeh et al., 2020). The anti-corrosive technologies like corrosion inhibitor, anodizing and coating. Hydrophobic coatings are preferred as they can reduce corrosion by reducing the contact between metals and water.

In recent years, lotus leaf has been the main inspiration for scientist to produce superhydrophobic surface. The superhydrophobic surface exhibits a water contact angle (CA) above 150 ° and sliding angle less than 10 ° Besides minimum contact with water droplet for achieving anti-corrosion, the superhydrophobic surface is also antifouling, self-cleaning, and antibacterial. Two main components for successful superhydrophobic surfaces which are appropriate air trapping technique and low surface with free energies. Superhydrophobic coating have various advantages of simple process and environmental protection in the current progress of technologies.

This type of technologies has been widely used in various industries such as anti-corrosion, oil/water separation, drag reduction, self-cleaning, anti-icing, and much more. Even that, there are two types of coating applicable which are using the organic and in organics coating materials.

During the projected period, the market for superhydrophobic coatings is expected to grow at a CAGR of more than 25%. The growing demand from the automobile industry is one of the primary reasons driving the market researched. Demand from the textile industry is projected to increase demand for superhydrophobic coatings as well. The textile and footwear industries dominated the market in 2014 and are predicted to continue to rise in the forecast period, owing to rising demand for sophisticated textiles and high-end footwear. Recent improvements in underwater electronics, as well as flexible and wearable electronics, are expected to create future industry prospects. Additionally, there are a few uses for superhydrophobic coatings in food packaging, which are anticipated to present future market potential. Asia-Pacific is predicted to develop the quickest of all regional categories, owing to strong demand from a variety of end-user industries in countries such as China and India.

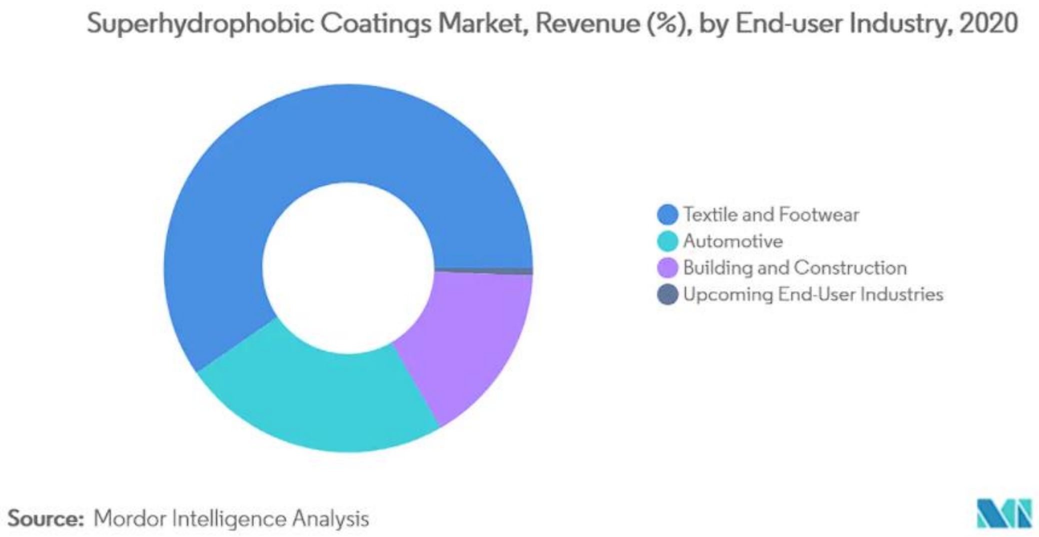

Figure 1-1 Superhydrophobic Coatings Market Volume, 2020 (*Superhydrophobic Coatings Market | Growth, Trends, COVID-19, and Forecast (2021 - 2026)*, n.d.).

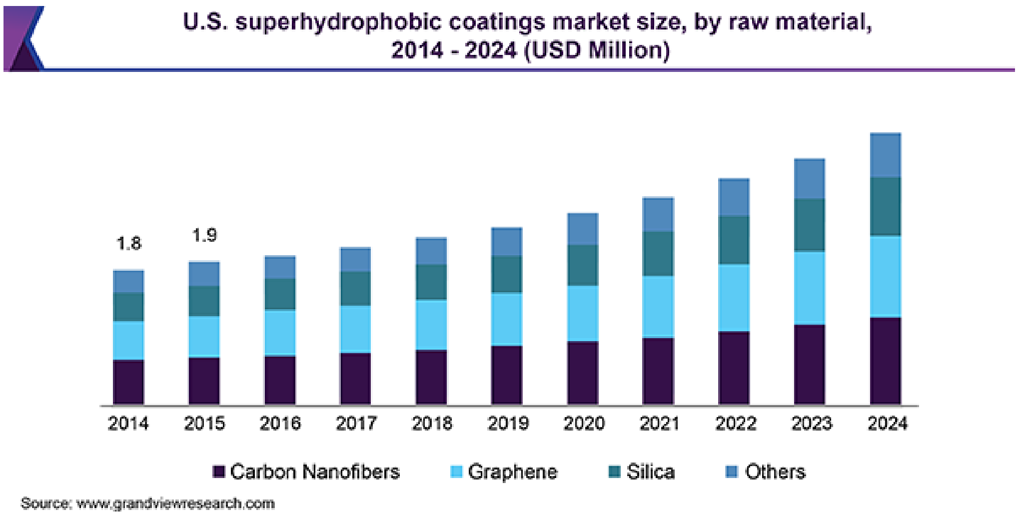

Figure 1-2 Market Size of the raw material for the superhydrophobic coating in US 2014-2024 (*Superhydrophobic Coatings Market Size & Share | Industry Report, 2024*, 2021)

As per before, the market volume above shows that the Anti-microbial superhydrophobic surfaces are increasingly gaining popularity in the healthcare sector, on account of their water-resistance, non-permeability, safety, and biocompatibility. Although hydrophobic coating is vastly popular, superhydrophobic coatings are yet to be commercialized to such a large extent, since their production processes are comparatively sophisticated with high investment costs.

1.2 Problem Statement

The creation of the coating with superhydrophobic surface is essential to avoid water to affect apparatus or cabling system nearby coastal areas. Current technologies of superhydrophobic coatings possess some flaws. The usage of carbon soot (CS) as a superhydrophobic coating method is questionable since it has weak interaction nonchemical bonding for long term application (Esmeryan et al., 2016). Blending and spraying of nanoparticles on polymer coatings to create superhydrophobic coating may not be cost effective since this method requires the use of nanoparticles (Esmeryan et al., 2016). Moreover, the preparation of superhydrophobic coating using fluorine-based silane and other siloxane chemicals with low surface energy is considered less sustainable (Esmeryan et al., 2016). Perfluorinated compounds (PFC) with good water and oil repellency to surfaces have been banned due to the existence of eight or more fluorinated carbon in its polymers backbone which can be disintegrated into toxic products (Naderizadeh et al., 2020). In this study, CS will be collected on the Polyvinylidene Fluoride (PVDF) adhesive before curing. PVDF/ACETONE composite will be subsequently cured to form antifouling and durable coating.

1.3 Research Objective

I. To identify the carbon soot obtained from candle can achieve superhydrophobic surface.

II. To compare the effect of PVDF/Acetone mixture on carbon soot with the before the dip-coating process.

CHAPTER 2
LITERATURE REVIEW

Chapter 2 discusses the literature review of this thesis. The method in the preparation of the dip-coating is discussed in detailed by and further development in modification which making it more sustainable. The following section will be discussed the comparison of methods for coating process.

2.1 Wenzel Model and Cassie-Baxter Model

The Wenzel model is an improved version of the Young's model, which was previously used to explain the contact angle for physically and chemically homogeneous surfaces:

$$cos\theta = \frac{(\gamma_{sg} - \gamma_{sl})}{\gamma_{lg}} \tag{1}$$

Where γ_{sg}, γ_{sl}, and γ_{lg} are the surface tensions of the solid-gas, solid-liquid, and liquid-gas interfaces, respectively (Azhaarudeen et al., 2012). Thus, we know in Wenzel model

$$cos\theta_w = rcos\theta \tag{2}$$

Where r is the roughness ratio of the actual to projected solid-liquid contact area, and θ_w and θ are the contact angles for the rough and smooth surfaces, respectively. (Wenzel, 1936). As illustrated below, a droplet placed on a rough surface will penetrate the rough grooves of the surface, demonstrating strong adhesion between liquid and solid surface. (Wenzel, 1949).

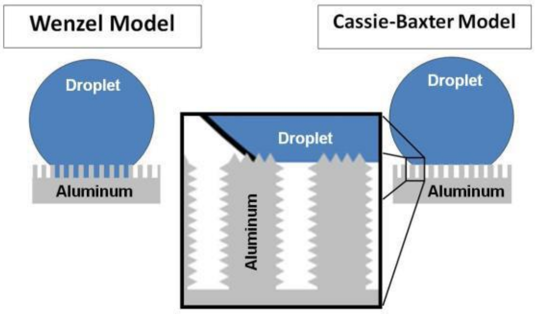

Figure 2-1 Comparison of Wenzel Model and Cassie-Baxter Model (Wenzel, 1949).

The Wenzel model is decommissioned in favour of the Cassie-Baxter model (Figure 1.1). Droplets deposited on the surface do not penetrate the rough grooves in the Cassie-Baxter model. Rather than that, the droplet will rest on top of the grooves, trapping air beneath. When the liquid-gas contact area exceeds the liquid-solid contact area, the droplet makes contact with a smaller surface area and rolls away when slightly tilted. The Cassie-Baxter model is defined by the equation below:

$$cos\theta_c = f_1 cos\theta - f_2 \quad (3)$$

where θ_c and θ represent the contact angles on the rough and smooth surfaces, respectively, and $f_1$and f_2 are the area fractions of the solid and air on the surface, respectively (Zhao et al., 2013).

2.2 Spray-coating modification methods

Superhydrophobic materials have a variety of applications in many fields like national defence, industry and agriculture, and daily life. The coating fabrication methods include sol-gel method, vapor deposition, etching and printing, template method, electrochemical method, self-assembly technique, and phase separation. The spray-coating methods are preferable as it is a facile and robust technique that can prolong the superhydrophobic surfaces. Water-soluble PVA was used to immobilize the silica nanoparticles on glass substrate (Gong et al., 2020). The PVA worked as the adhesive while the nanoparticles created rough surfaces. The PVA/silica coating was further modified by PDMS to form durable superhydrophobic coating. Raspberry structure, pore structure, nano fibre structure and trapezoidal structure were reported to be effective in the formation of superhydrophobic coating (Gong et al., 2020). The specific method that been organized is to use the fluorine-modified silica which are mixed with inorganic binder aluminium phosphate to form superhydrophobic coating through spraying method (Gong et al., 2020). In the research, the improvement of mechanical strength of superhydrophobic coating through coating are a bit of challenges in current situation. As below shown the schematic of spray-coat method Polyvinyl alcohol type 1788 (PVA) and mixture of hydrophilic nanoparticles with water (Gong et al., 2020). The surface then is sprayed for 3 or multiple time to ensure the coating are uniform.

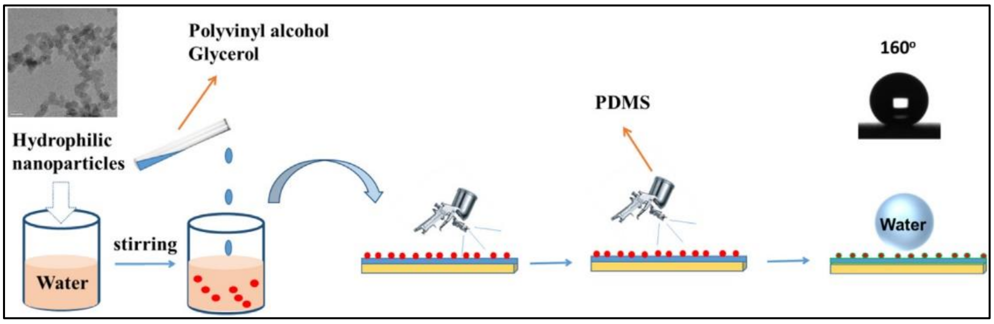

Figure 2-2 Fabrication of superhydrophobic PVA-SiO2-PDMS composite coatings.(Gong et al., 2020)

2.3 Candle soot based superhydrophobic coating

Superhydrophobic surfaces was also tested under the low temperature to study the coating endurance that might be affected by ice formation (Pan et al., 2016). A mixture of PMMA and silica nanoparticles was created and then sprayed over a substrate to create a superhydrophobic coating with a contact angle of 158° and a sliding angle of 2°. The superhydrophobic PMMA/silica coating showed anti-icing properties, which are most desired in the winter.

Superhydrophobic coatings have gained a remarkably increased interest. SiO_2 nanoparticles modified with different chemicals including the quaternary ammonium salt were extensively used to create roughness and reduce surface energy. Superhydrophobic coating was constructed using fluorine-free functionalized silica nanoparticles and functionalized silica nanoparticles and polystyrene-*b*-poly(ethylene-*co*-butylene)-*b*-polystyrene (SEBS) (Wang et al., 2020). SEBS which can be applied by scalable spraying or immersing techniques for glass, metal, and polymeric matrix.The coating showed great resistance towards mechanical, chemical, and physical durability tests. It was used to separate oil/water separation and it possesses self-cleaning properties as well. Paperboard is known as a biodegradability, renewability, mechanical flexibility, and affordability as the substrate of superhydrophobic coating. Liquid Fire Spraying (LFS) was used to deposit titanium dioxide (TiO_2) particles on paperboard with superhydrophobic surface (Teisala et al., 2010).

CS is a potentially advantageous nanomaterial for fabricating superhydrophobic surfaces. The superhydrophobic surface fabricated from the CS attained a water contact angle higher than 150 ° and a sliding angle less than 10 ° (Sutar et al., 2021). Carbon nanoparticles are present in CS as a result of the incomplete burning of hydrocarbons in a controlled atmosphere. (Sutar et al., 2021). Liang et al. (2020) established that inner flame soot particles with a diameter of 20–55 nm are extremely hydrophobic and oleophilic as a result of incomplete combustion of wax vapour. The soot was deposited on the surface due to the weak Van der Waals force of attraction to its fragile network (Sutar et al., 2021). Due to the fact that the polymers provided a stable and mechanically resistant coating on the substrates. It also strengthened the bonding between substrate and coating layer. The thermoplastic like polystyrene, polyethylene propylene and PVDF were also used to bond CS for the formation of superhydrophobic coating (Sutar et al., 2021). Fig. 2.2 the schematic process of fragile network of CS surface area on polymers by Applied Polymer (Sutar et al., 2021).

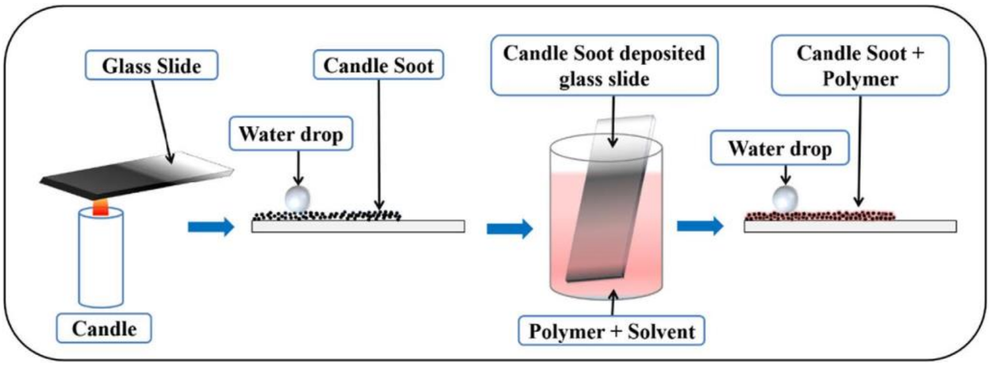

Figure 2-3 Preparation of superhydrophobic coating surface using candle soot (Sutar et al., 2021)

CHAPTER 3
METHODOLOGY

This chapter involves the methodology used in this study for the entire research work. **Figure 3.1** shows the flowchart for the overall research activities. The experiment is divided into four stages which are Carbon Soot Collection preparation, characterization test, coating with PVDF, and analysis of the process. This chapter outline the procedures to produce carbon soot glass slides coating. And further enhance the hydrophobic state of the carbon soot coating using PVDF/Acetone mixture. Subsequently, this research introduces the characterization study of this research work based on the performance glass slides study.

3.1 Materials

The materials used for the experiment are ethanol lamp and the candles which used as the sources for the collection of the carbon soot. For the chemical used, Acetone, Polyvinylidene Fluoride (PVDF), and ethanol wipes for cleaning the surface of the glass slides. For the candles, it can be easily obtained which is BT Lites candle 6'pcs from nearby shops which consist of wax.

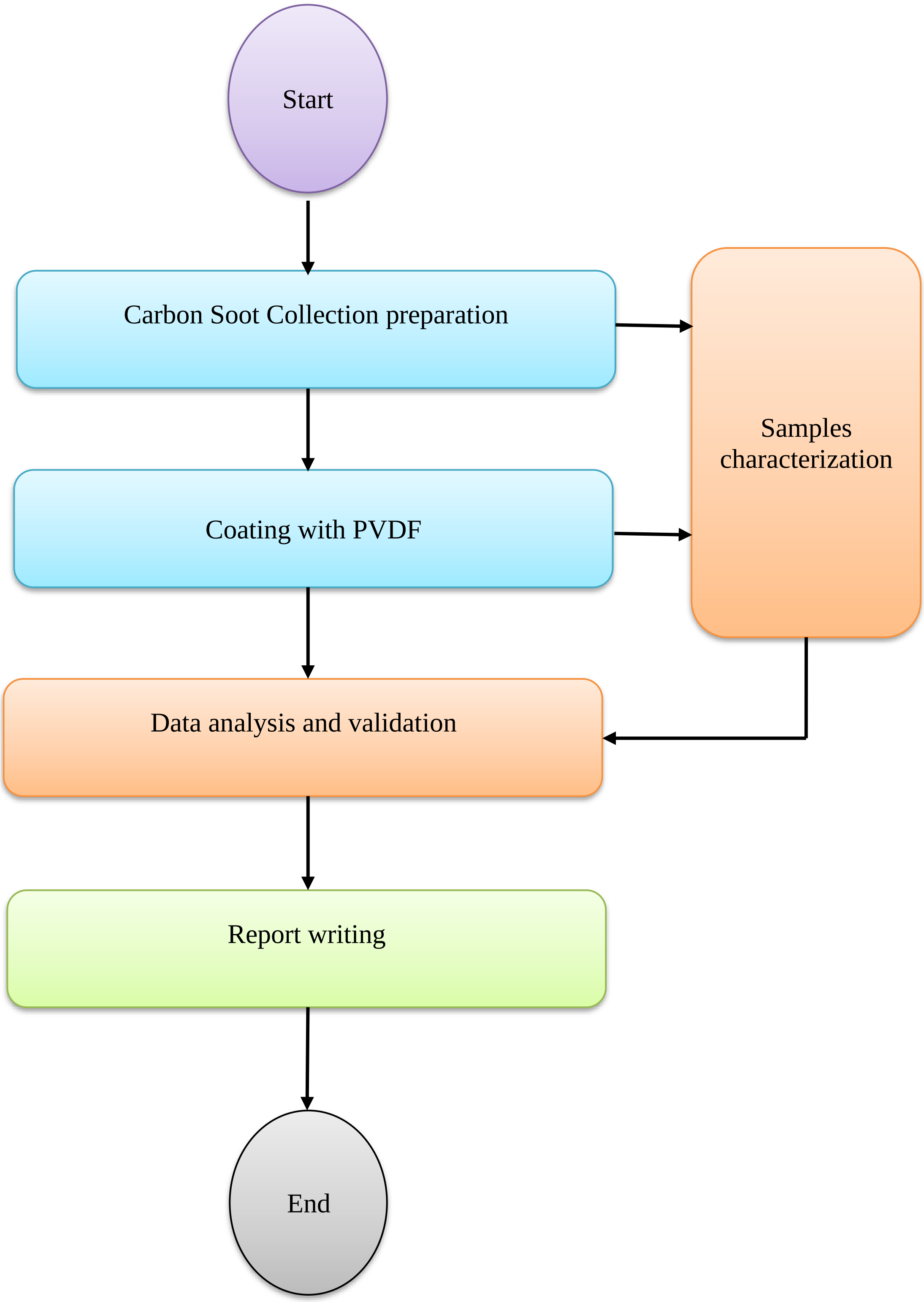

Figure 3-1 Flow diagram of research project on carbon soot collection with PVDF coating.

3.2 Preparation of Carbon Soot Collection

Ethanol lamp was chosed for the trial of the carbon soot collection. The first steps is collection of the carbon soot from the ethanol lamp into the ceramics. This have to be done to make sure the correct distance from the flame and the time taken for the collection. So that the parameters are properly taken. This equipment choose to verify the carbon soot on the glass slide. Next, set up a retord stand to hold up the glass slide. The glass slide are firstly clean with ethanol and the dried up at room temperature before the collection to occurs. Then, setup candles in the beaker to avoid dripping of candles wax on the experiment workplace. Next, place the glass slide in the hand of retord stand and adjust properly to avoid movement and dropping during the experiment. The setup of experiment was shown in **Figure 3-2**. The distance from the flame are can be shown in **Figure 3-3**. Thus here are the constant distance of the flame from the glass slides are decided from the trial of ceramics before. As a result, we can acquire the parameters listed in the table below.

Table 3-1 Parameters for carbon soot collections

Samples	*Time* (min)		
Carbon soot on glass slides	2	4	6