MICROENCAPSULATION OF WASTE SUNFLOWER OIL AS NATURAL SELF-HEALING CORROSION AGENT FOR COATING APPLICATIONS

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ZULKHIBRI BIN BAHAROM

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Special for my beloved mother, late father, brothers and sister. You are my everything.

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ABSTRACT

Corrosion is a material's destructive attack in reaction to its environment. The extreme consequences of corrosion have become a worldwide issue. Corrosion triggers plant shutdowns, waste of productive energy, loss of product pollution, decrease of productivity and expensive maintenance due to this type of degradation. The effect of the physicochemical interaction due to corrosion can also endanger human safety and generates global issues and economic loss. Microencapsulation is defined as wall formation process where urea formaldehyde (UF) is attached with emulsified waste sunflower oil (WSO) to form a microcapsule. The microcapsules containing WSO were used as smart material to be embedded in epoxy coating known as self-healing coating which can be applied to mild steel. The self-healing coating is used to prevent corrosion that induced by the existence of micro-crack on the coating surface. The WSO was aimed to be encapsulated via in-situ polymerization method with main parameter of stirring speed, reaction time and surfactant concentration. The microencapsulated WSO was characterized by using Field Emission Scanning Electron Microscopy (FESEM), Energy Dispersive X-ray (EDX) and Fourier Transform Infra-Red Spectroscopy (FTIR). The rare coating technique called sandwich method is used in this study. MS3E5R3 (microcapsules with 300 rpm stirring speed, 5 wt%. of Ethylene Maleic Anhydride, EMA and 3 h reaction time) showed an optimum result of microencapsulation of WSO with smooth and spherical structure of 46 % of yield of microcapsules (Y), 48 % of microencapsulation efficiency (ME) and 66 % of core content (CC). The scratch on the coating matrix autonomously healed after five days and the corrosion rate was also reduced. CS3E5R3 (coating with 300 rpm stirring speed, 5 wt%. of Ethylene Maleic Anhydride, EMA and 3 h reaction time) showed the optimum result of self-healing performance and mechanical strength with 1.47 mm coating thickness, fully healed of healing category, 654.25 N/mm^2 maximum stress on bending adhesion test, 6.14 HV of hardness and 83 μm of detachment length

on scratch adhesion test. The coating matrix that containing WSO also showed the anti-corrosion ability. CS3E5R3 showed the optimum result of anti-corrosion ability with the lowest mass loss (0.02062 g), corrosion rate (0.0574 mm/yr). The corrosion rate of CS3E5R3 compared to reference sample showed 57 % reduction of rate. The unique morphology of corroded mild steel named lepidocrocite is the novel finding that has not been presented by any researcher involve in the investigation of self-healing coating. This study revealed that the WSO as a new self-healing corrosion agent is viable self-healing corrosion agent to be microencapsulated. It can be concluded that microcapsules synthesized from a natural agent incorporated with recycling of waste oil could be very auspicious smart coating materials and beneficial for the advancement of corrosion control technology.

ABSTRAK

Pengaratan adalah serangan pemusnah pada bahan sebagai tindak balas dari persekitarannya. Pengaratan yang melampau telah menjadi isu di seluruh dunia. Pengaratan mencetuskan penutupan loji, pembaziran tenaga produktif, kehilangan pencemaran produk, penurunan produktiviti dan penyelenggaraan yang mahal berpunca dari kemerosotan bahan. Kesan interaksi fisioekimia akibat pengaratan juga boleh membahayakan keselamatan manusia dan menjana isu-isu global dan kemerosotan ekonomi. Mikroenkapsulasi didefinisikan sebagai proses pembentukan dinding oleh urea formaldehid (UF) meliputi minyak bunga matahari terpakai yang telah dielmusifikasi untuk membentuk kapsul mikro. Kapsul mikro yang mengandungi minyak bunga matahari diguna sebagai bahan pintar untuk dicampur bersama bahan epoksi, dinamakan pelindung pemulih-sendiri. Pelindung pemulih-sendiri itu kemudian disapu ke atas besi lembut. Pelindung pemulih-sendiri digunakan sebagai penghalang pengaratan yang berpunca dari retakan-mikro yang wujud pada permukaan pelindung besi. Minyak bunga matahari terpakai disasarkan untuk dienkapsulasi melalui kaedah polimerisasi terus dengan mempelbagaikan parameter kelajuan putaran, tempoh reaksi dan kepekatan ajen pembentuk. Minyak bunga matahari yang terkapsul dicirikan melalui alat Mikroskop Pengimbasan Pelepasan Medan, X-Ray Penguraian Tenaga dan Transformasi Fourier Spektroskopi Infra-Merah. Teknik sapuan pelindung yang digunakan di dalam kajian ini adalah teknik yang jarang diguna dan dinamakan 'Sandwich method'. MS3E5R3 (Kapsul mikro dengan 300 rpm kelajuan putaran, 5 wt%. Ethylene Maleic Anhydride, EMA dan 3 jam tempoh reaksi) menunjukkan keputusan optimum di dalam mikroenkapsulasi minyak bunga matahari terpakai dengan menghasilkan permukaan dinding kapsul mikro yang licin dan berbentuk sfera dengan 46 % penghasilan kapsul mikro (Y), 48 % keberkesanan mikroenkapsulasi (ME) dan 66 % kandungan isi (CC). Calar pada pelindung matrik dilihat telah pulih selepas lima hari dan mengurangkan kadar pengaratan. CS3E5R3 (Pelindung dengan 300 rpm kelajuan putaran, 5 wt%. Ethylene Maleic Anhydride, EMA dan 3 jam tempoh reaksi) menunjukkan keputusan optimum di dalam sifat pemulih-sendiri dan kekuatan mekanikal dengan mempunyai 1.47 mm ketebalan sapuan, kategori pemulihan lengkap, 654.25 N/mm^2 tekanan maksimum pada ujian lengkungan, 6.14 HV kekerasan dan 83 µm panjang pengelupasan di dalam ujian pencalaran. Pelindung matrik yang mengandungi minyak bunga matahari terpakai juga menunjukkan kemampuan anti-pengaratan. CS3E5R3 menunjukkan keputusan optimum di dalam anti-pengaratan dengan menunjukkan nilai kehilangan jisim terendah (0.02062 g), kadar pengaratan (0.0574 mm/tahun). Kadar pengaratan CS3E5R3 berbanding sampel rujukan berkurangan dengan kadar sebanyak 57 %. Keunikan morfologi lepidokrosit adalah penemuan yang belum pernah dibentangkan oleh penyelidik sebelom ini. Penemuan ini menjelaskan minyak bunga matahari terpakai adalah ajen pemulih-sendiri yang baru dan berjaya untuk dimikroenkapsulasi. Kesimpulannya, kapsul mikro yang dihasilkan daripada ajen semulajadi dan dari sumber kitar semula mampu mewujudkan bahan pelindung pintar dan memberi kelebihan kepada teknologi kawalan pengaratan yang terkehadapan.

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LIST OF SYMBOLS AND ABBREVIATIONS

ASTM	-	American Society for Testing and Materials
CC	-	Core content
DCPD	-	Dicyclopentadiene
EDX	-	Energy Dispersive X-ray
EMA	-	Ethylene maleic anhydride
FESEM	-	Field Emission Scanning Electron Microscopy
FTIR	-	Fourier Transform Infra-Red Spectroscopy
h	-	hour
LO	-	Linseed oil
ME	-	Microencapsulation efficiency
MUF	-	Melamine urea formaldehyde
NaCl	-	Sodium Chloride
OM	-	Optical microscope
PF	-	Phenol formaldehyde
PO	-	Palm oil
PVA	-	Polyvinyl alcohol
rpm	-	revolution per minute
SDBS	-	Sodium dodecyl benzene sulfonate
SEM	-	Scanning Electron Microscopy
SO	-	Sunflower oil
TGA	-	Thermogravimetric Analysis
TO	-	Tung oil
UF	-	Urea formaldehyde
WSO	-	Waste sunflower oil
XRD	-	X-ray Diffractometer
Y	-	Yield

CHAPTER 1

INTRODUCTION

This study investigates the microencapsulation of natural self-healing corrosion agent for coating applications. The study in this research is divided into three stages, namely microencapsulation of waste sunflower oil as a natural self-healing corrosion agent, self-healing coating embedded with microcapsules containing waste sunflower oil, and evaluation of the anti-corrosion ability of self-healing coating. The microencapsulated waste sunflower oil as a natural self-healing corrosion agent has generated characteristics pertaining to its diameter, shell structure, yield, microencapsulation efficiency, core content, functional properties and thermal stability. The sandwich method refers to microcapsules comprises of waste sunflower oil that are embedded with epoxy matrix through coating method. The coating matrix was analyzed for its self-healing performance and the mechanical strength involving bending adhesion, vickers hardness, and scratch adhesion were tested. The last stage of this research demonstrates the evaluation of the anti-corrosion ability of self-healing coating specified on the corrosion rate and the characteristics of the corroded mild steel. For the development of future corrosion prevention technologies, the results of this research are important as they also acknowledge the potential of recycled sources that are generated from waste production.

1.1 Background of study

Around the globe, the prevalence of corrosion is concerning and the expense of avoiding corrosion has caused significant problems especially in industries. According to Hou *et al.* (2017), in 2015, the cost of corrosion in China is estimated at around RM 1.347 trillion which make up about 3.34 % of the gross domestic product. Industries has made cost reduction for corrosions management their main priority. Acid rain generated in one country pollutes the environment and causes corrosion damage far beyond that country's borders and even beyond the borders of its neighbours. Toxic materials released from corroded equipment in one area can pollute the air and water far beyond one country's borders and toxic materials released into the world's waterways poisons sea life, killing many species and making others toxic to humans (Hays *et al.,* 2009). The application of organic coating is the most economical and common approach to combat corrosion. However, being the outermost layer on the component, these coatings are prone to micro level damages in service, either due to mechanical or chemical actions, decreasing their service life. Using coatings that are tailored to provide active capability to react against certain damage and heal the damage autonomously may solve these problems. Such coatings are termed as self-healing coatings (Yu *et al.,* 2015).

A prudent and common technique is the requirement for the use of natural coating to combat corrosion. However as an exterior layer, these natural coatings need to contend against the presence of micro level degradation that decreases the expected service life of the component. Yin *et al.* (2008) investigated the coating failure that starts from micro-cracks frame inside the materials. Further issues are created as the materials are exposed to the outside environment due to micro-cracks that are difficult to detect. The micro-cracks can then spread until failure happens and bring major damages. Conventional repairs, such as welding, will be limited to uncontrollable damage and further repairing can possibly worsen the damage. In addition, global companies require fast solutions, swift inspection is important as these techniques are not autonomous or immediate. (Ataei *et al.,* 2019).

These coatings, which are embedded in smart microcapsules, contain self-healing agents is expressed as self-healing coatings. Self-healing coatings can cause a normal recovery process, such as the damage repair for broken tissue. Thus, it is a promising material that can improve the durability of the coated component from chemical or mechanical damages. The basic principle of self-healing coating is to heal the damaged area by utilizing a buffer stock of either the raw materials or quick healing materials. (Blaiszik *et al.,* 2009). Self-healing or self-repairing of materials can recapture the unique properties that were lost by outer damages and can assess the capacity of a material for autonomous repair (Zheludkevich *et al.*, 2007). Self-healing materials can be either autonomous or non-autonomous which is in contrast with man-made materials that require exterior trigger (Bollinger *et al.,* 2001).

Shirzad *et al.* (2017) claimed that self-healing has a system that could detect the damage and thus trigger the release of the healing agent. The effectiveness of the self-healing process itself depends largely on how to set up the self-healing materials to be released only when cracking occurs. The self-healing strategy itself is divided into three main groups, namely encapsulation, expansive agent and mineral admixtures.

Among the different methods, self-healing may be attaining especially by means of microcapsules. For microcapsules-based self-healing, the healing agent is stacked under a grid material by utilizing microcapsules. When micro-cracks occur, the microcapsules will break and release the healing agent to polymerize or cure after reacting with the existing polymer such epoxy as coating matrix (Bollinger *et al.,* 2001).

The microencapsulation of sensitive materials and its incorporation in a suitable matrix is a versatile system for self-healing coatings. Besides that, considerable literature is available on the synthesis methods and parameter optimization for encapsulation. There are different techniques available for the encapsulation of reactive materials which can be classified on the basis of a wall formation mechanism as reported by Jagtap *et al.* (2016).

The evolution of natural resources as a potential self-healing agent has become of demand lately. Most natural resources that have been experimented on by previous researchers have come from vegetable oil involving both drying and non-drying types. A drying type of vegetable oil include tung oil (Thanawala *et al.,* 2015) and linseed oil (Mahmoudian *et al.,* 2018), which were chosen by the researcher due to its accelerate drying ability. Palm oil (Shahabudin *et al.,* 2016a) and coconut oil (Khorasani *et al.,* 2017; Safaei *et al.,* 2018; Ataei *et al.,* 2019) are non-drying types of vegetable oil that are also very attractive to be explored. There is a potential of vegetable oil as a self-healing agent at the core of microcapsules to conspire with potential materials such urea formaldehyde (UF), melamine urea formaldehyde (MUF) and phenol formaldehyde (PF) that performs as shell (Samadzadeh *et al.,* 2011; Rajendra *et al.,* 2013). The advantage of synthesizing the drying type of vegetable oil as a self-healing agent compared to the non-drying type is the fast drying ability (Samadzadeh *et al.,* 2011; Dlugogorski *et al.,* 2012; Szabó *et al.,* 2015; Taylor et *al.,* 2015) which suits coating requirement. The evolution of the natural self-healing agent towards current advancements includes manipulating cooking oil such palm oil (Shahabudin *et al.,* 2016) and coconut oil (Khorasani *et al.,* 2017) as a healing agent, which has become a challenge of future green resources. The encapsulation of palm oil needs more chemical procedures and needs to be synthesized in the form of a palm oil-alkyd base (Shahabudin *et al.,* 2016) to improve the drying ability. Sunflower cooking oil, also falls under the category of a drying type oil that makes it very unique as a self-healing agent in the microencapsulation process. This unique property of sunflower cooking oil has the potential to be further explored.

Globally, a prevalent issue is on the challenge of waste cooking oil disposal that pollutes the landfill sites (Ngadi and Mba, 2015). There is a demand currently for the exploitation of waste material to be transformed into core material. Lately, engineering technology advancements are looking for the ability to enhance the value of recycled materials to become useful resources. Due to this challenge, the investigation of waste sunflower oil as a recyclable material of a self-healing agent in microencapsulation was inclusively discovered in this research. Figure 1.1 shows the illustration of microencapsulation of waste sunflower oil by using the in-situ polymerization method to synthesize microcapsules. The microcapsules were embedded with epoxy coating by sandwich method and were applied to a mild steel substrate. Once the coated mild steel was scratched, the waste sunflower oil was released and polymerized, thus the scratch was healed.

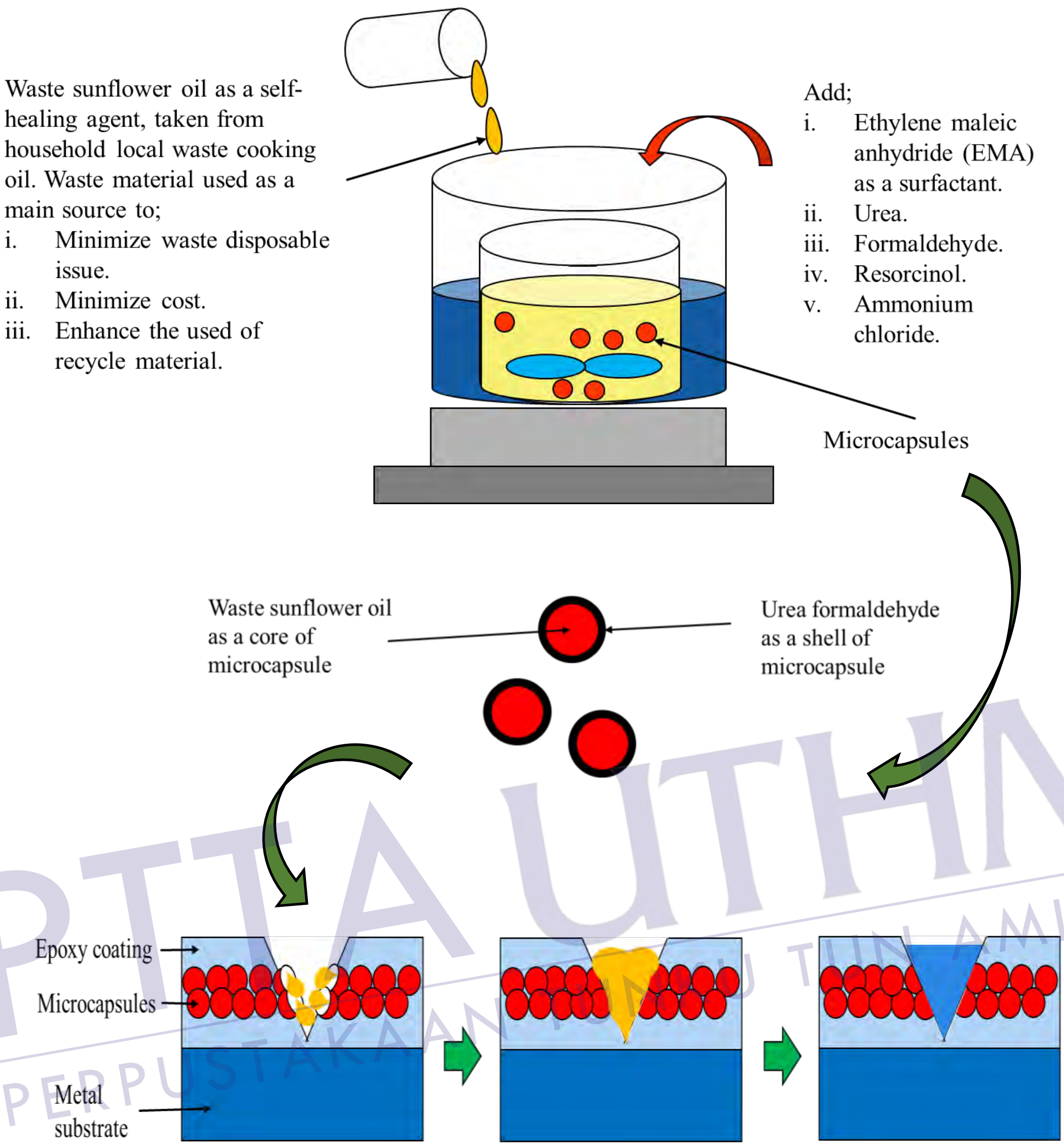

Figure 1.1: Production of self-healing coating containing microencapsulated waste sunflower oil.

The study of the ability of waste sunflower oil as a self-healing agent may demonstrate its competence and efficiency as collated with natural sunflower oils and other forms of discovered vegetable oils. The self-healing performance of the coating matrix embedded with microencapsulated waste sunflower oil performed has proposed for new materials for anti-corrosion coating application. Most preeminently, the embedment of waste sunflower oil as recyclable material of a self-healing agent was demonstrated to be environmentally friendly. Moreover, it is non-carcinogenic and safe material that is available in the market. Besides that, waste sunflower oil as waste resource could promote sustainable energy consumption.

1.2 Problem statement

National Association of Corrosion Engineers (NACE) reported that in 2016, the estimated global cost of corrosion was RM 6.59 trillion, 4 % of the global Gross Domestic Product (GDP). Malaysia as developed country was statistically showed RM 24.0 billion cost of corrosion (Isa *et al.,* 2019). Around 40 % of total cost of corrosion in Malaysia were critically came from industries (Koch *et al.,* 2016). Manufacturing industries are particularly were affected with damage issues on engineering materials due to corrosion that causes failure in metal functionality. The most widely applied solution to corrosion protection is coating. Coating on metal is also prone to heat and moisture attack that exposes it to corrosion. Generally, all industries use the manual re-coating approach or the replacement of damaged instruments (Huige *et al.,* 2014). In addition, during this global instability of the spreading pandemic of coronavirus disease 2019 (COVID-19), the labour force problem of manual re-coating maintenance has become a major obstacle. However, a number of studies have shown that the smart coating has been integrated into a self-healing concept that helps the coated part to recover on its own. The advantages of the self-healing concept adopted in coating matrix allows the coated metal to heal the micro-cracks (Samadzadeh *et al.,* 2010). This approach generates an alternative to the manpower issue, however, there is still room for improvement.

The previous research on self-healing approach has focused on polymer involving an agent such dicyclopentadiene (DCPD). However, this approach needs catalyst to induce the reaction whilst has a constraint on lifetime issue (Kirkby *et al.,* 2009). Later, modern researchers extended the non-catalyst approach by using natural self-healing agents from a drying type of vegetable oil such as tung oil (Thanawala *et al.,* 2014) and linseed oil (Abdipour *et al.,* 2018). The availability of the drying type creates the issue of availability of oil, especially in Malaysia. Taking on that challenge, Shahabudin *et al.* (2016) studied the potential of palm oil as a self-healing agent, however, the palm oil needed to be transformed to alkyd via an ethanolysis procedure that induces complexity of experimentation. As a result, the promise of a specific drying form of waste sunflower oil as a self-healing agent has given rise to the need to resolve issues of availability and complexity.

Waste cooking oil is widely available around the world, especially in developed countries. The waste management of oil creates significant challenges due to disposal problems and possible contamination of water and land resources (Ngadi and Mba, 2015). Since sunflower oil is used as a cooking oil, recycling of waste sunflower oil as a self-healing agent is considered as renewable energy consumption. The waste sunflower oil that undergoes the frying process can be filtered using a simple filtration process to remove unwanted particles, and the clean and purified sunflower oil can be used as a healing agent. The best part is that the utilization of waste sunflower oil as a self-healing agent that it will solve the availability issue of raw materials, minimize cost expenses, and bring economic advantages. Moreover, to date, there have been no attempt to study microencapsulation from waste sunflower oil as a natural self-healing corrosion agent for coating applications.

Microencapsulation of waste sunflower oil prompts an alternative of raw material as a natural self-healing corrosion agent. The process of microencapsulation involving waste cooking oils distinguishes a new difficulty in the chemical process by means of an in-situ polymerization approach to fit possible criteria that influence the character of the microcapsules. Waste cooking oil induces change in the viscosity of oil after the frying process (Maskan, 2003), thus, the ability to be emulsified during in-situ polymerization process will be presented in this research's findings. The characteristics of microcapsules synthesized from waste sunflower oil generates another challenge in order to be able to suit the embedment with epoxy coating in order to be implemented in coating applications. Besides that, the coating application method on mixing of epoxy-microcapsules via stirring approach established by previous researchers still have room to be improved. The findings of this research can be seen as a new solution to the global battle against corrosion, which may minimise the avoidance of corrosion, reduce material costs and drive forward the life of long-haul coated parts. Moreover, the studies with respect to waste sunflower oil as a self-healing corrosion agent will achieve the streamlining of renewable and sustainable energy development.

1.3 Objectives of study

This study embarks on the following objectives:

i. To synthesize microcapsules containing waste sunflower oil by using microencapsulation method.

ii. To characterize microcapsules containing waste sunflower oil.

iii. To determine the self-healing performance of coating matrix that embedded with microcapsules containing waste sunflower oil.

iv. To investigate the mechanical strength of coating matrix that embedded with microcapsules containing waste sunflower oil.

v. To evaluate the anti-corrosion ability of coating matrix that embedded with microcapsules containing waste sunflower oil.

1.4 Significance of study

The potential of waste sunflower oil as a self-healing agent has been established as a target to be explored in order to resolve the supply problem of drying form oil as an agent. Moreover, waste sunflower oil that is sourced from waste cooking oil generates an alternative and very significant cost saving raw material as a self-healing agent. The unique properties of waste sunflower oil fall under the drying type category of vegetable oil that is highly suitable as a self-healing agent due to its fast-drying ability. Moreover, sunflower oil can be used as a cooking oil, which creates availability. Meanwhile, tung and linseed oil are also a drying type of oil but cannot be used in cooking due to rancidity (Stenberg *et al.,* 2005). The frying process leads to the enhancement of the viscosity of sunflower oil (Oth, 2012). The enhancement of viscosity is significant to be studied, especially the performance of the drying ability as compared to the established self-healing agent of tung and linseed oil.

Microencapsulation of waste sunflower oil as a natural self-healing corrosion agent via in-situ polymerization method as the basic principle of the in-situ polymerization method is significant with the effects of variant parameters such as stirring speed, reaction time and surfactant concentration. Adopting new materials as a self-healing agent reflects the effects of variant parameters as mentioned above. The characteristics of microcapsules synthesized from waste sunflower oil aims is hoped to be able to be embedded in epoxy coating. The new coating application method, named 'sandwich method', allows for a particular microcapsules diameter and shell thickness to match the appropriate coating thickness so that the self-healing mechanism performs accordingly.

The self-healing principle was significantly developed to maintain and prolong the service life of engineering materials (Zhang and Li, 2016) as a major issue that has been discussed in the problem statement section. During this coronavirus diseases 2019 (COVID-19) pandemic, the self-healing of coated metal has become an essential method to replace the manpower issue for corrosion prevention maintenance in all industries globally. Self-healing on coated materials have the ability to reverse the damage by corrosion attacks and increases the lifetime and the reliability of the material, and thus of the device significantly (Huige *et al.,* 2014). Such new levels of performance are of particular relevance to materials that are used with or without limited access by humans, such as in medical applications as well as in civil, aerospace, automotive and power engineering. If it is possible to incorporate a self-healing system for harm incurred by the manufacturing process, this greatly improves the successful longevity and durability of potential novel products, besides being cost effective due to the reduced need for monitoring and controlling. In addition, a substantial saving of resources and energy could be anticipated due to the reduction of hitherto necessary safety margins for the constructive geometry of mechanically, thermally and corrosively exposed components in almost all technical areas. Self-healing materials would greatly improve materials' reliability and thus revolutionize component construction and design. Moreover, it benefits the extension of the lifetime of critical components (Glass, 2001; Tait, 2018).

1.5 Scope of study

This research investigates the potential of waste sunflower microcapsules as natural self-healing corrosion agent for metal coatings. The research is divided into three stages. Each stage represents each objective in this study.

The first stage (from objectives 1 and 2) was involved the experimental procedure of the microencapsulation process that was prepared by an in-situ polymerization method. The scope of raw material and microencapsulation conditions were specified below:

i. Raw material: waste sunflower oil collected from own household resources that has been used to fry fish cracker for twice. The waste sunflower oil was undergoing heating process under cooking temperature of 100-200 ºC. Hexane were used as a solvent to during vacuum filtration process on microcapsules.
ii. The parameters of in-situ polymerization method:
    a. Stirring speed (200, 300, 400 rpm).
    b. Reaction time (2, 3, 4 h).
    c. Concentration of Ethylene Maleic Anhydride, EMA as a surfactant (2.5, 5.0, 7.5 wt%.) 5.0 wt%. adopt from established researcher, while 2.5 and 7.5 wt%. embark as a research gap.
    d. pH was fixed at 3.5.
iii. Characterization of microencapsulated waste sunflower oil:
    a. Surface morphology of microcapsules was undergoing Field Emission Scanning Electron Microscopy (FESEM).
    b. Chemical properties of microcapsules analysed by Fourier Transform Infra-Red Spectroscopy (FTIR).
    c. Compound analysis on the shell structure was undergoing X-Ray Diffractometer (XRD).
    d. The thermal stability of microcapsules containing waste sunflower oil was analysed by Thermogravimetric Analysis (TGA).

The second stage (from objectives 3 and 4) in this study involved the preparation of self-healing coating embedded with microcapsules containing waste sunflower oil. The coating was applied to substrate using a sandwich method with the fixed weight ratio microcapsules over epoxy resin (1 g: 100 g). The self-healing coating was applied on a substrate named S275JR Grade mild steel (without any preparation). The substrate was a grade of mild steel which widely used in manufacturing industries today. The self-healing coating was analysed with specified characterization and testing scoped below:

i. Coating thickness analysed under optical microscope (OM).
ii. The self-healing performance of artificial scratch (Chapter 3) on coating surface was analysed by Scanning Electron Microscopy (SEM).
iii. The self-healing coating went through mechanical testing as specified below:
    a. Bending adhesion test (adhesion analyzation).
    b. Vickers hardness test (hardness analyzation).
    c. Scratch adhesion test (thin layer adhesion analyzation).

The third stage (from objective 5) in this study was involved the evaluation of anti-corrosion ability of self-healing coating that applied on mild steel. The evaluation of anti-corrosion ability permits with immersion of coated mild steel in 3.5 wt%. sodium chloride (NaCl) solution for 672 h (28 days). The analysis of anti-corrosion ability of self-healing coating was specified below:

i. The visual assessment on anti-corrosion ability of self-healing coating was analysed by digital camera.
ii. The compound analysis of corrosion that was existed on coated mild steel after immersion test was characterised under X-Ray Diffractometer (XRD).
iii. Surface morphology of the corrosion species that generated from mild steel was analysed under Field Emission Scanning Electron Microscopy (FESEM).

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

Microencapsulation is defined as a wall formation process of prepolymer, for instance, urea formaldehyde (UF) that attached with self-healing agent as a core, in which the prepolymer will form a shell and cover the core to form a microcapsule. Self-healing agent can be identified as a core material that was protected by a shell polymer. The core has the potential to release and polymerized to heal specific damaged zone on coating matrix (Khorasani, *et al.*, 2017). Microencapsulation of self-healing polymeric materials were used mostly in epoxy coatings. Epoxy coating embedded with microcapsules containing reactive regent of healing agent is called self-healing coating. Self-healing coating applied on the surface of mild steel acted as a barrier from corrosion. The existence of crack on the coating surface was healed by the unleashed of the healing agent from ruptured microcapsules. Once the healing agent was polymerized, the crack area was healed. This study aimed to demonstrate the potential of waste sunflower oil to be encapsulated. The encapsulated oil was applied as smart microcapsules in coating matrix to provide self-healing mechanism and provide anti-corrosion ability to protect mild steel that were used in engineering equipment. According to Blaiszik *et al.* (2010), self-healing mechanism was classified into three main classes; capsule base, vascular and intrinsic. The concept, technique, preparation method, materials and characteristics of microcapsules produced from the microencapsulation process, specifically capsule base, was discussed in this chapter. The key component in microencapsulation were the materials and methodology. The major raw material was a self-healing agent and considered as a reactive reagent as a core of microcapsule. The self-healing agent was divided into two categories; organic and inorganic. Details regarding organic self-healing agents extracted from natural vegetable oils was addressed in this chapter. The microencapsulation process was divided into five techniques; in-situ polymerization, interfacial polymerization, pickering emulsion template, mini-emulsion polymerization, solvent evaporation/solvent extraction and sol-gel reaction. In-situ polymerization approach is mainly tailored to the microencapsulation of natural self-healing agents and offers the flexibility of parameter adjustment to achieve the characteristics of the microcapsules. The analysis on the validity of materials, definition, methodology, characteristics, characterization and testing for the study of microencapsulation of natural self-healing corrosion agent for coating applications were discussed further in this chapter.

2.2 Self-healing agent

Self-healing agent as an organic material that been embedded in coating matrix has been proposed to extend the lifetime of metal against corrosion and recover from cracks caused by external or internal environment. Therefore, in self-healing coating, healing mechanism occurred when smart coating start to minimize the cracked from spread and reduce the penetration of oxygen, water and ions to the substrates (Khorasani, *et al.*, 2017; Safaei *et al.,* 2018; Ataei *et al.,* 2019). In recent years, many attempts have been made to produce an optimized self-healing material with microcapsules that contain healing agent, especially in industrial coating and some healing agent was modified to use in epoxy resins as matrix. The consumers and interest's industry in the development of materials that are eco-friendly have led to the environmentally friendly agricultural resources as feedstock in the polymer industry. Today, due to the approach of discipline through research and technological innovation in the fields of chemistry, bioscience, biotechnological and engineering, it is possible to design an eco-friendly specialty chemicals that come from the nature's abundant renewable resources (Alam *et al.*, 2014).

Nowadays, vegetable oils have been increasingly used as self-healing agents in coating industrial. Alam *et al.* (2014) stated that vegetable oils are non-toxic, non-exhaustible, domestically abundant, biodegradable resource and non-volatile. Most importantly, vegetable oils were cheaper and their unique structure of chemical has enabled them to undergo various chemical transformations in process to produce low molecular weight polymeric materials with particularly as main ingredients in coatings. There are numerous types of vegetable oils that have been employed as smart coating materials such as tung oil, linseed oil, sunflower oil, coconut oil and palm oil. Figure 2.1 shows the summary of category of self-healing agent that been discovered by previous researcher.

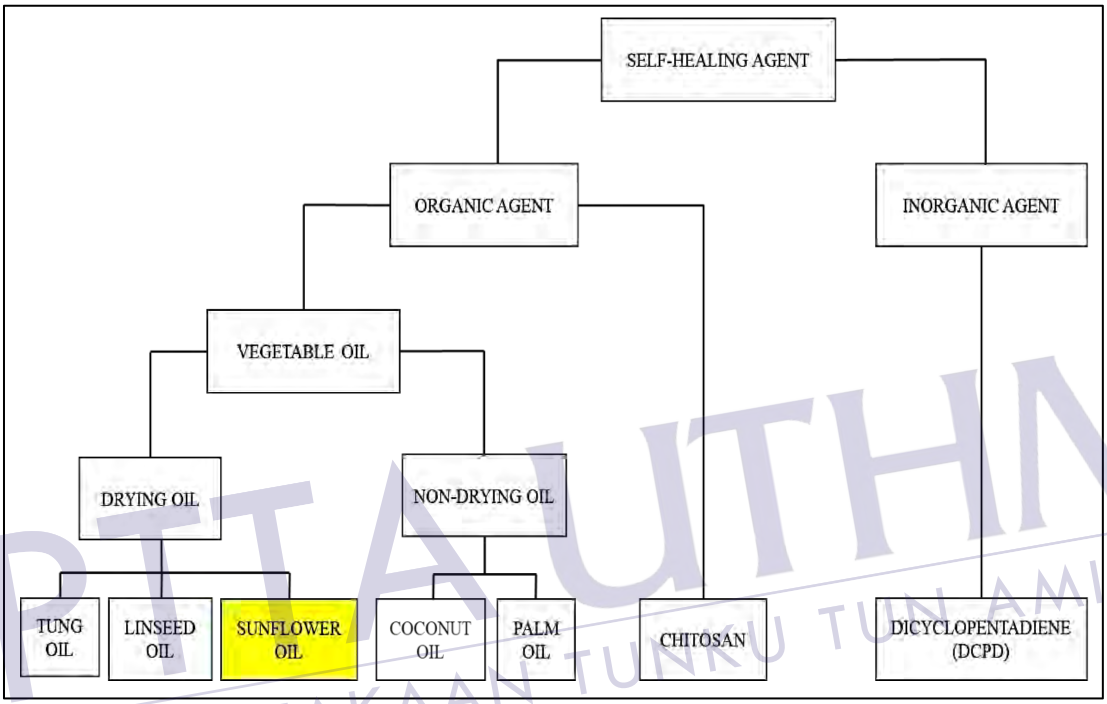

Figure 2.1: Category of self-healing agent.

In general, vegetable oil was separated into two categories; drying oil and non-drying oil. Drying oil was defined as type of oil that can dry fast whereas non-drying oil would dry slower in comparison. Ataei *et al.* (2019) reported that drying oil was defined as oil that consist of long-chain triglycerides unsaturated fatty acids (Figure 2.2) that was able to react with atmospheric oxygen without the occurrence of catalyst. This reaction is called autoxidation and drying oil has potential autoxidative self-healing agent. The number of double bond conjugate lead to the drying rate, whereas the fast polymerization was influenced by the amount of unsaturated fatty acids. During oxidation, trans-isomer was formed, breaking the long carbon chain and generates volatile by-products.

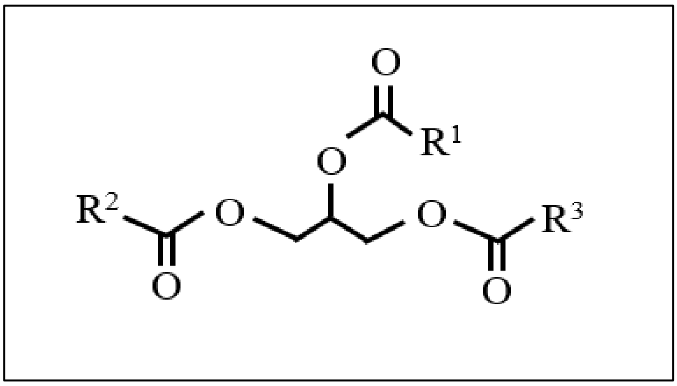

Figure 2.2: Triglycerides unsaturated fatty acids, where R=fatty acids hydrocarbon chain (Ca *et al.,* 2013).

The polymerization of drying oil consists of crosslinking reaction to form dry film. Drying oil such linseed and tung oil contain more that 50 % linoleic (C18:3) and elestrostearic (C18:3) acids where both were triglycerides unsaturated fatty acids that can lead to increasing oxidation activity with atmospheric oxygen (Ataei *et al.,* 2019). The composition of fatty acids on drying and non-drying oil showed in Table 2.1. Soybean, coconut and palm oil were described as non-drying oil because of small concentration of triglycerides fatty acids (Ataei *et al.,* 2019).

Table 2.1: Fatty acids composition of drying and non-drying oil (Ataei *et al.,* 2019)

Type of oil	Elostearic C18:3	Linolenic C18:3	Linoleic C18:2	Oleic C18:1	Lauric C12:0	Myristic C14:0	Decanoic C10:0	Palmitic C16:0
Linseed		52	17	25				5
Tung	80	3	4	8				5
Soybean		7	53	24				12
Coconut				6.5	48	16	8	9.5
Palm			9	45				39

According to Soucek *et al.* (2012), linoleic fatty acids were pigmented and have basic fillers that act as corrosion resistance. Linoleic fatty acids also have diene structure that induced oil autoxidation but is limited. Linoleic fatty acids existed as free radical structure that react with oxygen and with the hydrogen abstraction, the autoxidation process was accelerated. The complete autoxidation process involved the cessation of carbon-carbon to cross-linked activity and the generation of polymerization. The limitation occurred because there are secondary oxidation reactions which do not produce crosslinks.

Among the drying type of vegetable oil; linseed and tung oil were widely explored by most researcher as microencapsulation agent due to the fast drying capability that is most suited for coating applications (Dlugogorski *et al.,* 2012). Few researchers have begun to develop the usage of non-drying vegetable oil such coconut and palm oil as self-healing agent. These self-healing agents require additional additive and experimentation to form as an alkyd resin to fasten the drying ability (Shahabudin *et al.,* 2015; Shahabudin *et al.,* 2016a; Shahabudin *et al.,* 2016b; Khorasani *et al.,* 2017).

2.2.1 Drying oil

In recent decades, the use of smart materials has shown itself to be a promising material in the development of self-healing technology advancements. The self-healing concept incorporated in the microencapsulation method is one of the practical and effective methods for producing metal self-healing coatings. The use of natural resources as self-healing agent has recently increased in demand due to its environmental friendliness. As an organic resource, vegetable oil was one of the most promising self-healing agents.

According to Sharma and Kundu (2006), drying oil can be define as a type of oil that can be polymerized in air condition to produce a robust elastic film. The elastic film hardens by polymerization process with reaction with air. This excellent natural drying oil was a produced biopolymer that classified as renewable, biodegradable and non-toxic.

The autoxidation of oil was interrelated to drying ability. Autoxidation of vegetable oil signify as a biological autoxidation due to the natural process of oxidation. Dlugogorski *et al.* (2012) studied on the oxidation of linseed oil that consist of 60 % linoleic acids and found that the higher the concentration of linoleic acids generate higher drying ability. The formation of thin film from oil was occurred during mechanical stage while lipid oxidation that create crosslink ability was existed during chemical stage. Dlugogorski's finding has influenced the potential of various type of drying oil to be explored more. One of the possible choices of vegetable oil that have high concentration of linoleic acids is a sunflower oil.

The drying ability depends mainly on the concentration of polyunsaturated fatty acid (linoleic) to proceed an autoxidation process by reaction with ambient air while monounsaturated fatty acid (oleic) only proceeds an autoxidation process on particular elevated temperature (Dlugogorski *et al.,* 2012).

The thermal activity such as heating, or cooking process mostly affects the concentration of saturated fatty acids but not much on the concentration of unsaturated fatty acids. The concentration of unsaturated fatty acids bring the vegetable oil to be classified as a drying or non-drying type oil (Chen *et al.,* 2017). Chen's finding can be used as a justification to show that the implementation of recycle vegetable oil that used after heating or cooking process was possible to be explored as a potential of self-healing agent.

Xia and Larock (2010) reported that vegetable oil was unique in chemical properties because of renewable polymers, biodegradability and low toxicity. The polymerization of unsaturated fatty acids of vegetable oil by reaction with oxygen in air makes it benefited to be implemented for coating applications.

Oth (2012) defined drying process as a curing process of oil that generates by autoxidation with an oxygen through a crosslinking action (Figure 2.3). The details of autoxidation process were as follows:

i. The existence of an oxygen in the air reacts with carbon-oxygen bonds of unsaturated fatty acid to form hydroperoxide. The hydroperoxide were important to create a crosslinking reaction.
ii. Then, the hydroperoxide react with neighboring unsaturated fatty acid to form a polymer network. The polymer network was visibly existing as a thin film that elastic, stable and inflow. The formation of this thin film was called as a polymerization process.

The diene structure derived from polyunsaturated fatty acids in the drying oil was active in the reaction with oxygen, while monounsaturated fatty acids such as oleic acids were less stable in the reaction with oxygen to dry.(Oth, 2012).

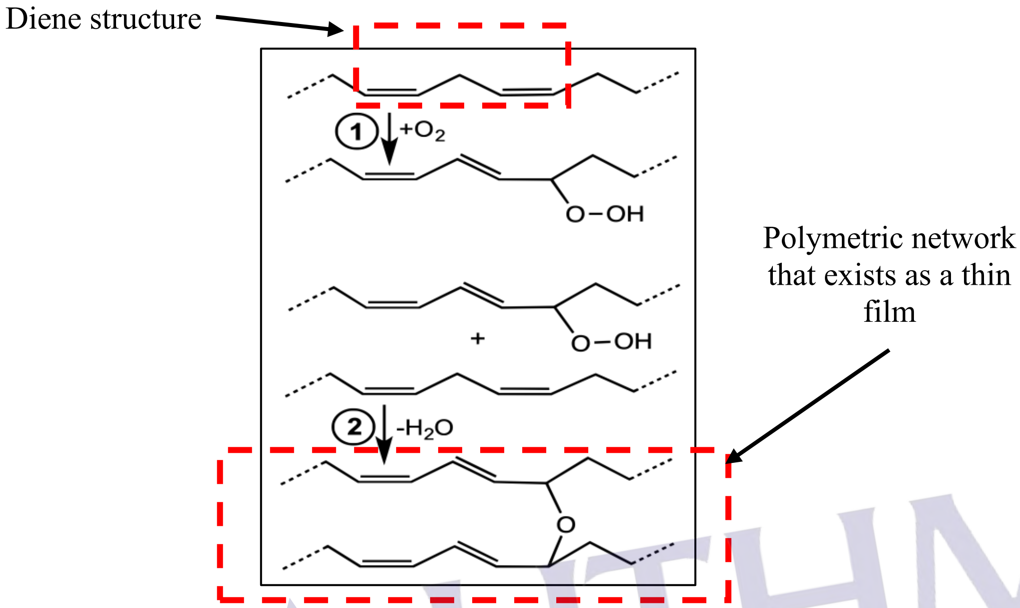

Figure 2.3: Chemical reaction during drying process (Oth, 2012).

The other unique property of drying oil was having an excellent drying property even without the reaction with oxygen due to the long aliphatic hydrocarbon chain and double bond in fatty acids. Apart from that, the molecular structure of unsaturated fatty acids in drying oil had also produced an excellent flow movement to form a thin film during polymerization process. The thin film with aliphatic structure were hydrophobic which was stable with water or soluble agents (Oth, 2012).

Drying ability was related with weight increment of oil during heating process and during exposure to air. Upon drying, the weight of oil was found to be increasing. The higher the weight, the higher the autoxidation rate (Coni *et al.,* 2004). According to Homas (2012) and Oth (2012), the drying process relates with the weight changes in a thin film. The oil film absorbed oxygen during reaction process which led to the increase of weight. Linseed oil increases 17 wt%. during drying process. Once the oil ages, the original ester bonds in oil molecules were hydrolysed and remove individual fatty acids, so that the thin oil film decreases the weight.

Drying ability was also related with the oil viscosity. Zahir *et al.* (2017) identified that the changes of viscosity of oil during heating was related to the changes of triglyceride molecule. This shows that viscosity changes depend on the chain length and unsaturation process. The viscosity of oil was changed with the effect of polymerization, thus also influenced on the drying ability.

Sudhir and Sharma (2007) claimed that during cooking process, heat and water content has induced the hydrolysis of triglycerides to enhance the concentration of fatty acids in oil. Cooking process had also increased the viscosity of oil due to the presence of glycerides. Thus, during cooking, the water content decreased due to reaction of heat and increased the viscosity. Maskan (2003) investigated the effect of frying process on sunflower oil and found that the waste cooking sunflower oil has higher viscosity value compared to natural sunflower oil due to the heating process. Most drying oils had rapidly increased in viscosity after heating in the absence of air. If the oil is subjected to raised temperatures for a long time, it will become oil-insoluble substance with rubbery texture (Oth, 2012).

Microencapsulation process that incorporated drying type oil as self-healing agent mostly experimented with in-situ polymerization (Thanawala *et al.,* 2014) and solvent evaporation (Behzadnasab *et al.,* 2017). In-situ polymerization is a process that involved emulsification and wall forming at a single stage of the process. (Thanawala *et al.,* 2014) while solvent evaporation was a two-stage procedure involve emulsification of oil in first stage and second stage procedure involving wall formation process (Tripathi *et al.,* 2017).

Herein, the specified potential of vegetable oil as self-healing agent for corrosion coating will be discussed further. Tung oil, linseed oil, soybean oil, poppy oil and sunflower oil, walnut oil and candlenut oil were part of drying oil available in market and some need to be extracted from the origin sources (Kouzu and Hidaka, 2012; Ca *et al.,* 2013; Taylor *et al.,* 2015).

Tung and linseed oil were widely used in China as a finishing material applied to wooden products; to look presentable, glossy and shinning (Serviss *et al.,* 2007). The high concentration of triglycerides of fatty acids in tung and linseed oil allow them to dry rapidly in contrast to soybean and poppy oil with lesser triglycerides fatty acids concentration. Some researcher classified soybean and poppy oil as semi-drying oil

(Ataei *et al.,* 2019). The fast-drying ability and yellowish attractive color of those oil has created a great demand in China. Tung and linseed oil is advantageous in terms of high extraction process therefore it can easily fulfil the increasing demand (Serviss *et al.,* 2007). The high demand of tung and linseed oil attract more researcher to investigate the potential of those oil as self-healing agent. The fast-drying ability and high viscosity of tung and linseed oil create the possibility of emulsification and cross-linking with other material such an epoxy. On the other hand, sunflower oil classified as a drying oil with lower viscosity as compared to tung and linseed oil (Esteban *et al.,* 2012). To date, no study has reported on the investigation of sunflower oil as self-healing agent in metal coatings.

2.2.1.1 Linseed oil

Popa *et al.* (2012) mentioned that, linseed oil is commonly known as flaxseed oil. Linseed oil was extracted from the dried, ripened seeds of Linum usitatissimum or also known as flax plant (Figure 2.4). Linseed oil was yellowish and some even colorless. The extraction method of linseed oil was using solvent extraction and natural pressing procedure.

Figure 2.4: Linseed plant (Linum usitatissimum) (Popa *et al.,* 2012).

Linseed oil was classified as a drying type oil due to high concentration of triglycerides fatty acids of linolenic acid (26-60%), which means it can be polymerized and became solid (Popa *et al.,* 2012). The organic and characteristics of linseed oil create a suitability to be a core material as self-healing agent in microencapsulation process for coating applications. The fatty acids composition of linseed oil was indicated in Table 2.2.

Table 2.2: Fatty acids composition of linseed oil (Popa *et al.,* 2012)

Composition	
Palmitic acid (C16:0)	6.58 %
Stearic acid (C18:0)	4.43 %
Oleic acid (C18:1)	18.51 %
Linoleic acid (C18:2)	17.25 %
Alpha-linolenic acid (C18:3)	53.21 %
Other	0.02 %

Dlugogorski *et al.* (2011) studied the drying ability of linseed oil to match with the performance of coating matrix such as paints. The drying properties of linseed oil were induced with high concentration of polyunsaturated fatty acids, where molecules of unsaturated fatty acids able to react with oxygen from atmospheric air with one another and crosslinked to create polymeric network. The drying process of linseed oil mentioned as autoxidation process that allow the conversion of liquid film to solid thin layer. Dlugogorski *et al.* (2011) also defined the autoxidation process by below statements;

"Autoxidation is a chemical chain-reaction process propagated by radical intermediates. The process involves initiation, propagation and termination steps".

The potential of linseed oil as self-healing agent start to be investigate deeply by Suryanarayana *et al.* 2008. The researcher concludes that linseed oil as self-healing agent in microencapsulation has been successful cross-linked by urea formaldehyde as shell of microcapsules. The results proved; microcapsules able to withstand shear force that induced during mixing into a paint matrix as a metal coating. The microcapsules able to mix into paint matrix due to agglomerated surface morphology of the shell. The crack that against by the microcapsules was healed and provided good corrosion prevention on the painted component. The adhesive stability of microcapsules in coating matrix also supported by Boura *et al.* (2012). Boura found that the microcapsules incorporated with linseed oil had rough, non-porous and agglomerated wall surface were ensured the good bonding to the coating.

The potential of linseed oil as self-healing agent also was discovered by many researcher such Lang and Zhou (2017). The researcher analyzed the potential of linseed oil to be encapsulated with urea formaldehyde (UF) via in-situ polymerization method. It was found that the microcapsules containing linseed oil as self-healing agent were stable with high core content and suitable to perform as smart material to be embedded in epoxy coating. Apart from that, the epoxy coating embedded with microcapsules containing linseed oil showed excellent healing performance on the artificial cracks.

2.2.1.2 Tung oil

Tung oil comes from the seeds of several species of Aleurites, primarily Aleurites fordii, a deciduous shade tree native to China. It belongs to the Euphorbia Family (Euphorbiaceae) along with the candlenut tree, another species with seeds were rich in unsaturated oils (Figure 2.5). Tung oil has been used for paintings and waterproof coatings for decades, and as a part of caulk and mortar. It is one of the ingredients in "India ink" and is commonly used for a lustrous finish on wood. In fact, the "teak oil" sold for fine furniture is usually refined tung oil. Some woodworkers consider tung oil to be one of the best natural finishes for wood (Serviss *et al.,* 2007).

Figure 2.5: Tung fruits (Aleurites fordii) (Serviss *et al.,* 2007).

According to Systematic Treatment of Fruit Types by Richard Spjut (Memoirs of New York Botanic Garden, Volume 70, 1994), the tung fruit is called "bacca." It is technically not a drupe because it lacks a stony endocarp. Tung oil is composed primarily of eleostearic acid, with smaller amounts of oleic, linoleic and palmitic glycerides. Eleostearic acid is a crystalline unsaturated fatty acid that exists in 2 stereoisomeric forms; an alpha acid occurring as the glycerol ester especially in tung oil, and a beta acid obtained from the alpha acid by irradiation (Serviss *et al.,* 2007).

Tung is also known as Aleurites fordii (Atabani *et al.,* 2013). It is a kind of drying oil obtained from tung tree by pressing the seed from the nut. Tung oil usually used for finishing or protecting wood. When exposed to air, tung oil will become hardens and showing a deep, almost wet look even though the coating was transparent. Table 2.3 presents the fatty acids composition of tung oil discovered by Atabani *et al.,* (2013). The concentration of linoleic acids was induced the tung oil to be drying oil due to fast drying ability that bring the suitability of tung oil to be a self-healing agent in microencapsulation process (Ataei *et al.,* 2019).

Table 2.3: Fatty acids composition of tung oil (Atabani *et al.,* 2013)

Composition	
Palmitic saturated (C16:0)	1.8 %
Stearic saturated (C18:0)	2.1 %
Oleic monounsaturated (C18:1)	5.3 %
Alpha-eleostearic acid	82.0 %
Other/Unknown	8.8 %

Samadzadeh *et al.* (2010**)** discover the potential of encapsulated tung oil as a scratch healing agent for metal coating. Tung oil was successfully encapsulated with urea formaldehyde synthesized with diameter of 40-100 µm. Incorporated tung oil microcapsules through epoxy structure gave self-healing ability for coated component without presence of catalyst. In order to give better corrosion resistance, Thanawala *et al.* (2015) investigated the encapsulation of tung oil with corrosion inhibitor. The synthesized microcapsules were dispersed in zinc phosphate-based epoxy premier coating. The optimization of microencapsulation enabled the encapsulated tung oil to heal crack and resist corrosions.

2.2.1.3 Sunflower oil

According to Oth (2012), sunflower scientific name was Helianthus annus, sunflower oil extracted from the sunflower seeds (Figure 2.6). Sunflower oil was widely used as a cooking oil and cosmetics. The extracted sunflower oil is light amber color and rich with vitamin E. Sunflower oil was also used in a coating industry such as paint industry due the non-yellowing color. The extraction method of sunflower oil was mainly by using a chemical solvent such as hexane and other method was using an expeller pressing instrument.

Figure 2.6: Sunflower (Helianthus annus) (Oth, 2012).

Sunflower oil was mainly a triglyceride. Sunflower oil composed of a combination of monounsaturated fatty acids, oleic acid (25.2 % of the total) and polyunsaturated fatty acids, linoleic acid (63.1 % of the total) (Ramos *et al.,* 2009). The high percentage of polyunsaturated fatty acids in sunflower oil makes it considered as a drying oil (Table 2.4).

Table 2.4: Fatty acids composition of sunflower oil (Ramos *et al.,* 2009)

Composition	
Palmitic saturated C16:0	6.2 %
Stearic saturated C18:0	3.7 %
Oleic monounsaturated C18:1	25.2 %
Linoleic polyunsaturated C18:2	63.1 %
Other/Unknown	1.8 %

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