EFFECT OF POLY VINYL ALCOHOL (PVA) ON THE SIZE OF LINSEED OIL (LO) MICROCAPSULE SELF-HEALING COATING

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This report submitted in accordance with requirement of the Universiti Teknikal Malaysia Melaka (UTeM) for the Bachelor Degree of Manufacturing Engineering (Engineering Materials) (Hons.)

by

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APPROVAL

This report is submitted to the Faculty of Manufacturing Engineering of UTeM as a partial fulfillment of the requirements for the degree of Bachelor of Manufacturing Engineering (Engineering Materials) (Hons.). The member of the supervisory is as follow:

……

(Supervisor)

(Associate Professor Dr. Zulkifli Bin Mohd Rosli)

ABSTRAK

Kajian ini membincangkan kesan kepekatan (wt. %) dan isipadu (ml) Poli Vinil Alkohol (PVA) terhadap pembentukan 'Linseed oil (LO) microcapsule' dan diameter saiz. Terdapat beberapa kajian dibincangkan mengenai kepekatan PVA terhadap struktuk pembentukan 'Linseed oil microcapsule'. Walaubagaimanapun, tiada kajian yang sistematik pada tajuk ini. Dalam in situ emulsi pempolimeran, biji rami minyak Poly urea formaldehid digunakan sebagai teras dan karung pembentukan untuk menghasilkan 'microcapsule' salutan penyembuhan secara automatik.PVA bertindak sebagai penstabil untuk emulsi pembentukan microcapsules. Seterusnya, PVA dimanipulasi untuk mengkaji kesan pelbagai kepekatan dengan isipadu yang berbeza terhadap fenomena saiz microcapsule dan pembentukan microcapsule itu. Kemudian, semasa pemprosesan sampel melalui in situ kaedah emulsi pempolimeran, suhu malar , kadar pergerakan dan masa tindak balas yang digunakan yang 50ºC , 500rpm dan 4h. Terdapat beberapa pengubahsuaian pada kadar pergerakan mengurangkan kepada 300 rpm. Oleh itu , sampel dicirikan menggunakan SEM untuk mencirikan saiz microcapsule dan struktu pembentukan dan juga analisis FTIR untuk memeriksa komposisi teras dan karung bahan.

ABSTRACT

This research involves studying the effect of various concentrations (wt. %) with different volume (ml) of Poly vinyl Alcohol, PVA on the encapsulated linseed oil microcapsule size. There are several studies discussed about the essence of various concentrations of Poly vinyl Alcohol, PVA on the linseed oil microcapsule attributes. However, on that point is no systematic research on this claim. In the *in situ* emulsion polymerization, linseed oil-Poly urea formaldehyde are used as a core and shell material to produce microcapsule self-healing coating. PVA act as stabilizers for a stable emulsion of the microcapsules. Next, PVA is manipulated to investigate the influence of various concentrations with different volume on the microcapsule size phenomena of the microcapsule formation. Then, during the sample processing via in situ emulsion polymerization method, the constant temperature, agitation rate and reaction time are used which are 50ºC, 500rpm and 4h. Simply, some modification on an agitation rate reduce to 300 rpm. Thus, the sample is characterized using SEM to characterize the microcapsule size and formation and also the FTIR analysis to examine the composition of the core and shell material.

DEDICATION

Dedicated to
my beloved father, Abdul Yazid bin Othman
my appreciated mother, Zuraidah binti Sulaiman
and my adored siblings, Fatin, Aliff, Aiman and Damia
for giving me moral support, cooperation, encouragement and also understandings.

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LIST OF ABBREVIATIONS AND SYMBOLS

LO - Linseed Oil

PUF -Poly urea formaldehyde

PMF -Poly melamine formaldehyde

PVA -Poly vinyl alcohol

HCL -Hydrochloric acid

H_20 -Water

DO -Distilled water

SDS -Sodium dodecyl sulphate

℃ - degree Celsius

ml - millilitre

wt. % - weight percent

CHAPTER 1

INTRODUCTION

This chapter traces the background of the research, the problem statement and the aims of the research. Furthermore, it also states the scope covered by student in this research.

- **Background of the Study**

Nowadays, corrosion becomes a major issue that pertained to the materials and causes a huge economic losses in particular to automotive, marine, pipeline, oil and gas and aerospace industries. It is fixed as the deterioration reaction of an electrochemical between the metal and its environment by Nuenghatai et al. (2014). Therefore, self-healing, anti-corrosive coating called smart materials have been suggested as a corrosion prevention. Self-healing are defined as self-repairing upon exposure to an external stimulus and composing of healing agent encapsulated microcapsules. In addition, Tatyana et al. (2011) noted that the aim is to develop materials with a built in capability to retain functionalities and restore their structural integrity astronomically after the damage.

The most realistic approach is self-healing polymer coatings and it is founded on the incorporation of microcapsules filled with reactive chemicals. Also, the microcapsule are spherical particles with a typical diameter of 10-200 μm, consisting of a solid polymeric shell and liquid core material stated by Tatyana et al. (2011). Thermosetting polymer such as urea-formaldehyde usually used to make microcapsule shell and healing factor, namely core, can be a

synthetic chemical substance or an organic and natural meat. In gain, drying oil usually used for corrosion resistance and linseed oil was chosen as a healing agent, the significance being its ability to forge a film by oxidative drying (Kouhi et al. 2013, Jadhav et al. 2013). Moreover, due to its high content of unsaturated esters of oleic acid and linoleic acid, which susceptible to polymerization reactions upon exposure to oxygen in air, results in the rigidification of the material and protect the metal from corrosion ability stated by Avinash et al. (2013). In this study, microcapsules with urea-formaldehyde as a shell and linseed oil as a core are synthesized by ***in situ*** emulsion polymerization method.

Furthermore, on that point are many parameters that influence the shape, morphology, and functioning, size and shell thickness of the shell of microcapsules. There are agitation rate, type of stabilizers, and concentration of stabilizers, pH, temperature and the reaction time of the encapsulation reaction. During this work, concentration and volume of stabilizers are focusing on parliamentary procedure to synthesize the size of microcapsules. Polyvinyl alcohol, PVA was applied as a stabilizer to stabilize the emulsion and adjust microcapsule size. If the size of microcapsule is too large and tend to agglomerate the microcapsule are not free flowing powder which related to less stability stated by Tatyana et al. (2011).

The PVA act as the stabilizer plays effective parts in manipulating the microcapsules size. A study done by Yuan et al. (2006) increase the stabilizers concentration leads to the output of smaller capsules. As the concentration of PVA increases to 30ML, the size of microcapsule form at range 10 µm -200 µm stated by T. Nesterova et al. (2012).

Therefore, it is important to consider the essence of concentration and volume of PVA stabilizers on the synthesizing the microcapsule size dimension and structures.

- **Problem Statement**

Generally, paints are usually used for substrates modification either for aesthetic appearance or for corrosion prevention, for painting water and oxygen exposure application, the mean size of microcapsule was ideally between the 10 µm-200 µm. Research by Nuenghatai et al. (2014), the comparison self-repairing coating contained different size microcapsules, the coating prepared from smaller size could prevent corrosion better than larger sizes. Hence, it is possible to disperse in the epoxy paint matrix homogeneously and when the coating was damaged, the microcapsules could release the linseed oil to repair the damages. In reality, the researchers faced the problems in producing the encapsulated microcapsule and difficult to control the microcapsule size. The microcapsule size that always obtained were bigger in size and not suited for the coating water and oxygen exposure application.

Furthermore, to take on this problem, there are many parameters that influence in reducing the microcapsule size. The most important parameter that influences the size, shape, morphology, and thickness of the shell microcapsules are agitation rate, type of stabilizer, concentration of stabilizer, pH, temperature and the duration of the encapsulation reaction stated by Karan et al. (2014). In summation, by that, the research of this subject area is highlighted along the effect of concentration of stabilizer and its volume on the microcapsule size dimension. Increasing the absorption of the stabilizers will decrease the dimension size of the microcapsules. In parliamentary law to get the stability of the microcapsules, the capsule must free flowing powder which tends smaller in size and not to agglomerate.

PVA solution was chosen as the stabilizer to investigate the changes of microcapsule size. Furthermore, increasing the concentration and volume of PVA solution, will decrease the size of microcapsules.

Hence, the simultaneous influence of PVA concentrations and its volume will be the chief theme in this study focusing more on the microcapsule size of linseed oil microcapsule produce by in situ emulsion polymerization method. It also proposed that by increasing the concentration and volume PVA is required. Indirectly, a sustainable development can be attained.

- **Objectives**

The objectives of this study are:-

- To synthesize the microencapsulated self –healing microcapsule via ***in situ emulsion polymerization method.***
- To investigate the influence of concentration and volume PVA as stabilizer on the structure and microcapsule size adjustment.
- To characterize the microcapsule size and examine the composition of microcapsule via SEM and FTIR analysis.

- **Scope**

The scope of this research will be focusing on the producing encapsulated microcapsule powder with a linseed oil healing agent via in situ emulsion polymerization method. In this task, the capsule must possess small size with average range are 10 μm-200 μm and freely flowing powder. The attributes of the microcapsules formed are under the influence of the effect of various concentrations with different volume of PVA solution during in situ emulsion polymerization method. The concentration was carried out by three different weight percentage (wt. %) and each concentration will test with different volume. Concentration: 10 wt. %, 20 wt.

% and 30 wt. %. Volume: 5 ml, 10 ml, 20 ml and 30 ml. Analysis of microcapsule properties was derived from four constant parameters which are the pH value of the 1M HCl used is 3.0, temperature is the 50ºC, time duration is 4h and agitation rate is 300rpm.

In summation, this research will only discuss on the in situ emulsion polymerization method use to synthesize the encapsulated linseed oil microcapsule powder. The linseed oil powder was filtered using filter paper and dried in a fume cupboard for 1 day. The samples are characterized using Scanning Electron Microscopy (SEM) to investigate the microcapsule size, structure and the surfaces of the microcapsules while Fourier Transmission Infrared Spectroscopy (FTIR) was used to analysis the composition bonding in the formation of linseed oil healing agent and PUF shell of the microcapsule self-healing coating.

CHAPTER 2

LITERATURE RIVIEW

This chapter will primarily discuss the wide survey of previous research on microcapsule self-healing materials, encapsulation techniques and the important parameters by in situ emulsion polymerization method. Furthermore, this chapter is aimed to present a clear stages on in situ emulsion polymerization method in order to assist student deciding the parameters to be used in the research later. Most importantly, two of the variables that will be used in the path producing linseed oil microcapsules- various concentrations of polyvinyl Alcohol, PVA and its volume will be covered and critically analyzed in this chapter.

2.1 Self-Healing Anti Corrosive Coating

Corrosion-resistance self-healing coating have become an intense discipline in the late years. The self – healing coating was categories in the family of smart/multifunctional materials based on witnessing growth and success on laboratory design and synthetic thinking. The aim is to develop a powerful system that can retain functionalities and restore their structural economically after damage with their capabilities of smart material. The ability to repair themselves should be less maintenance, prolonged material service life, and therefore potential cost reduction. Furthermore, self –healing with active coating can be attained from the smart release systems that are integrated into the polymer matrix and a section of theses application is a relatively recent concept in the corrosion protection technology started by (Karan et al. 2014) In addition, a large bit of review articles (Feng et al. 2007, Murphy et al. 2010, Solomon et al. 2008, Wool et al., 2008) focusing on the different facets of self-healing phenomena, have been brought

out recently. In parliamentary law to inflict self-healing processes in thermoset polymeric systems, different triggering mechanisms have been suggested. In the other hand, initiating self-healing process can be levied based on the complex system which are mechanical, thermal, photo, electrical or other outside stimuli (Feng et al. 2007, Murphy et al. 2010). Presently, judging by Murphy et al. (2010), the most realistic approach for self-healing systems utilizing mechanical stimulus, are self-healing polymers coating with based on incorporation of microcapsules, filled with reactive chemicals. The schematically one of microcapsule shown in Figure 2.1, are spherical particles with a typical diameter of 10-200μm, consisting of a solid polymeric shell and a liquid core material. Ideally, when fracture upon impact or high strain on the coating, microcapsule should release the low viscosity healing agent to the damaged site for subsequent healing and filling of the micro-cracks (Wu et al. 2008). Therefore, the microcapsules for coating can perform their function well stated by Tatyana et al. (2012).

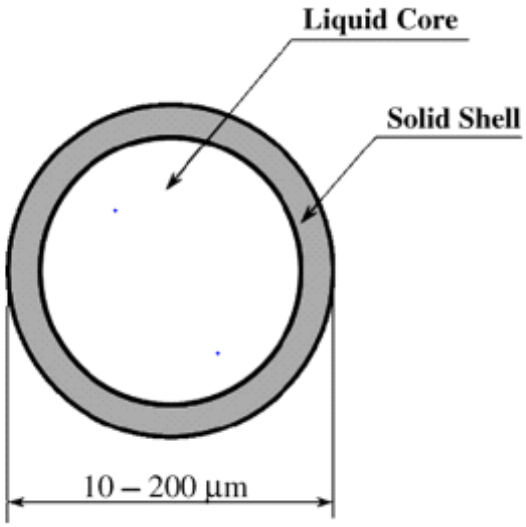

Figure 2.1: A simplified illustration of a microcapsule. (Tatyana et al. 2011)

2.2 Self-Healing Approaches

Adapted from Hayes et al. (2007), Wool et al. (2008), and also Wu et al. (2008) noted that Carolyn Dry as an innovator of self-healing approaches. In collaboration with N. Sottos in 1996, a hollow fiber system containing a reactive fluid which released into the damage sites upon fracture, reacted and healed the crack was developed stated by Sorensen *et al.* (2009). Since that the time various approaches to the thermoset polymers healing have been aimed and tested and the bearing of a healing agent is the only common thing for all of them whereas the triggering mechanism is of a principal difference. Temperature stimulus, UV-light, pH change, and as well as mechanical action are generally studied by Feng et al. (2007) as the healing system.

- **Temperature/UV –light-activated self-healing system**

Thermally reversible polymers. Wu et al. (2008) state that, a new class of highly cross-linked polymeric materials with mechanical properties similar to epoxy has been developed. These stuffs can be added to thermoset systems for healing and do not involve solvents or catalyst to lead off their study.

The attack is based on retro Diels-Adler (DA) reaction: it was found that the push to break DA adduct is much lower than to break a covalent bond of the matrix and that stands for the retro-DA reaction will be the primary pathway for crack propagation research by Chen et al. (2003). Being reheated up to 120ºC, furan and maleimide moieties, contained in the system, will reconnect again healing the fracture. The capability of multiple healing with retaining about 60% of the material's original strength was reported by Chen et al. (2003) and co-authors.

However, the healing process could not be considered as truly autonomous as the external trigger-temperature or UV-light- is needed (Benthem et al. 2007). This is the main disadvantage of the proposed system.

***Inclusion of thermoplastic additives*.** Wu et al. (2008) reported that the first self-healing system based on inclusion of thermoplastics into the thermoset matrix was developed in 1999 by Zako and Takano. Thermoplastic epoxy particles, incorporated into epoxy matrix, melt under the heating, flew into internal cracks and healed them.

"Solid-state" self-healing system was patented by Jones and Hayes in 2005 stated by Wu et al. (2008). In their approach, a linear polymer is dissolved into the thermosetting epoxy matrix and bonding to the matrix through hydrogen bonds. Under heating the added polymer becomes mobile and can diffuse through the matrix bridging the cracks. When diglycidyl ether of bisphenol-A was added as a healing polymer to bisphenol-A-based epoxy matrix, 43-50% healing efficiency was identified (Hayes et al. 2007). The systems are capable of healing small or not very open cracks.

Chain rearrangement. Polymer molecules at the crack surface possess enhanced mobility due to a higher level of freedom (Wool et al. 2008). The chain rearrangement that may occur at ambient or elevated temperature simply due micro-Brownian motion heals the cracks in the matrix through inter diffusion of dangling chains or chain slippage (Wu et al. 2008). "These ends and segments penetrate like (bent) prongs of a fork into the opposite matrix. Through kinks in the primary range and through the side groups, each prong forms a bit of physical cross-connections with the matrix" (Benthem et al. 2007). The qualifying of the mountain range ends with suitable reactive groups can contribute to improved healing performance of such systems (Benthem et al. 2007)**.**

- **pH change-triggered self-healing systems.**

Polyelectrolyte species are deposited along the surface of containers as the films – layer by layer. The containers could be complex organic molecules, or hyper branched polymers, or oxide particles, or naturally occurring halloysites filled with corrosion inhibitor. The stage of dissociation of the polyelectrolyte shell changes with the pH of the spiritualist. In case of a coating damage, the corrosion begins and the accompanying alkalinity causes release of the inhibitor from the nano container. Once pH returns to initial value, the dismissal of the inhibitory stops research by Andreeva et al. (2008). The authors described the absence of corrosion products when 2-(benzothiazol-2-ylsulfanyl) -succinic acid was applied as an inhibitor. They also noted the capability of migration of the polyelectrolyte shell and of the subsequent healing of the coating defect.

- **Mechanically triggered microcapsule-based self-healing systems**

Based on the approach originally proposed by White et al. (2001), different kinds of self-healing systems, utilizing a chemical reaction of species embedded into the polymer matrix for healing of micro fractures, have been produced. All of them employ a liquid healing agent that needs to be encapsulated into a polymeric shell in order to prevent its spontaneous mixing with the matrix material during proceeding or storage.

The overall concept of the glide path is illustrated by Figure 2.2. Microcapsules filled with healing factor as well as the catalyst are embedded into the polymer matrix. In one case a damage-induced crack propagates a capsule, release of the healing agent occurs through the capillary activity. The healing agent dissolves the catalyst which leads up a response in the fracture plane, and the forming polymeric material binds the faces of the plane together repairing the matrix‘s structural integrity. The approaches differ by organization of healing process (e.g. Number of reagents involved, their condition in matrix) and healing chemistry and will be looked at in this critique, based along the latter.