EFFECT OF AGITATION RATE AND REACTION TEMPERATURE ON THE SIZE OF LINSEED OIL MICROCAPSULE SELF- HEALING

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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 Material) (Hons.)

by

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DECLARATION

I hereby, declared this report entitled “Effect Of Agitation Rate And Reaction Temperature On The size Of Linseed Oil Microcapsule Self - Healing” is the results of my own research except as cited in references.

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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 Material) (Hons.). The member of the supervisory is as follow:

………………………………

(Project Supervisor)

ABSTRACT

This research involves studying the effect of various agitation rate and reaction temperature on the Linseed oil microcapsule size. There are several studies discussed about the effect of various agitation rate and reaction temperature on Linseed oil microcapsule attributes. In the *in situ* polymerization, Linseed oil-Poly urea formaldehyde are used as a core and shell material to produce microcapsule self-healing coating. The ideal capsule size using in paint application are in range of 200 μm to 150 μm for easily dispersed in paint matrix. The selected parameter on agitation rate and reaction temperature will determined the capsule particle size. From previous research, the higher the agitation rate, the finer capsules. But too vigorous speed also may contribute to unstable emulsion and irregular shape of capsule. The correct choice of temperature also will effect the particle size. The agitation rate parameter used to synthesized microcapsule is 200, 250, 300, 350 and 400 rpm while the temperature parameter used is 50 º C, 60º C and 70º C. It was found that the reduction of dimension microcapsules are successful as increasing the agitation rate and reaction temperature. Nevertheless, the agitation rate and reaction temperature are limited to certain points which is the capsule were not formed. Besides, it was also observed the structure of microcapsule when manipulate the variables. In a nutshell, the dimension of microcapsules are reduced when increasing agitation rate and reaction temperature.

ABSTRAK

Kajian ini melibatkan mengkaji kesan pelbagai kadar pergolakan dan suhu tindak balas pada saiz kapsul minyak biji rami. Terdapat beberapa kajian yang dibincangkan tentang kesan pelbagai kadar pergolakan dan suhu tindak balas kepada sifat kapsul minyak biji rami. Dalam in situ pempolimeran, minyak biji rami digunakan sebagai teras, dan Poly urea formaldehid digunakan sebagai shell bahan untuk menghasilkan salutan penyembuhan diri. Saiz kapsul yang ideal adalah menggunakan dalam aplikasi cat dalam lingkungan 150 μ m sehingga 200 μ m untuk mudah tersebar dalam cat matriks. Parameter kadar pergolakan digunakan untuk kapsul disintesis adalah 200, 250, 300, 350 dan 400 rpm manakala parameter suhu yang digunakan ialah 50 ºC, 60 ºC dan 70 ºC. Ia telah didapati bahawa pengurangan kapsul berjaya semasa meningkatkan pergolakan kadar dan suhu tindak balas. Walau bagaimanapun, kadar pergolakan dan suhu tindak balas adalah terhad kepada had- had tertentu yang kapsul tidak terbentuk. Selain itu, ia juga diperhatikan struktur kapsul apabila memanipulasi pemboleubah. Secara ringkas, dimensi kapsule dikurangkan apabila meningkatkan kadar pergolakan dan suhu tindak balas

DEDICATION

Dedicated to
my beloved father, Muhamad Nor Bin Md Daud
my appreciated mother, Noraini Binti Mohamed Isa
and my adored siblings, Azlin, Alyssa, and Amir
for giving me moral support, cooperation, encouragement and also understandings.

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LIST OF ABBREVIATIONS

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
DCPD	-	Dicyclopentadiene
SEM	-	Scanning Electron Microscopy
FTIR	-	Fourier Transform Infrared Spectroscopy
MUF	-	Melamine Urea Formaldehyde
rpm	-	Revolution per minutes
ENB	-	5-ethylidene-2-norbornene

CHAPTER 1
INTRODUCTION

This chapter describes the background of the research, the problem statement, objective and also the scope of the research that covered by the student.

1.1 Background of Study

Nowadays, self- healing materials receiving a lot of attention among the researchers due to their wide range of advantages, for example, higher structural reliability when apply loads, the service life of the product are prolonged, less maintenance thus reducing the costs, and also less material replacement. A self healing process, which is able to repair minor damages automatically without the need for detection. The self-healing ability is required, especially for protective coatings such as in painting application that act as an anticorrosive coating that will enhance their long-term durability and reliability stated by Xiuxiu Liu et al. (2012).

There are various approaches, such as microcapsule embedment, hollow fiber embedment and the microvascular system were applied to create self- healing coatings stated by M.L Zheludkevich et al. (2010), J.W.C. Pang et al. (2005), N.R, Sottos et al. (2009). Among these approaches, the microcapsule embedment are the most commonly used for self healing because of microcapsules facile application and easy dispersion in a matrix that suitable in painting application.

Additionally, the microcapsules are spherical particles with a diameter of 10-200 μm, consisting of a solid polymeric shell and a liquid core material. When a microcrack start initiate that originating from internal stress or a physical damage, the crack will start propagates trough the coating, and the microcapsules are supposed to rupture and release healing agents. The healing agents will flow to the fracture plane due to capillary forces. The healing agents then start to react, thus, form a polymer network and 'glue' the crack.

In the present study, students have been researching the Poly urea formaldehyde (PUF) microcapsules containing fatty as healing agents due to their own properties for corrosion resistance. The methods used to prepare microcapsules are the in- situ polymerization. During in- situ polymerization, water in oil emulsion is produced under vigorous agitation. This method offers many advantages, such as controllable microcapsule size and shell thickness, simplicity of procedure, low costs and ease of industrialization.

There are important parameter that influence the size, shape, morphology, and thickness of shell of microcapsules such as stirring speed, type of emulsifier, pH, temperature and the duration of the encapsulation reaction. In the present study, the effect of temperature and the stirring speed to the microcapsule size containing fatty oil as healing agents is investigated. Tatyana Nesterova et al. stated that the higher the agitation rate and temperature, the smaller the capsules were obtained. Moreover, there are the limits of agitation rate and temperature that can make the emulsion unstable.

In a conclusion, it seem to be essential to study the effect of agitation rate and temperature to the PUF microcapsule containing linseed oil as healing agents and also to analyze the microcapsule size upon exhibit those parameter.

1.2 Problem Statement

Paints are usually used for substrates modification either for aesthetic appearance or for corrosion protection. During its service life, the paint film leading to formation of microcracks due to the changes in mechanical properties which subsequently propagates and exposes substrates to atmospheric moisture and oxygen. Hence, the concept of self-healing is used in paint application to provide longer durability.

Ideally, the mean microcapsules size in painting is from 200 μm to 150 μm. The coating prepared from smaller size could prevent corrosion better than the larger size. It is possible that the small microcapsules could disperse in the paint matrix homogeneously. In reality, the researchers facing the problem to adjust the size of microcapsule.

There are a few parameters that influence the size of microcapsules which is stirring speed, type of emulsifier, concentration of emulsifier, pH, temperature and the duration of the encapsulation reaction. In the present work, more focus on two physical parameter, stirring speed and also temperature to get the ideal microcapsule suitable in painting. Based on the research, the higher agitation rate and temperature, the finer capsules. Thus, both parameter may reduce the microcapsules size and get the ideal size.

1.3 Objective

The objectives of this study are:-

1. To produce the linseed oil microcapsule using in-situ water oil-in- emulsion polymerization.
2. To study the effect of agitation rate and reaction temperature on the structure and dimension of linseed oil microcapsule.
3. To characterize the linseed oil microcapsules using SEM and FTIR.

1.4 Scope of this Research

The scope of this research will be focused on the microcapsule size of which is the healing agents or core are linseed oil and the shell are Poly Urea Formaldehyde (PUF). Analysis of microcapsules sizes that suitable in painting application which derived from five different agitation rate and three different temperature will be carried.

Besides, the research will only discuss on the oil-water emulsion by in-situ polymerization used to synthesis the microcapsules. The parameter of agitation rate will be carried out at five different speeds: 200 rpm, 250 rpm, 300 rpm, 350 rpm and 400 rpm. The parameter of temperature will be carried out at three different temperature: 50ºC, 60ºC, and 70ºC. Both physical parameter will be carried out to determine the influence of agitation rate and temperature on the microcapsule size. Analysis of microcapsule properties is derives from four constant parameters which are the pH value of the 1M HCL used is 3.0, concentration PVA is 10 wt%, volume PVA is 10 ml and 4h time duration.

The powder was filtered using filter paper and dry in the fume cupboard for 1 day. The microcapsule is going to be characterized using Scanning Electron Microscopy (SEM) to investigate structure, surface, and dimension of linseed oil microcapsule. Lastly, the microcapsule will undergo Fourier Transform Infrared Spectroscopy (FTIR) to analysis the presence of material in the formation of microcapsule.

CHAPTER 2
LITERATURE REVIEW

This chapter will mainly discuss the large and wide scope of self healing microcapsule, PUF containing linseed oil as healing agents. This chapter will also discussing about the preparation techniques and the important parameter in synthesizing the microcapsule.

2.1 Self healing anti-corrosive coating and its mechanism

In the 1980s, different kinds of self-healing system have been developed by researchers and their stated demonstrated the repair of polymeric materials via the addition of solvents and adhesives. However, an approach was introduced by White et al. since the other approaches used lacked the ability to initiate and complete the repair automatically. The first microcapsule-based self-healing material was introduced by White et al. and thus enable to synthesis of a truly self-healing material that initiated and completed self-repair without any outside intervention.

Irrespective of their particular characteristics, every proposed microcapsule-based self-healing system should meet the following requirements. All the reagents and newly formed polymeric materials should be compatible with the polymer matrix and exhibit good adhesion. Both the reagents and the capsule shell should survive for a long time being stable to degradation and various chemical reactions including self-polymerization.

The overall concept of the approach is illustrated by Fig. 1. The specific details of any given encapsulation- based self-healing material may differ, but the basic mechanism for the incorporation and activation of the functionality remains the same. Microcapsules filled with healing agent as well as the catalyst are embedded into the polymer matrix. Once a damages-induced crack propagates a capsule, it release the healing agent and pulled into the damages by capillary action, where contact with a catalyst or a released cross-linker phase initiates polymerization. After contact with the catalyst/cross-linker, the healing agent polymerizes and bonds the crack faces together. S.R. White et al. stated that, one of the advantages of the microcapsule approach is that cracks are attracted to the midplane of a microcapsule when the modulus of the capsule is less than that of the surrounding matrix.

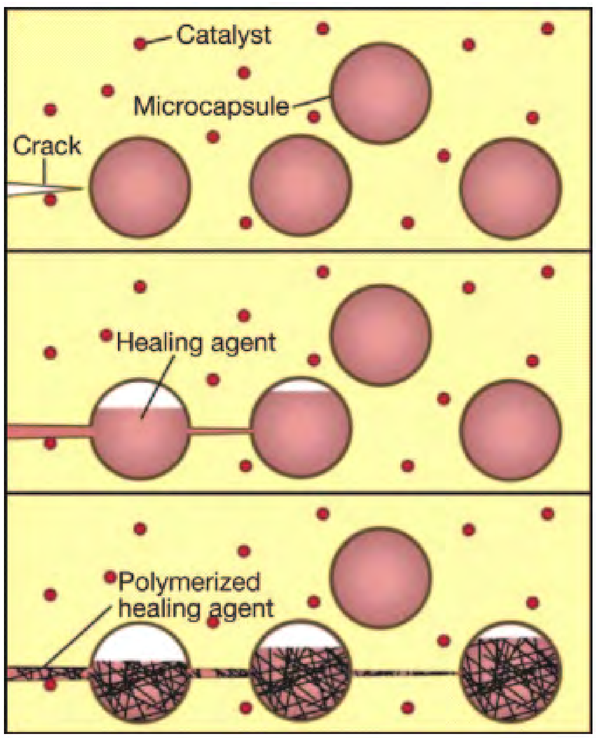


Figure 2.1 : Self healing mechanism

2.1.1 Microcapsule Requirement

To perform their function well, microcapsules for a coating use have to meet the following requirements:

- Remain intact during storage, coating formulation and application.
- Contain sufficient amount of chemicals with fast reaction kinetics.
- Rupture readily when a coating is damaged.
- Exhibit good adhesion with the polymer matrix.
- Not deal mechanical properties of the matrix.

2.1.2 Self-healing systems based on microcapsule

In self-healing approaches using microencapsulated healing agents, at least one component of the healing agent must be flow-able and stored in the microcapsules. Following addition to the polymer that requires healing, the capsules should be broken upon cracking of the matrix, thereby releasing the healing agent to the target areas via capillary effects.

Among the different classes of microencapsulated healing agent systems, as stated by Dong Yu Zhu et al. (2015), five types of healing agent systems such as single-capsule, the capsule/dispersed catalyst, the phase-separated droplet/capsule, double-capsule, and also the all-in-one microcapsules system have proven in Table 1.

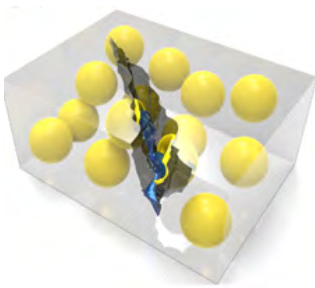
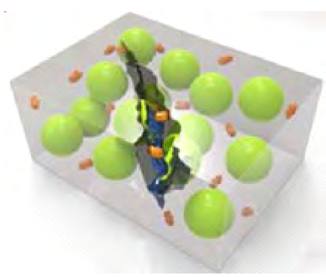
The single-capsule system consists of only one type of encapsulated healing agent. The healing agent can be a reactive chemical, suspension, solvent, or a low-melting point metal. Release of the healing agent commences reaction with the latent functional groups of the matrix, polymerization induced by the surrounding moisture environment or light, chain entanglement across the fractured surfaces, or conductive bridging.

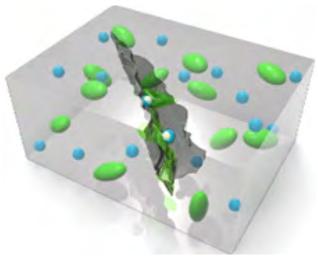
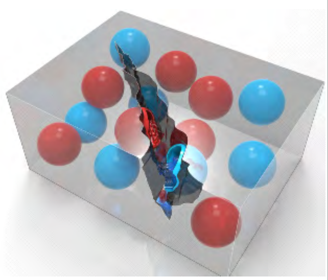
The capsule/dispersed catalyst system is based on monomer-loaded capsules and catalysts dispersed (or dissolved) in the matrix. Soon after breakage of the microcapsules due to crack propagation in the matrix, the released monomer is polymerized under the action of the neighboring catalyst.

Besides, in the phase-separated droplet/capsule system, at least one healing component undergoes phase separation, whereas the remaining component is encapsulated. The two fluids react with each other upon release from capsules. The double-capsule system is often employed if two or more reactive liquid healing agents require compartmentalization. Furthermore, the self-healing material is subjected to stringent processing conditions,i.e., heating and shear mixing.

The all-in-one microcapsules system is entirely self-contained. Both the healing agent (monomer) and a required catalyst (initiator) are either held in the core and shell wall of the same capsule and isolated from each other by layers (thus generating a multilayer microcapsule) or are encapsulated in separate smaller spheres that are stored within a larger sphere (thus generating a capsule-in-capsule). When the capsules are ruptured, the released healing agent comes in contact with the catalyst and is subsequently polymerized the absence of additional chemicals.

Table 2.1 : Typical healing systems based on microcapsules.

Type	Healing agent	Material to be healed	Healing chemistry	Healing conditions/ efficiency
Single capsules 	Encapsulated epoxy	4,4- Bismaleimido diphenyl-methane/ diallyl bisphenol A	Nucleophilic addition reaction	220 ºC, 5 h/57-79 %
	Encapsulated epoxy	Cyanate ester resin	Nucleophilic addition reaction	220 ºC, 1h/85 %
	Encapsulated linseed oil/ tung oil	Epoxy resin	Free radical polymerization	RT, 24 h/recovery of corrosion resistance.
Capsule/ dispersed catalyst 	Encapsulated DCPD (or ENB, ENB + CL) + Grubbs' catalyst (or wax protected Grubb's catalyst)	Epoxy resin; polyethylene oxide (PEO)	Ring- opening metathesis	RT, 24 h;RT, 3 h/ 75%; 93%.

Phase- separated droplet/ capsules 	Phase separated + encapsulated DBTL solution	Epoxy vinyl ester	Polycondensation	Air, 50 ºC, 24 h: water,50 ºC, 24 h/ 90%; 25%
Double-capsule 	Encapsulated epoxy + encapsulated polyetheramine	Epoxy resin	Nucleophilic addition reaction	RT, 24 h / 84.5%