One-part self-healing anticorrosive coatings via microencapsulation of reactive agents

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**NANYANG
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UNIVERSITY**

**ONE-PART SELF-HEALING ANTICORROSIVE
COATINGS VIA MICROENCAPSULATION OF
REACTIVE AGENTS**

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2013

One-Part Self-Healing Anticorrosive Coatings via Microencapsulation of Reactive Agents

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Abstract

Corrosion is a worldwide open issue and corrosion control has been one of the most important factors in the fields of materials design and application. Various traditional approaches have been developed and applied to address this problem. However, most of such methods are passive and lack of active response to damage events. Recently the concept of self-healing has been employed to develop anticorrosive coatings with different chemistries via microencapsulation. To date most of such coatings are based on two-part chemistries to trigger healing reaction, which increases manufacturing complexity and environmental concern. In this study, two novel reactive agents were adopted and successfully microencapsulated as self-healing additives to protective coating for active corrosion control upon damage events. The healing agents are reactive with water that is the essential media to facilitate corrosion process. Two self-healing anticorrosive coating systems were developed and comprehensively characterized.

The first healing chemistry is based on a highly reactive liquid diisocyanate monomer, hexamethylene diisocyanate (HDI), which is encapsulated into polyurethane microcapsules through a facile interfacial polymerization reaction. The synthesized capsules are integrated into epoxy to prepare self-healing anticorrosive coatings. The HDI-filled microcapsules are characterized by different analytical techniques, and the influences of reaction variables such as reaction time, temperature, agitation rate, *etc.* on the resultant capsules are investigated. The shelf life of the microcapsules in different environment is studied, and it is found that the barrier property of the microcapsule is yet to be improved. The corrosion protection performance of the prepared HDI microcapsules based self-healing coating is evaluated by an accelerated salt immersion test and a comprehensive salt spray test

following industrial standard. DC electrochemical test and electrochemical impedance study are also performed to quantitatively assess the self-healing and anticorrosive property of the coatings. The test results reveal that the HDI based coatings provide excellent corrosion protection upon manual scratches towards metal substrates via a self-healing mechanism.

The second self-healing chemistry is based on *1H,1H',2H,2H'*-perfluorooctyltriethoxy silane (POTS), a commercial organic silane. In this study, it has been encapsulated into poly(urea-formaldehyde) microcapsules through an *in situ* polymerization reaction. The produced microcapsules are comprehensively characterized and the influences of the reaction parameters on the resultant microcapsules are investigated. The microcapsules show good environmental stability. The synthesized POTS-filled microcapsules are used to develop self-healing coatings, and the excellent corrosion protection ability of the prepared coatings to metal substrate is demonstrated by different test methods.

The anticorrosive mechanisms of the new microcapsule-based coatings via self-healing reaction are discussed. The healing or sealing performance is directly related to the availability of healing agents. Based on a simplified damage model, the influence of the variables on the crack sealing performance of the prepared coating is discussed, and it is found that the amount of available healing agents in a crack is proportional to the microcapsules size, weight fraction of microcapsules in coating and the coating thickness, which is agreeable with the experimental observation. In addition, the anticorrosive mechanism is briefly discussed for the intact coating where self-healing microcapsules serve as numerous reservoirs to trap and react with the diffused water and thus to retard the corrosion process.

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List of Abbreviations

AC	alternating current
AFM	atomic force microscopy
CNT	carbon nanotube
CMC	critical micelle concentration
DCPD	dicyclopentadiene
DC	direct current
EIS	electrochemical impedance spectroscopy
EDX	energy-dispersive X-ray spectroscopy
FTIR	Fourier transform infrared spectroscopy
HDI	hexamethylene diisocyanate
IPDI	isophorone diisocyanate
MBT	mercaptobenzothiazole
MDI	methylenediphenyl diisocyanate
MRT	minimum reaction time
OM	optical microscopy
POTS	<i>1H,1H',2H,2H'</i> -perfluorooctyltriethoxy silane
PU	polyurethane
PUF	poly(urea-formaldehyde)
PMF	poly(melamine-formaldehyde)
SEM	scanning electron microscopy
SVET	scanning vibrating electrode technique
SNAP	self-assembled nanophase particle
TGA	thermogravimetric analysis
TDI	toluene diisocyanate

Chapter 1 Introduction

1.1 Background

Corrosion is a worldwide open issue and it causes huge economic loss annually. According to a corrosion costs study conducted by the National Association of Corrosion Engineer, the direct cost of corrosion in the U.S. was USD 468.1 Billion in 2011, taking up 3.1 % of the USD 15.1 Trillion U.S. gross domestic product (GDP), and it is estimated that the total cost of corrosion will exceed USD 1 Trillion in 2012 in the U.S. [1]. Sometimes corrosion may even lead to catastrophic accidents such as collapse of buildings and bridges. Corrosion is problematic especially in the field of automotive, aerospace, petroleum industries and many other industrial fields. Prevention and control of metal corrosion is one the most important concerns for materials applications, and to date many strategies have been developed to alleviate corrosion damage. Traditional approaches for corrosion control include material selection, cathodic protection, addition of corrosion inhibitor, engineering design, *etc.* [2-4] Among those approaches, the application of coating and painting is the most straightforward and convenient one, which takes the about 88.3% of the total corrosion cost [3]. A coating layer will primarily provides a barrier layer that directly separates metal from corrosive environment, and it may also serve as a sacrificial layer that offering cathodic protection to the underlying metal [5]. Usually anti-corrosive pigments or corrosion inhibitors are integrated into coatings in order to further retard corrosion process of the underneath metal [6].

For the coatings protected structures, even for heavy duty protective coatings, there are still high risks to induce microcracks in those surface layers during storage, transportation, and service of those structures. When damages or microcracks are

formed in a coating, a path will be created through which external corrosive agents will attack the underlying metals and result in corrosion. There is no solution to solve this issue for the commercial coatings. As a novel strategy to address this problem, the concept of self-healing has recently been proposed. A self-healing coating is able to autonomously repair the damaged area and therefore seal the path. Hence, the corrosion will be effectively retarded or suppressed.

Research of self-healing materials started from last century [7-14]. However, most of early self-healing materials are not real “self” healing because they require manual intervention such as energy input to deliver healing agent to the damaged locations [11, 15] or to activate the healing process via heating or irradiation [16]. The first generation of real self-healing materials was developed by White *et al.* in 2001 [17], which was based on encapsulated dicyclopentadiene (DCPD) and dispersed Grubbs’ catalyst particles. When the material is damaged, the autonomous healing process does not require any detection or manual intervention to initiate the healing reaction.

In modern self-healing coatings, healing species are stored in reservoirs such as microcapsules that are randomly distributed in host material. For most existing self-healing coatings, the healing reaction often requires catalyst, which is directly dispersed within the host matrix. Nevertheless, the dispersed catalyst may interact with the components of polymer, and this interaction may not only deactivate the catalyst, but also induce detrimental effects to matrix materials. To prevent this problem, a dual-capsule system was proposed, in which healing agents and catalyst were encapsulated separately [18, 19], and the two types of microcapsules were both distributed in host matrix. Dual-capsule system is also employed when the healing behavior is based on a two-part reaction between resin and hardener, For example, Jin

et al. reported a self-healing epoxy, in which the self-healing was achieved with a dual-microcapsule epoxy-amine chemistry [20]. However, the introduction of extra microcapsules may bring some unfavorable effects to the matrix, and the procedure for the self-healing coatings preparation will be more tedious and complex.

Considering the limitations of existing self-healing coatings as mentioned above, the present study aims to develop one-part and catalyst free self-healing anticorrosive coatings based on novel chemistries. Compared with the existing self-healing coatings, herein the whole fabrication process is greatly simplified, the potential unfavorable impact of microcapsules to the host polymer matrix is reduced, and the use of catalyst is avoided, which is of considerable economic importance.

1.2 Objective

The final target of the present study is to develop effective anticorrosive coatings via adopting novel self-healing chemistries. To implement this target, the detailed breakdown objectives are:

- a) to explore novel chemistries which can be adopted to develop one-part self-healing additive;
- b) to investigate proper methods to microencapsulate the targeting reactive chemicals;
- c) to characterize the quality of the synthesized microcapsules;
- d) to develop and comprehensively evaluate various formulations of self-healing coatings via incorporation of microcapsules;
- e) to analyze the anticorrosive mechanisms in the scratched and intact coatings after introducing self-healing microcapsules.

1.3 Scope of work

The present study is focused on microcapsules based self-healing anticorrosive coatings. Fabrication of microcapsules based self-healing system generally consists of two steps. In the first step, microcapsules filled with healing agents are synthesized, and in the second step, the synthesized microcapsules are integrated into polymer matrix to create the self-healing anticorrosive coatings. Hence, the scope of the present study is as follows:

(a) Microencapsulation of healing agents

Synthesis of microcapsules containing different healing agents is realized through different methods such as interfacial polymerization and *in situ* polymerization. The reaction parameters are delicately monitored to investigate their influences on resultant microcapsules, and the synthesis process is optimized to produce microcapsules with optimum properties for self-healing application. The prepared microcapsules are characterized by different analytic techniques such as optical microscopy (OM), scanning electron microscopy (SEM), Fourier transform infrared spectroscopy (FTIR) and thermogravimetric analysis (TGA), *etc.* The stability of the produced microcapsules in different environment is investigated.

(b) Fabrication and characterization of self-healing anticorrosive coatings

The synthesized microcapsules are integrated into polymer matrix to generate self-healing coating, and the self-healing and corrosion protection performance of the prepared coating are evaluated by different test methods such as salt immersion corrosion test, salt spray test, DC electrochemical test and electrochemical impedance spectroscopy (EIS) measurement. The self-healing mechanism is proposed to explain the excellent corrosion protection function of the prepared coatings. In addition, some parameters of the coatings such as the weight fraction of the microcapsules in the

coating, microcapsules diameter and coating thickness are tuned to study their effects on the anticorrosive properties of the coatings, and a model is proposed to explain these effects.

1.4 Thesis outline

This thesis is organized as follows:

Chapter 1 gives a brief introduction to the background of the present research, and highlights the objective and scope of my project.

Chapter 2 presents the literature review related to the topic of my research, which mainly includes backgrounds of corrosion, conventional approaches for corrosion control and self-healing anticorrosive coatings.

Chapter 3 describes the experimental procedures and characterization methods. It includes the materials used in the project, synthesis and characterization of microcapsules, as well as the preparation and characterization of self-healing anticorrosive coatings.

Chapter 4 presents the results for the microencapsulation of hexamethylene diisocyanate (HDI) and the HDI microcapsule based self-healing coating. The microcapsule synthesis and the influences of reaction parameters are discussed, and the self-healing anticorrosive property of the prepared coating are demonstrated by different methods.

Chapter 5 describes the results for the microencapsulation of *1H,1H',2H,2H'*-perfluorooctyltriethoxy silane (POTS) and the POTS microcapsule based self-healing coating. The microcapsules synthesis and the anticorrosive performance of the POTS-based coating are carefully investigated.

Chapter 6 discusses the self-healing mechanism of the excellent anticorrosive properties of the microcapsules-based coatings. A model is proposed to explain the

influences of several factors on the self-healing anticorrosive performance of the prepared coatings.

Chapter 7 concludes this report with the highlights of future works.

Chapter 2 Advances in Self-Healing Anticorrosive Coatings

2.1 Corrosion and traditional protection methods

2.1.1 Background of corrosion

Corrosion of metal is one of the most destructive processes that results in material failure, and it will cause huge economic loss annually. Corrosion is a destructive attack of a metal by chemical or electrochemical reaction with the environment, and it is an electrochemical process that involves anodic reaction and cathodic reaction [2, 21]. Reduction reactions and oxidation reaction occur at the cathodic area and anodic area, respectively, while the corrosion of metal usually occurs at the anodic area.

As an example, the corrosion of iron is demonstrated in Figure 2.1. It can be seen that, when an iron panel is immersed in corrosive electrolyte solution, the cathodic reaction consists of the reduction of dissolved oxygen, hydrogen ion and water, while the oxidation reaction at the anodic area dissolves iron to produce Fe^{2+} , leaving voids in the iron panel. Usually Fe^{2+} will react with OH^- in the solution to yield $\text{Fe}(\text{OH})_2$, and after a serial of further reactions, finally Fe_2O_3 will be produced, and this is the rust that one usually see on a corroded iron.

There has not been an universally accepted classification for corrosion, but most corrosions that people encounter can be categorized into uniform corrosion, galvanic corrosion, cosmetic corrosion, crevice corrosion and pitting corrosion based on their mechanism and the appearance of the corroded materials [22].

Corrosion control is one of the most important issues when people use metals. To date many strategies have been developed to alleviate corrosion damage, and

Figure 2.1 Mechanism of iron corrosion in water.

traditional approaches include material selection, cathodic protection, addition of corrosion inhibitor, engineering design, and the forth [2-4]. Material selection means that more corrosion resistant material is used, and one of the most common examples of such material is stainless steel. For cathodic protection, the metal to be protected is made as the cathode in an electrochemical cell, while the anode is a more active metal, which is also called sacrificial anode. This strategy has been widely used in many fields such as fuel pipelines, storage tanks, ships, offshore oil platform, and so forth. Use of corrosion inhibitor to suppress or retard corrosion process is also very common. For example, it has been a long history that chromates are added into primer to provide corrosion protection function to metal substrates. Engineering design plays a significant role in corrosion control as well. For example, the structure should be designed so that stagnant zones is avoided, and try to use welding instead of bolted or riveted joints to minimize crevice corrosion.

2.1.2 Traditional approaches for corrosion control

Use of corrosion inhibitors for anticorrosion application has a long history [23, 24], and they are still extensively used in anticorrosive products. For example, the anticorrosion function of most commercial anticorrosive primer or coatings is from

various anticorrosive pigments. Corrosion inhibitor is a chemical that is able to inhibit or suppress corrosion process, and usually only small amount of it is used. Some inhibitors retard the anodic reaction or the cathodic reaction, while some others may interfere with both reactions [5].

According to the modes of inhibition, corrosion inhibitors can be classified into three types: passivator, adsorption inhibitor and barrier inhibitor [25]. Passivators are anodic inhibitors that cause a large anodic shift of the corrosion potential, forcing the metallic surface into the passivation range. They are usually inorganic oxidizer, and they deactivate the anodic site on the metal surface by causing the local current density to exceed the amount required for passivation. Chromates (CrO_4^{2-}) and nitrites (NO_2^-) are the most popular passivators, and they exhibit excellent passivating performance on steel even in deaerated solutions. However, it is noteworthy that the use of chromates has been restricted in many countries due to their environmental toxicity [26]. Adsorption inhibitors are usually organic molecules or mixture of them, and they have slight effect on the corrosion potential. Most of adsorption inhibitors contain a polar group such as amine, sulfide or hydroxyl groups, by which the molecules can attach themselves to the metal surface. For example, thiourea [27] and some benzotriazole derivatives [28] have been proved to exhibit excellent corrosion protection to aluminum. However, when adsorption inhibitors are employed for anticorrosion purposes, it is important to ensure the adsorbed inhibitor to reach a critical concentration in order to realize inhibition. Otherwise, the corrosion process may be even accelerated [21]. Barrier inhibitors are able to form a surface layer on metal, which serves as a barrier to prevent the attack of external environment to the metal and hence suppress corrosion process. For example, phosphate is extensively employed as an additive in boiled water in pickling baths for metals. Phosphate is able

to combine with ferrous or ferric ions to form a layer of phosphate precipitation. Silicates are also widely used as barrier inhibitors for corrosion protection application.

Usually corrosion inhibitors are directly added into coating to yield a corrosion inhibition function. However, for direct loading, it is noteworthy that the inhibitor should not interact with the coating components. Otherwise, the coating may be degraded to lose its barrier property, and in the meantime, the inhibition function of the corrosion inhibitor may be compromised [29]. To overcome such problems, corrosion inhibitor can be stored in micro- or nano- reservoirs before addition. The reservoirs can be capsules or other forms of containers [30]. The containers serve not only to protect the inhibitor but also to control the release rate of inhibitor, which is favorable for long term anticorrosion performance. For example, Fix *et al.* loaded corrosion inhibitors, 8-hydroxyquinoline and benzotriazole, into halloysite nanotubes to develop an anti-corrosive sol-gel coating, and it was found that the coating performed excellent corrosion protection function for a long period of immersion in salt solution [31].

2.2 Self-healing polymeric materials

2.2.1 Background of self-healing materials

Damage and degradation of polymeric materials is a very common issue in the field of materials. Conventionally, material failure control involves damage detection, damage prediction and repair or replacement. However, the conventional approaches are highly limited in real application because they always require manual intervention, and sometimes, such as in case that the damage is deep in materials, manual detection and repair are almost impossible. If polymer is able to autonomously repair the damage at the early stage, the lifespan of materials will be extended. Self-healing

materials can effectively diminish the cost of repair and replacement and therefore are of considerable importance in many fields.

Self-healing behaviors is a ubiquitous phenomenon in nature. For example, animals are able to self-heal via a “bleeding” mechanism when their skin experiences injury or scratches [11]. In such a process, the biological system responds to external stimuli, injury for example, and transfers healing species to the injured location to heal the injury. Inspired by nature, modern self-healing materials are also able to sense damage and release healing agents to realize self-healing function. Healing species are stored in reservoirs that are distributed in host material. Damage and degradation of polymeric materials often start from the formation of micro-cracks, and the stored healing species will be released when the reservoirs are ruptured by the propagating micro-cracks. The healing species then flow into the crack plane, undergoing healing reactions to form a film to re-bond or seal the cracks. The reservoirs can be hollow tube [4], inter-connected microvascular network [32, 33] or microcapsules, and microcapsules are most popular for healing applications because they are applicable in more situations. Self-healing is advantageous over traditional techniques including welding, patching and *in situ* curing of resin for repairing materials because it is much more time and cost efficient [9].

Based on the application, self-healing polymer can be generally categorized into self-healing bulk polymer composite and self-healing coating. Self-healing bulk polymer composite is usually used for structural purpose, while self-healing coating is mainly applied on the surface of an object to provide protection or decoration function. Although self-healing bulk materials and coatings basically share the same healing mechanism, they differ in many aspects including manufacturing and application, *etc.*

Compared with thin coating, bulk polymer composites allow for the use of capsules with larger diameter for healing, and this is very beneficial to achieve higher healing efficiency since larger capsules can store more healing agents. At the same time, larger capsules are more likely to sense the crack and get ruptured to initiate the healing process [34]. In addition, some self-healing techniques can only be used in bulk polymer composites rather than polymer coating due to the restriction of mass and volume of the host matrix. For example, microvascular network [33] or hollow fiber [35] containing healing agent can be embedded into bulk polymer to induce healing function, but they are hard to be integrated into thin film. However, in some other cases, some self-healing strategies suitable for thin coating may not be applicable for bulk composites. For example, if the healing reaction of a self-healing system is triggered by UV radiation, it may not be used in composites because UV radiation is hard to penetrate the composite and reach the crack where self-healing behavior is desired [36].

Different from bulk materials and composites, polymeric coatings mostly provide decoration and protection function to the substrates on which coatings are applied, and therefore their design and preparation is greatly different from those for bulk materials. For example, since coatings are often applied on the surface of objects, the influences of external environment including moisture, UV radiation, temperature shift, oxygen and many other factors have to be taken into consideration when self-healing coatings are designed [8]. In addition, coatings are typically thin and it also brings some limitation to the design of self-healing coatings. For instance, when microencapsulation technique is used to fabricate a self-healing coating, the diameter of the capsules should be more delicately monitored so that other properties of the coating are not compromised.

Due to their great importance, self-healing materials have been the focus of researchers since last century, and many approaches have been developed for their manufacturing. However, most of early self-healing materials actually are not really self-healable because they require manual intervention such as heating and irradiation. For example, Jud *et al.* [16] reported the self-healing performance of a thermoplastic polymer, but the healing was realized at elevated temperature that allowed for molecular inter-diffusion. Chung *et al.* [37] reported the self-healing behavior of a poly(methoxy methylacrylate) coating, but light irradiation was necessary to trigger the cyclo-addition reaction of cinnamoyl groups to achieve the healing purpose.

In an ideal self-healing system, the healing behavior should be completely autonomous without any manual intervention. In this sense, the first self-healing material was developed by White *et al.* [17] in 2001. Dicyclopentadiene (DCPD) monomer was stored in poly(urea-formaldehyde) (PUF) microcapsules, which were evenly distributed in a polymer matrix. The self-healing function was realized via the polymerization of DCPD when the monomer contacted pre-dispersed Grubbs' catalyst particles. The whole process did not require any detection or manual intervention to initiate the repairing behavior and thus was deemed as self-healing. To date, a number of self-healing materials have appeared, and the progress on this topic can be found on many review papers [10-12, 38, 39].

2.2.2 Preparation of self-healing materials

To date a large number of self-healing materials have been reported. In self-healing polymeric materials, healing agents are usually stored in reservoir that is distributed in the host polymer, and they will be released in response to external stimuli. Based on the reservoirs used, self-healing materials can be generally divided into three groups: microcapsule-based [40, 41], hollow tube-based [4] and

microvascular-based [32, 33]. Some systems use interfusion to induce the self-healing ability and they also exhibit good self-healing ability, but most of them actually require external intervention. For example, an oxetane-substituted chitosan precursor incorporated polyurethane (PU) that displayed good self-healing performance was reported [42], but UV radiation was necessary to trigger the healing reaction. The methods people used to manufacture self-healing materials are highly dependent on the particular system.

Preparation of microcapsules based self-healing materials involves microencapsulation, a technique of encapsulating core material into microcapsules. Microencapsulation has been applied in various fields such as agriculture, pharmaceuticals, foods, textiles, coatings, flavoring and fragrances, adhesives, *etc.* for a long time [43], and it has also become one of the most important methods to design self-healing materials because it can be used for both bulk polymer composites and thin polymer coatings, and the amount of healing agent could be monitored by tuning the microcapsules size. The healing function is usually realized by the polymerization reaction of healing agent that is stored in microcapsules, and in most cases, catalyst is necessary for triggering such a reaction. In a typical microcapsule-based system, the microcapsules containing healing agents are ruptured when cracks form in the host polymer matrix, and the encapsulated healing agents are hence released. Upon contact with catalyst, the healing agents undergo polymerization, forming a film to heal the cracks (Figure 2.2) [10]. The self-healing polymer may be based on mono-capsules basis, in which the healing agent is encapsulated and catalyst is directly distributed in host matrix. Alternatively, self-healing polymer may be based on a dual capsules basis, in which healing agent and catalyst are both encapsulated in discrete capsules, and the capsules are then randomly distributed in host polymer matrix. Samadzadeh *et al.*

Figure 2.2 Mechanism of healing in a microcapsule-based system [10].

reviewed the recent progress of microcapsules-based self-healing materials [44].

Microencapsulation can be reached via a number of methods such as coacervation [45, 46], interfacial polymerization, spray drying [47, 48], *etc.* The microencapsulation techniques can be generally classified into chemical process and physical or mechanical process [49]. However, it is noteworthy that sometimes one microencapsulation may involve both chemical and physical process. Among the numerous methods for microencapsulation, interfacial polymerization and *in situ* polymerization are most common for self-healing materials development.

Interfacial polymerization usually takes place in a normal oil-in-water emulsion system, which is prepared by dispersing a water immiscible organic liquid (oil phase) into aqueous continuous phase with the assistance of surfactant. In a typical interfacial polymerization reaction, one reactant of the polymerization and target core materials are contained in the oil phase, while the second reactant is in the

aqueous phase. Polymerization reaction between the two reactants from different phases occurs to generate a polymer wall at the interface between the aqueous and organic phases, with core material being encapsulated [50].

Although interfacial polymerization has been widely used for microencapsulation [18, 19, 44], its application for self-healing has appeared in only a few publications, and the capsules were mainly restricted to PU and polyurea. Yang *et al.* [51] reported the microencapsulation of isophorone diisocyanate (IPDI) by PU microcapsules via an interfacial polymerization. In this study, a toluene diisocyanate (TDI) based PU prepolymer was prepared at first, which was mixed well with IPDI, the target core material, to form the oil phase. After the generation of oil-in-water emulsion system by adding the oil phase into aqueous continuous phase, addition of chain extender 1,4-butanediol initiated its polymerization reaction with more reactive TDI prepolymer from the oil phase, while the less reactive IPDI was encapsulated as core material.

The IPDI filled polyurethane microcapsules had smooth surface (Figure 2.3). As illustrated in Figure 2.4, the diameter and shell thickness of the obtained microcapsules were highly dependent on agitation rate during the reaction. When the agitation rate was 500 RPM, the prepared capsules had a diameter of about 413 μm and a thickness of about 17 μm . This is the first successful encapsulation of liquid

Figure 2.3 Surface and shell morphology of IPDI-filled PU microcapsules [51].

Figure 2.4 (a) Microcapsules size histograms at different agitation rates; (b) average microcapsules diameter as a function of agitation rate [51].

state reactive isocyanate monomer, whose high reactivity with water makes it potential for the development of one-part and catalyst-free self-healing system.

In a similar fashion, Cho *et al.* [18, 19] encapsulated organotin including di-*n*-butyltin dilaurate, dimethyldineodecanoate tin and tetrakis-(acetoxidybutyltinoxy)-silane for self-healing polymer. Organotin effectively catalyzes the poly-condensation of hydroxyl end-functionalized polydimethylsiloxane and polydiethoxysiloxane. The siloxane-based healing agents, either phase separated or encapsulated, and the encapsulated organotin catalysts were both randomly distributed in vinyl ester matrix to yield a self-healing system.

If the core material to be encapsulated is water soluble, the microencapsulation via interfacial polymerization can be realized in an inverse emulsion, in which aqueous phase is dispersed into organic continuous phase to produce a water-in-oil emulsion system. Core material and one reactant are contained in the water phase. After the addition of the second reactant to the organic phase, polymerization of the reactants also occurs at the interface between aqueous and organic phases to produce capsules. For example, McIlroy *et al.* [52] prepared polyurea microcapsules containing a reactive amine through interfacial polymerization in an inverse emulsion. DEH-52 is a reactive amine, and it can be used as curing agent for epoxy resin. In this

study, DEH-52 was mixed with diethyltriamine to form the aqueous phase, which was added into a prepared oil continuous phase to create a water-in-oil reverse emulsion system. After the addition of TDI into the continuous phase, the polymerization reaction between TDI and diethyltriamine generated polyurea microcapsules at the phase interface.

Sometimes the microencapsulation via interfacial polymerization can also be reached in oil-in-oil emulsion system. For example, Kobaslija *et al.* [53] demonstrated the preparation of polyurea microcapsules containing coumarin-1 through interfacial polymerization reaction in an oil-in-oil emulsion. The continuous phase was cyclohexane, and the disperse phase was methanol, formamide, or *N,N*-dimethylformamide. Polyethylenimine, one reactant contributing to the capsule shell, and the target core material coumain-1 were contained in the disperse phase, while polyisobutylene as polymeric stabilizer was contained in the continuous phase. When the oil-in-oil emulsion system was created by adding the disperse phase into the continuous phase, addition of TDI into the continuous phase resulted in microcapsules at the phase interface, and coumarin-1 was encapsulated.

When interfacial polymerization is used for encapsulation, the capsules size can be controlled by adjusting the reaction parameters such as agitation speed and surfactant concentration. Generally speaking, higher agitation speed and higher surfactant concentration result in smaller capsules. If capsules with even smaller size are desired, some other assisting techniques such as ultrasound agitation should be used. For example, Torini *et al.* [54] prepared nano-scale PU capsules via a modified interfacial polymerization reaction. The mixture of cyclohexane and IPDI as oil phase was added into a sodium dodecyl sulfate aqueous surfactant solution under stirring to develop an emulsion, and then ultrasound was applied to create a mini-emulsion.

Figure 2.5 SEM image of polyurethane nanocapsules prepared from interfacial polymerization in mini-emulsion [54].

Another reactant 1,6-hexanediol was then introduced into the mini-emulsion system, and the polymerization reaction between 1,6-hexanediol and IPDI yielded capsules, while cyclohexane was encapsulated as core material.

The prepared nanocapsules had smooth surface as shown in Figure 2.5, and the average diameter was about 200 nm. However, it could be observed that most of the yielding capsules agglomerated, and this is a very common problem for nanoparticles due to their high surface area-to-volume ratio [55].

In situ polymerization has been one of the most popular methods to encapsulate active agents for self-healing application. Similar to interfacial polymerization, *in situ* polymerization also takes place in an emulsion system, but the reactants for the polymerization are from the same phase.

PUF is an excellent material that has been widely used in self-healing material. Microcapsules made from PUF are robust enough to withstand processing for self-healing materials manufacturing, and they can also be ruptured easily by propagating micro-cracks [56]. Yuan *et al.* [57, 58] reported the preparation of PUF microcapsules containing epoxy resin through a two-step reaction. In the first step, urea-

formaldehyde prepolymer was synthesized in aqueous phase, and in the second step, epoxy resin, the target core materials, was added into the obtained prepolymer solution to create an oil-in-water emulsion. The *in situ* polymerization of the urea-formaldehyde prepolymer yielded PUF microcapsules with epoxy resin encapsulated inside.

Brown *et al.* [40] reported a single-step reaction for the preparation of PUF microcapsules through *in situ* polymerization, and it has become a standard procedure for PUF microcapsules synthesis. In their study, DCPD was encapsulated into PUF microcapsules and the procedure is outlined in Figure 2.6. To ethylene maleic anhydride surfactant solution, urea, ammonium chloride and resorcinol were added. After dissolution of these chemicals, the pH value of the solution was adjusted to 3.5 by adding sodium hydroxide and hydrochloric acid. DCPD liquid was added into the aqueous solution under stirring to create an oil-in-water emulsion system. 37 wt.% formaldehyde solution was then introduced into the system. Ammonium

Figure 2.6 Synthesis of PUF microcapsules via *in situ* polymerization [40].

chloride served as hardeners while resorcinol was a further brancher involved in the polymerization reaction with urea and formaldehyde [59]. Resorcinol also behaved to improve the resistance of PUF bonds to the influence of water in the synthesis [60]. The *in situ* polymerization between urea and formaldehyde in the aqueous phase produced PUF microcapsules surrounding the DCPD oil droplets.

SEM images of the shell structure of the prepared PUF microcapsules as shown in Figure 2.7 revealed that the capsule shell was comprised of a smooth inner surface and a rough outer surface. The thickness of the inner surface was between 160-220 nm, and it was largely independent on synthesis parameters. The outer surface was an agglomeration of PUF nanoparticles. The microcapsules as prepared contained 83-92 wt.% DCPD, and the capsules diameter ranged from 10-1000 μm depending on agitation rate.

The influence of synthesis parameters on the resultant PUF microcapsules including the size, surface morphology, storage stability, solvent resistance and mechanical strength was extensively studied. The microcapsules size and shell thickness were primarily controlled by agitation rate [40]. The higher agitation rate

Figure 2.7 SEM image of shell structure of PUF microcapsules prepared via *in situ* polymerization [40].

used in the synthesis, the smaller the diameter and shell thickness of capsules. Surfactant concentration also dramatically influenced the capsules size and size distribution, and higher concentration yielded smaller capsules with a narrower size distribution. It was found that the microcapsules size was also dependent on the initial weight ratios of core/shell materials. Higher weight ratio resulted in larger microcapsules, and it was explained by the fact that larger amount of core materials led to larger core oil droplet size in the emulsion, which in turn determined the larger diameter of the final microcapsules. The same observation was also reported by other researchers [61].

The method as described above has been used as a standard method to prepare PUF microcapsules. For example, Suryanarayana *et al.* [62] reported the microencapsulation of linseed oil by PUF microcapsules via an *in situ* polymerization following a very similar procedure, and García *et al.* [63] also similarly encapsulated a water reactive silyl ester for self-healing purposes.

Poly(melamine-formaldehyde) (PMF) microcapsules are also extensively used for self-healing application, and they are advantageous over PUF microcapsules in their mechanical properties, stability and chemical resistance [64-66]. PMF microcapsules can also be prepared via *in situ* polymerization following a procedure similar to that for PUF microcapsules. For example, Yuan *et al.* [64] reported the microencapsulation of polythiol by PMF microcapsules in an oil-in-water emulsion system. Poly(styrene-maleic sodium) was synthesized as emulsifier first. The Target core material polythiol was added into the emulsifier solution under stirring to develop an emulsion. Melamine-formaldehyde prepolymer was prepared separately, which was then added into the emulsion to allow for the polymerization reaction at a certain pH value and temperature. The polymerization of melamine-formaldehyde

prepolymer occurred in the continuous phase, and the resultant microcapsules were produced surrounding the polythiol oil droplets. Again, the diameter and size distribution of the capsules were found to be highly dependent on the agitation rate and emulsifier concentration. DCPD filled PMF microcapsules were also similarly prepared via an *in situ* polymerization in an oil-in-water emulsion system [65].

Similar to that for interfacial polymerization, it is able to manufacture capsules with even smaller size when a normal *in situ* polymerization procedure is slightly modified. For example, as demonstrated by Blaiszik *et al.* [67], during the microencapsulation of DCPD by PUF microcapsules following the established procedure [40], if the solution was agitated by ultrasound for 10 min after the addition of urea, ammonium chloride and resorcinol into the ethylene maleic anhydride surfactant solution, the diameter of the resultant capsules could reach as small as about 1.5 μm . When co-stabilizer such as hexadecane or octane was added into DCPD to decrease the Ostwald ripening [68], the diameter of the resultant capsules could be even reduced to about 220 nm, as shown in Figure 2.8.

Interfacial and *in situ* polymerization reactions have been extensively explored for microencapsulation. However, when microencapsulation is applied to develop

Figure 2.8 Image of nanocapsules prepared by a modified *in situ* polymerization [67].

self-healing materials, microcapsules made from single component may not meet the complicated and strict requirement in practical application [69]. For example, PU microcapsules possess excellent mechanical and thermal property, but they are likely to agglomerate due to the cross-linking of residual isocyanate functional groups and hence the distribution into host matrix may be problematic [70]. PUF microcapsules also have good mechanical property and they can be easily distributed into host polymer, but they are unable to withstand high temperature, which is usually required in materials processing. To overcome these limitations, researchers developed techniques to prepare multi-layered microcapsules to encapsulate active agents for self-healing applications. Microcapsules composed of two or more materials possess the combined advantage while avoid the disadvantage of each single material and hence are superior.

Multi-layered microcapsules can be prepared via a procedure combining interfacial polymerization and *in situ* polymerization. It can be achieved from a multi-step procedure. Initial single-layer microcapsules are synthesized first, which are then used as template for the second microencapsulation to create multi-layered capsules. For example, Li *et al.* [71] reported the preparation of polyurea-urea-formaldehyde double layered microcapsules through a two-step procedure. Polyurea microcapsules

Figure 2.9 Cross section micrograph of (a) single-layered polyurea microcapsules and (b) double-layered microcapsules under optical microscope [71].

containing red oil were prepared at first by interfacial polymerization of TDI and triethylene tetraamine in polyvinylpyrrolidone surfactant solution. In the second step, the prepared polyurea microcapsules were used as template, and the second layer of PUF shell was manufactured by an *in situ* polymerization. The produced PUF deposited on the initial polyurea template and finally yielded double-layered microcapsules as shown in Figure 2.9. The average diameter of the double-layered polyurea-urea-formaldehyde capsules as prepared were bigger than that of the single layered polyurea capsules, and this is the reasonable consequence of the deposition of an extra layer of PUF on the inner polyurea shell structure.

Alternatively, multi-layered microcapsules can be fabricated through a single step procedure. Caruso *et al.* [72] demonstrated the microencapsulation of ethyl phenylacetate by PU-PUF double layered microcapsules by combining interfacial and *in situ* polymerization in a single batch process. Compared with the normal *in situ* polymerization approach as described elsewhere for making PUF capsules [40], herein after the addition of urea, ammonium chloride and resorcinol into the surfactant solution and pH adjustment, a mixture of the core material and a PU prepolymer, rather than the core material alone, was added into the above aqueous solution to generate an oil-in-water emulsion system. The rest operation including the further addition of formaldehyde solution, temperature control and product collection

Figure 2.10 AFM images of (a) PUF single-layer microcapsules and (b) PU-PUF double-layered microcapsules [72].

were all the same as those for normal *in situ* polymerization.

The double-layered structure of the resultant microcapsules was revealed by atomic force microscopy (AFM) characterization. As shown in Figure 2.10, two distinct phases were observed on the AFM phase images. As a control, a single layered PUF capsules was also observed. It could be seen that the shell of the PU-PUF microcapsules consists of a PU inner shell and a PUF outer shell. Thermogravimetric analysis (TGA) of the prepared capsules revealed that the PU-UF capsules exhibited much better protection to the core materials compared with single-layered PUF capsules.

Aside from the microcapsules-based system as discussed above, hollow-tube based system is another important type of self-healing material. Healing agents are stored in hollow tubes, which are embedded into polymeric host matrix to induce the desired self-healing function [73-75]. For self-healing polymer composite based on hollow tubes, the embedded tubes serve as both the reservoir for healing agent storage and reinforcement fillers [76].

Compared with microcapsules, hollow tubes can store more healing agents and hence the healing performance will be better [38]. The mechanism of self-healing behavior of hollow tube based self-healing materials can be illustrated in Figure 2.11. Once cracks form in a polymer composite, the embedded hollow tubes will be ruptured to release the stored healing agents into the cracks site. The polymerization reaction of the healing agents will re-bond the cracks and therefore realize the self-healing function.

Glass fibers are the most important material used as hollow tubes for self-healing materials. It is firstly due to the fact that glass fibers are inert to most of healing agents and host polymer matrix. In addition, they can be broken easily by

Figure 2.11 Mechanism of healing in a hollow tube-based system [73].

cracks formed in the host matrix to release the containing healing agents [77]. On the contrary, tubes made from other materials such as copper or aluminum may be difficult to sense the crack and therefore the healing behavior will not be triggered [9]. Compared with microcapsules based self-healing system, in a hollow tube based system, special attention should be paid to the compatibility of the healing agents with the hollow tubes, and hence various properties of the healing agents, such as their surface wettability, viscosity, chemical reactivity, *etc.* should be comprehensively considered [12]. For example, healing agents with too high viscosity may be unable to be introduced into the tubes, and even after the self-healing system is eventually developed, the healing agents are less likely to flow into the cracking sites where healing behavior is desired. In addition, the wettability of the healing species in the tubes is also a critical concern.

The first generation of hollow tube based self-healing systems was developed by Dry *et al.* [78] in 1990s [78-80]. In their efforts to manufacture self-healing

polymer materials, 100 μl of cyanoacrylate as adhesive was filled in 4 inches long glass pipette tubes, which were then integrated into polymer samples. The release of fill materials from the hollow tubes was examined under microscope, and it was confirmed that the contained adhesive was released when the tubes were broken by applied tension. When the samples were subject to bend tests to assess the self-healing performance, it was found that the released adhesive flowed into the matrix cracks and re-bonding occurred. Another hollow tubes based self-healing polymer system was similarly fabricated by integrating glass fibers containing methyl methacrylate as healing agent into a polymer matrix [79].

Trask *et al.* [81] also demonstrated a self-healing composite laminate based on hollow glass fibers. The host composite laminate in this investigation was manufactured from E-glass and 913 epoxy. The self-healing function was realized by introducing a layer of hollow glass fibers that contained Cycom 823 resin as healing agents. Cycom 823 is an epoxy resin with low viscosity, and it cures in 15 min at 95 $^{\circ}\text{C}$. The healing agents were introduced into the hollow fibers before or after the fibers were integrated into the host composite laminate, and the migration of the healing epoxy resin in case the fibers were broken was indicated by a pre-mixed UV dye. As shown in Figure 2.12, when overloading was applied on the self-healing composite laminate, the embedded hollow glass fibers were broken by cracks and the stored healing epoxy resin was released. Polymerization of the epoxy resin would repair the

Figure 2.12 Optical micrograph of impact damaged cross-section of a glass fibers/epoxy composite laminate. The fibers were filled with Cycom 823 and UV dye [79].

damaged area and hence restore the mechanical property of the composite. Mechanical test to the self-healing glass fibers/epoxy composite laminate revealed that although the incorporation of the hollow fibers healing layer into the host composite laminate caused initial strength reduction of 16 %, the self-healing composite could recover 87 % of its strength after damage was induced.

Carbon nanotubes (CNTs) are important fillers for materials reinforcement, and they can be also used as reservoirs for hollow tube based self-healing applications [82]. Lanzara *et al.* [83] explored the potential of CNTs for self-healing through a molecular dynamics study, and particularly investigated the CNTs capacity of delivering the stored agents. The study showed that the organic molecules, stored in CNTs, could be released into the outer space, and the molecules quantity was dependent on the size of the crack on the CNT wall.

However, the application of CNTs for self-healing is still in the development phase, and some important problems still have to be addressed before CNTs can be widely used in hollow-tube based self-healing system. For example, effective introduction of healing species into the tiny CNTs is still a main challenge, because the amount of healing species that can be stored is highly dependent on many factors including the CNTs diameter, length, orientation and dispersion, *etc.* In addition, it is still difficult to ensure that the CNTs can sense the host matrix damage and form a crack on the walls so that the stored healing agents can be delivered.

The research on microcapsule or hollow tube based self-healing materials has achieved great advancement. Nevertheless, neither of the them is able to repair the same location for more than once [38]. For example, in a microcapsule based materials, when the healing process was triggered due to the capsules rupture, the healing agent will be depleted, leaving voids in the host matrix. Then when another

healing is desired at the same location, no healing agent will be available to meet the purpose. The same case will happen to hollow tube based self-healing system, because the healing agents stored are still finite even though they are in larger volume compared with those in microcapsules. Moreover, in most case the second fracture will tend to occur at the same location as the initial one, because it is hard for the materials to reach a complete recovery in either the material integrity or the mechanical property. To overcome this problem, microvascular was proposed as an alternative approach for self-healing materials development [15, 84, 85].

In a microvasuclar based self-healing system, a three dimensional vascular network is embedded into the polymer host matrix, and healing agents are stored in the network. Once damage or cracks in the host matrix rupture the vascular, the healing agents will be transported to the damaged site via the vascular network. Figure 2.13 illustrates the mechanism of healing process in skin and a microvascular based self-healing system. It can be seen that in such a self-healing system, the

Figure 2.13 (a) Schematic diagram of a capillary network in the dermis layer of skin with a cut in the epidermis layer; (b) schematic diagram of a microvascular based self-healing structure with a microvascular substrate and a brittle epoxy coating [84].

healing process is a better imitation to the nature [11]. The healing agents can be supplied from other places via the interconnected network, and their supply will not be exhausted at one location, hence microvascular based system can achieve multiply healing [86].

Toohy *et al.* [33] demonstrated the self-healing performance of a microvascular based self-healing materials. In such a system, a rectangular three dimensional microvascular network was integrated throughout a polymer substrate via a direct-write assembly of a fugitive organic ink [87], and an epoxy layer modified by different percentage of Grubbs' catalyst particles was then deposited on the substrate. The interconnected microvascular channels ($d = 200 \mu\text{m}$) were filled with DCPD as healing agents. Once crack formed on the top epoxy layer, the underneath channels were broken and the stored DCPD was released from the vertical channels to the crack sites. Upon contact with the embedded Grubbs' catalyst, the polymerization of DCPD formed a film to repair the crack. In the healing process, the horizontal channels severed as the passage through which DCPD could be transported throughout the whole network to ensure the system was always filled with healing agents, and therefore enabled the multiple healing possible. The healing efficiency of the manufactured system was assessed, and the test showed as high as 70 % recovery

Figure 2.14 Procedure to a microvascular sandwich composite [89].

of the fracture toughness after damage in a four-point bending protocol.

In another effort to develop a microvascular based self-healing system, Williams *et al.* [88] fabricated a sandwich structured self-healing composites. As shown in the Figure 2.14, the vascular network was produced by integrating polyvinyl chloride tubes with 1.5 mm internal diameter and 2.5 mm external diameter into E-glass epoxy laminate, and liquid healing agents were filled in the network after the completion of all the manufacturing processes. Test to the produced self-healing composite revealed that the samples could restore their mechanical properties when impact damages were induced.

2.3 Self-healing concept for corrosion control

Applying coating on an object is the most straightforward approach to provide corrosion protection function to metal substrates. Coating provides a direct barrier layer to separate the underneath metal from external corrosive environment. In addition, corrosion inhibitor can be loaded into the coating layer to provide further corrosion suppression function. However, the degradation of coating is always a problematic issue. If coating degradation and failure are not timely detected, the underlying metal will be directed exposed to corrosive environment and may suffer from severe corrosion rapidly. In this case, if the coating can autonomously respond to the degradation and failure to recover its integrity or other function, its service life will be dramatically extended, and the corrosion protection function will be prolonged as well.

The concept of self-healing has been recently proposed for anticorrosion applications, and this novel approach has become a promising direction to develop anticorrosive coatings. Usually degradation of coating starts from the formation of micro-cracks. In a self-healing coating, the micro-cracks formation will rupture

embedded reservoir where healing agents are stored. The healing agents flow into the crack plane, undergoing healing reaction to re-bond the cracks. In self-healing polymeric materials, the reservoir can be capsules, hollow tubes or micro-vascular, but consider the small thickness of coating, only microcapsules can be employed in a coating system. When microcapsules are incorporated into polymer to introduce self-healing anticorrosion function, the capsules should fulfill some strict requirement. On the one hand, it should be robust enough to remain intact during processing and storage; on the other hand, it should be able to be ruptured on demand [89].

Sauvant-Moynot *et al.* [90] explored the application of self-healing for anti-corrosion purposes. In this study, a water-soluble and self-curable epoxy eletrodepositable adduct was synthesized and then directly incorporated into a polymer matrix. When the adduct came into contact with water, it would cure and deposit in the cracks to exhibit self-healing capabilities. When electrochemical impedance spectroscopy (EIS) test was performed on a steel panel coated with such a coating, it was revealed that the self-healing coating greatly improved its anticorrosion ability.

Suryanarayana *et al.* [62] reported a microcapsule based self-healing anticorrosion coating. Linseed oil as film former was encapsulated into PUF

Figure 2.15 Evolution of a scribe on self-healing coating. Optical microscope image of (a) initial scribe; (b) scribe after 90 second [62].

microcapsules via an *in situ* polymerization, and the prepared microcapsules were integrated into epoxy resin to generate a self-healing coating. A corrosion test was performed, and the results clearly demonstrated the excellent anticorrosion performance of the prepared coating. The mechanism behind the anticorrosion function of the coating is that linseed oil, released from ruptured microcapsules when scribes were applied on the prepared self-healing coating, solidified when it contacted atmospheric oxygen, forming a continuous film in the crack and separating the metal substrates from corrosive salt solution. The self-healing behavior of the self-healing coating was demonstrated in Figure 2.15. When a crack was applied on the coating, the length of the crack gradually reduced and the crack was completely filled after 90 s.

Following a very similar procedure, Samadzadeh *et al.* [91] also manufactured an anticorrosive coating by mixing encapsulated Tung oil into epoxy. Encapsulation of Tung oil by PUF microcapsules was realized via an *in situ* polymerization, and the prepared microcapsules were then distributed into epoxy coating. When cracks formed in such a coating, Tung oil would flow out of the ruptured microcapsules, undergoing polymerization upon contact with air to generating a film at crack planes.

Figure 2.16 Specimen after immersion in 3.5 wt.% NaCl solution for 10 days. (a) coated with blank coating; (b) coated with self-healing coating [92].

Although the mechanical property of the repaired area may be different from that of the initial epoxy coating, the creation of a barrier layer at the crack area definitely serve to protect the underneath metal substrates from external environment and therefore induce anticorrosion function. The anticorrosion ability of the self-healing coating was assessed similarly. As demonstrated in Figure 2.16, after exposure to salt solution for 10 days, severe corrosion was observed at the scribed area when the steel panel was coated with blank epoxy coating. By comparison, the specimen coated with self-healing coating was free of corrosion. This result clearly showed the excellent anticorrosion ability of the prepared self-healing coating.

García *et al.* [63] recently developed a self-healing anticorrosive organic coating based on an encapsulated water reactive silyl ester. In this work, self-synthesized silyl ester was encapsulated in PUF microcapsules and then distributed into epoxy to yield a self-healing coating. The self-healing function was realized by the hydrolysis and polycondensation of the silyl ester.

2.4 Assessment methods of self-healing anticorrosive performance

Self-healing anticorrosive coatings effectively protect the metal substrates via new film forming mechanisms to autonomously seal damage in the coatings. Different methods have been developed to evaluate the self-healing performance for corrosion resistance, such as visual inspection, measurement of the coating adhesion, and electrochemical testing.

Visual inspection is the most straightforward method to evaluate the recovered corrosion resistance of a self-healing coating, and it is very efficient especially when the substrate is steel since the corrosion product of steel shows a very visible reddish

Figure 2.17 Specimens after immersion in 5 wt.% salt solution after 120 h (a) coated with control coating (b) coated with self-healing coating [18].

color. Cho *et al.* [18] fabricated a self-healing coating based on polydimethylsiloxane-based healing agent. The coating was coated on steel substrate, scribed using razor blade and then immersed in 5 wt.% salt solution for 120 h. In the meantime, a neat coating was prepared as control and treated in the same manner. As shown in Figure 2.17, after immersion extensive corrosion was observed on the control sample, while the prepared self-healing coating was free of rust. This dramatic difference clearly illustrated that the scribed areas were self-healed to resist or retard the diffusion of corrosive species onto the metal substrate and therefore realize the corrosion protection function. This direct visual inspection was also used in other self-healing coatings systems [62, 91].

Corrosion in coating is often accompanied by physical change such as delamination or detachment of the coating to the substrate. Hence, adhesion measurement is also often employed to assess the self-healing anticorrosive property of self-healing coatings. The adhesion of coatings towards the underlying substrates is usually measured by cross hatch test in accordance with standard test methods such as ISO 2409 and ASTM D3359, *etc.* In a typical test, depending on the coating thickness, a cutter with suitable blade spacing is used to cut the given coating with approximately 20 – 30 mm of cut length, and another cut at 90° angle with the first cut is then made in the same fashion. After cleaning the detached flaks or ribbons with a

soft brush, an adhesive tape is applied on the cut area and then pulled off. The cutting area is inspected and the adhesion is then rated by comparing to reference.

Kumar *et al.* [92] prepared self-healing anticorrosive coatings by integrating different healing agents filled PUF microcapsules into coating matrix. The coatings were coated on steel substrates, and the specimens were then scribed and allowed for corrosion. The corrosion of the steel substrate was characterized by cross hatch test according to standard test method ASTM D3359. It was found that initial adhesion strength of coatings was reduced by addition of microcapsules while after scribing and healing Tung oil system showed the highest recovered adhesion strength. The result indicated the excellent anticorrosion property of the Tung oil based coating.

Corrosion is a very slow process, and it always takes an extremely long time to complete a test. In addition, corrosion occurring naturally somehow lacks reproducibility since it is hard to obtain exactly the same condition in field test. To avoid these problems, corrosion process is usually studied in an accelerated manner under a monitored condition according to some standard methods such as ASTM D5894 [93]. Typically, the samples are exposed to salt fog and UV radiation for a given number of cycles in a specially designed cabinet [94]. This condition simulates the natural environment to which the samples will be exposed, but it is delicately monitored so that the corrosion process is greatly accelerated.

Visual inspection and adhesion evaluation as discussed above are rapid and convenient to assess the self-healing performance of coatings. However, sometimes more quantitative information is required to further look into the corrosion process. Corrosion is inherently an electrochemical process and hence it can be studied by electrochemical measurement.

DC electrochemical measurement is the simplest electrochemical test to evaluate the self-healing performance of coatings. The principle of the measurement is very straightforward. Consider a coating is applied on a metal substrate, and the specimen is scribed and then exposed to electrolyte solution to form an electric circuit. When a potential is applied to the circuit, the current passing through the scribed coating will be high. But if the scribe of the coating is repaired, the current will be lower since the circuit is to some extent blocked. From the change of the current passing through the coating, the self-healing performance of a self-healing coating is characterized.

Cho *et al.* [18] measured the current passing through coatings to evaluate the anticorrosion behavior of a self-healing coating. In the testing, scribes were made on a prepared self-healing coating that was coated on a steel substrate. The damaged coating was then allowed to heal at 50 °C for 24 h. After that, a DC potential of 3 V was applied for 200 s and the current passing through the coating was measured. Before the scribes were induced, the current passing through the intact self-healing

Figure 2.18 Current versus time for scribed control and self-healed sample when a constant potential was applied in a DC electrochemical test [18].

Figure 2.19 Equivalent circuit of an organic coating on a metal substrate overlaid on a schematic of a painted metal surface.

coating and control coating was identical. As revealed in Figure 2.18, after scribing and healing, the current passing through the self-healing sample was $12.9 \mu\text{A}\cdot\text{cm}^{-2}$ - $1.4 \text{ mA}\cdot\text{cm}^{-2}$ compared to 26.6 - $58.6 \text{ mA}\cdot\text{cm}^{-2}$ of the control samples. This dramatic difference indicated that the self-healing coating was efficiently healed and the scribes were sealed. Other researchers varied the potential when the DC electrochemical test was performed to characterized self-healing coatings [95].

Although the DC electrochemical test as discussed above was often used to characterized self-healing performance, EIS is the most common electrochemical technique to evaluate a corrosion process and the self-healing ability of coating. When the corrosion in coating and the underlying metal substrate occurs, an electrochemical reaction is initiated to form an electrochemical circuit. Figure 2.19 demonstrated the equivalent circuit of an organic coating that is coated on a metal substrate. It can be seen from the equivalent circuit that a corrosion process will result in the change in the circuit parameters, and in turn, the circuit parameters of the equivalent circuit provides indicative information of the corrosion behavior. EIS can quantitatively

Figure 2.20 EIS (Nyquist plot) of Q235 carbon steel in 0.12 L of 0.1 M H_2SO_4 solution containing H_2NCSNH_2 -filled PVA microcapsules [27].

measure both resistances and capacitances of the equivalent circuit, and therefore indicate the extent of corrosion and corrosion rate [92].

Kuang *et al.* [27] employed EIS to study the corrosion behavior of Q234 carbon steel that was protected by corrosion inhibitor. In this study, thiourea (H_2NCSNH_2) as corrosion inhibitor was encapsulated by glutin or polyvinyl alcohol microcapsules, which were then added into corrosive 0.1 M H_2SO_4 solution. Q235 carbon steels were then put in this solution, and EIS was performed every 6 hours. It was clearly shown in Figure 2.20 that the polarization resistance (R_p), which was equals to the diameter of the arc, increased with time until 48 h. It suggested that the corrosion of the steel was inhibited after 48 h, attributed to the thiourea released from the microcapsules. It was also concluded that the releasing time of the thiourea from the polyvinyl alcohol microcapsules was 48 hours because the R_p did not further increase.

Similarly, García *et al.* [96] employed EIS to evaluate the anticorrosion performance of an epoxy self-healing coating. The coating was based on encapsulated silyl ester, which will experience hydrolysis and crosslinking to produce a barrier

layer to realize self-healing function. García *et al.* [97] also used EIS to evaluate the corrosion process of an epoxy coated low-carbon steel substrates when the panels were immersed in 3.5 wt.% NaCl solution. In addition, Sauvante-Mounot *et al.* [90] applied EIS to characterize corrosion process during their studies on corrosion protective coatings.

EIS is powerful in the evaluation of the corrosion in coatings, but it often takes a very long time to complete a sufficient number of runs in order to achieve good results, and sometimes several months are needed for a complete EIS measurement. To shorten the testing time, a rapid AC/DC/AC method has been developed by combining direct constant (DC) and alternating current (AC) measurement. In this technique, after an initial AC test, a constant DC is applied to the sample, followed by another AC test again. The change in the recorded impedance contains the information indicating the corrosion process [98].

Suay *et al.* [99] used both EIS and AC/DC/AC technique to characterize the corrosion behavior of epoxy-coated steel panels, and several variables influencing the protection performance of the coating were studied. When the coated steel panel was placed in 3.5 wt.% NaCl solution, corrosion occurred to form an electrochemical circuit, and then some parameters such as pore resistance (R_{po}), polarization resistance (R_p) and double layer capacitance (C_{dl}) were measured by both EIS and AC/DC/AC method. Figure 2.21 showed the pore resistance (R_{po}) of the equivalent circuit collected from EIS and AC/DC/AC measurement respectively when coatings with different thickness were applied on the steel substrates. It could be seen from Figure 2.21a that the pore resistance was higher when thicker coating was used, suggesting that panels with thicker coating had less pores and therefore were less degraded when all other variables were identical. As illustrated in Figure 2.21b, the R_{po} collected

Figure 2.21 Pore resistance (R_{po}) of the equivalent circuit from (a) EIS and (b) AC/DC/AC measurement when the coating thickness is 25 μm and 20 μm , respectively [100].

from AC/DC/AC measurement also afforded the same results. When other parameters such as C_{dl} and R_p of the equivalent circuit were measured, it was found that EIS and AC/DC/AC method also produced the same results. However, it can be seen that the test time for the AC/DC/AC method was only 3000 min (approximately 50 h), compared to the as long as 250 days for the EIS test. Hence, it is seen that AC/DC/AC measurement is much more time efficient.

Another electrochemical technique that is also widely utilized to characterize corrosion and the corrosion protection performance of coatings is scanning vibrating electrode technique (SVET). SVET operates with a non-intrusive scanning, vibrating probe to measure and map the electric field generated in a plane above the surface of an electrochemically active sample, and it is capable of indicating localized corrosion activity [94, 100, 101].

Khramov *et al.* [102] applied SVET measurement to characterize the corrosion inhibition of a sol-gel derived hybrid coating towards AA 2024-T3 aluminum panel. In the study, a hybrid approach termed self-assembled nanophase particle (SNAP) coating process was used to prepare a SNAP coating. Organic corrosion inhibitor mercaptobenzothiazole (MBT) was encapsulated in β -cyclodextrin, and then integrated into SNAP coating. An artificial Al-Cu galvanic couple was made on the

Figure 2.22 Current density distribution maps for Al/Cu artificial defects on AA 2024 coated with SNAP coating. (a) blank coating without inhibitor; (b) coating doped with inhibitor MBT [101]

specimen surface by applying a small drop of CuCl_2 solution. A small area of the specimen was exposed to corrosive Harrison's solution, and a platinum microelectrode was used as the vibrating probe for the SVET measurement. The SVET results show the current density within the detected area, and it represents the corrosion current flow associated with anodic and cathodic corrosion activities and hence reveals the degree of corrosion. As shown in Figure 2.22a, for the SNAP coating without corrosion inhibitor, the current density was higher than $400 \mu\text{A}/\text{cm}^2$ after 30 min. This result implied the rapid pitting corrosion when the specimen was exposed to corrosive Harrison's solution. On the contrary, when the coating was modified by encapsulated MBT, as shown in Figure 2.22b, the current density declined to a negligible level after exposure to the corrosive solution for 8 days. It meant that the incorporation of MBT effectively suppressed the corrosion of the SNAP coating, while the negligible current flow after long time immersion indicated the self-healing effect of corrosion inhibitor.

Andreeva *et al.* [101] and Shchukin *et al.* [29] both employed SVET to evaluate the anticorrosive property of anticorrosion coatings that were prepared by

layer-by-layer (LbL) deposition techniques. The prepared specimens were mechanically scratched, and the defected area was subject to SVET analysis. In both cases, the SVET analysis of the specimens demonstrated that the corrosion at the defect was effectively suppressed for the anticorrosive coatings compared with control specimens.

2.5 Summary

Corrosion control is one of the most important concerns in the field of materials. Applying coating is an efficient method to protect metal from corrosion because it provides a direct barrier to separate the metal substrates from corrosive environment. Corrosion inhibitors play significant roles in corrosion control. To develop anticorrosive coating, inhibitors can be directly added into the coating. Alternatively, they can be encapsulated prior to addition, and this method has at least two advantages over direct addition. First of all, the release rate of inhibitors is more controllable. Secondly, the interaction between the inhibitors and components of coating can be prevented.

Self-healing materials are able to autonomously repair micro-crack without manual intervention, and they are of considerable importance in terms of extending the service life of materials and therefore eliminating the cost for maintenance and replacement. In most self-healing systems, healing agents are stored in reservoirs and they will be released on demand. Based on the reservoirs, self-healing materials can be generally divided into microcapsule based, hollow tube based and microvascular based, whilst the first one is most widely used because it is applicable in more situations. A number of microcapsules based self-healing materials have been developed.

The concept of self-healing can be also used for anticorrosion coating, and this novel approach offers a promising route for corrosion control. Currently most of self-healing anticorrosive coatings are based on microencapsulation, in which the healing agents are stored in microcapsules. Self-healing coatings are able to autonomously repair micro-cracks and hence exhibits corrosion protection function. The self-healing anticorrosive performance of coatings can be assessed by different techniques, such as visual inspection, adhesion measurement and electrochemical test.

Chapter 3 Experimental Section

3.1 Materials

Hexamethylene diisocyanate (HDI), gum arabic, 1,4-butanediol, ethylene diamine, ethylene maleic anhydride copolymer, ammonium chloride, urea, resorcinol, 1-octanol, toluene, hexane, *o*-xylene, ethanol, methanol, sodium hydroxide, sodium chloride, hydrochloric acid, bromophenol blue and *n*-dibutylamine were obtained from Sigma-aldrich. Methylenediphenyl diisocyanate (MDI) prepolymer Suprasec 2644 was obtained from Huntsman. *1H,1H',2H,2H'*-perfluorooctyl triethoxysilane (POTS) was obtained from Alfa Aesar. Epoxy resin and hardener EPOLAM 5015/5014 were obtained from AXSON. Silicone resin and hardener Sylgard 184 were obtained Dow Corning. All chemicals in this study were used without further purification unless otherwise specified.

Figure 3.1 Structures of key chemicals for the microcapsules synthesis

3.2 Synthesis of microcapsules

3.2.1 Microencapsulation of HDI via interfacial polymerization

Polyurethane (PU) microcapsules containing HDI as core materials were synthesized via interfacial polymerization in an oil-in-water emulsion. At ambient temperature, gum arabic aqueous solution was prepared as surfactant in a 250 ml beaker. The beaker was suspended in a temperature-controlled water bath on a programmable hot plate with an external temperature probe. The solution was agitated with a digital mixer (Caframo) driving a three-bladed propeller. 2.9 g of Suprasec 2644 liquid was mixed well with HDI, and the mixture was then added into the prepared surfactant solution under agitation to create a stable emulsion system. After the addition, the system was heated to the set temperature at the heating rate of 7 °C /min to 40 °C. 3.0 g of 1,4-butanediol was diluted by 3 ml of deionized water and then dropwisely added into the emulsion to initiate the interfacial polymerization at the oil/water interface. The reaction was held for 1 h, and the resultant microcapsules

Figure 3.2 Procedure for the microencapsulation of HDI.

oil/water interface. The reaction was held for 1 h, and the resultant microcapsules were filtered and washed with distilled water for several times. HDI microcapsules were collected for air-drying at ambient temperature for 48 h before further analysis. A typical procedure for the synthesis is outlined in Figure 3.2.

3.2.2 Microencapsulation of POTS via *in situ* polymerization

Poly(urea-formaldehyde) (PUF) microcapsules containing POTS as core materials were synthesized through an *in situ* polymerization reaction in an oil-in-water emulsion system [40]. The facilities used for the synthesis of POTS microcapsules were the same as those used for interfacial polymerization as described above. At ambient temperature, 50 ml of deionized water and 12.5 ml of 2.5 wt.% aqueous solution of ethyl maleic anhydride copolymer were mixed in a 500 ml beaker. Under mechanical agitation, 1.25 g urea, 0.125 g ammonium chloride and 0.125 g resorcinol were dissolved in the solution. The pH of solution was raised from ~2.60 to 3.50 by drop-wise addition of 1 M sodium hydroxide solution. One drop of 1-octanol

Figure 3.3 Procedure for the microencapsulation of POTS.

was added to eliminate surface bubbles. 10 g of POTS liquid was dissolved in 5 g of toluene to form the oil phase, which was then slowly added into the above aqueous solution to generate emulsion. After stabilization for 10 min, 3.17 g of 37 wt.% aqueous solution of formaldehyde was added. The emulsion was covered and heated to 55 °C at a heating rate of 1°C/min. After 4 h of continuous agitation, the stirrer and hot plate were switched off. The resultant microcapsules were filtered and washed with distilled water for several times. Microcapsules were collected for air-drying at ambient temperature for 48 hours before further analysis. A typical procedure for the synthesis is outlined in Figure 3.3.

3.3 Characterization of microcapsules

The microcapsule formation during the reaction process was observed under Axiotech optical microscope (Zeiss) equipped with a device camera (Sony). The surface morphology and shell thickness of the synthesized microcapsules were examined by using SEM (JEOL JSM 5600LV SEM). During the sample preparation for SEM examination, microcapsules were placed on a conducting carbon tape that was attached to the holder, and the sample was sputtered with gold (JEOL JFC 1600 Auto Fine Coater). Mean diameter of the prepared microcapsules and their size distribution were determined from data sets of at least 200 measurements from SEM images and analyzed in software ImageJ.

Chemical constituent of the microcapsules were analyzed by using FTIR spectroscope (FT-IR, Nicolet 6700). Small amount of pure HDI, pure POTS, pure capsule shell, pure capsule core material and full capsules mixed with KBr pellet were prepared separately. The spectrum in the range of 400 - 4000 cm⁻¹ was used for the observation. In order to obtain the FTIR spectrum of pure capsule shell, small

amounts of microcapsules were crushed and washed by diluted ethanol for several times. After filtration and drying, pure shell was obtained for analysis.

The thermal stability and the core fraction of the resultant microcapsules were characterized by using TGA (Hi-Res Modulated TGA 2950). 10 - 20 mg of microcapsules was put in a platinum pan and heated under nitrogen atmosphere at a rate of 10 °C/min. The peak width of the derivative of the weight loss curve of capsules was used to roughly determine the core fraction of microcapsules. Pure capsules shell was obtained using the same way as that for FTIR analysis.

3.4 Shelf life of microcapsules in environment

The shelf life of microcapsules was estimated by the change of core fraction when the capsules were exposed to environment, while the core fraction of a microcapsule is the weight ratio of the encapsulated liquid to the whole microcapsule. The synthesized microcapsules were exposed to open air, water or different organic solvent. After a period time of exposure, the core fraction of the microcapsules was determined by TGA analysis.

For HDI-filled PU microcapsules, the shelf life, or the barrier property of the microcapsules in organic solvent was also characterized by the amount of isocyanate (NCO) functional group in solvent when capsules were immersed in solvents. 0.5 g of PU microcapsules was immersed into 25 ml of organic solvent to form a suspension. After a period of immersion, the suspension was filtered and the filtrate was transferred into a 250 mL Erlenmeyer flask. The quantity of NCO groups in the filtrate was determined by titration as below:

- a) Prior to the titration, 0.1 wt.% bromophenol blue indicator solution was prepared by mixing 0.1 g of bromophenol blue with 1.5 mL of 0.1 mol/L sodium hydroxide solution and diluting to 100 mL with distilled water;

- b) 50 mL of 0.1 mol/L *n*-dibutylamine toluene solution was added to the flask and allowed for sufficient mixing by swirling the flask for 5 min;
- c) 50 mL of ethanol and 5 drops of 0.1 wt.% bromophenol blue indicator were then added;
- d) The solution was then titrated using 0.1 mol/L hydrochloric acid to yellow end point;
- e) A parallel blank titration was also performed to 25 mL of toluene following the same procedure.

The quantity of NCO in the organic solvent is determined as follows:

$$NCO \text{ (mol)} = (B - V) \times N \quad (3.1)$$

where:

B = volume of HCl for titration of 25 mL of blank organic solvent, L;

V = volume of HCl for titration of collected filtrate, L;

N = normality of HCl, which equals to 0.1.

If the NCO groups are assumed to completely come from the encapsulated HDI, the equivalent weight of HDI dissolved in the organic solvent during the immersion can be calculated as:

$$W \text{ (g)} = \frac{(B-V) \times 0.1 \times 168.2}{2} \quad (3.2)$$

where :

168.2 is the molecular weight of HDI monomer; 2 in the denominator means the two NCO groups in each of HDI molecule.

The total weight of HDI contained in a certain amount of microcapsules was also determined by titration. 0.5 g of microcapsules was crushed in a beaker, and 25 mL of toluene was then added to create a suspension. The NCO in the suspension was titrated, based on which the weight of HDI was calculated.

3.5 Contact angle measurement

The contact angle of liquid on metal substrate was measured by using Theta Optical Tensiometer (KSV Instrument) equipped with software Attension Theta. 5 μL of liquid was dropped on the substrate, and the contact angle was measured by the software. The final contact angle was calculated from the average value of five measurements at different locations on the substrate. Prior to the measurement the steel panel was pretreated as stated in next section.

3.6 Preparation of self-healing anticorrosive coatings

3.6.1 Substrate treatment

Carbon steel panels with the size of 5 cm $\times$ 8 cm were used as substrates for the coating application in the study. Prior to coating, steel substrates were abraded with sand paper (grain size: 400), washed with deionized water and acetone for three times and dried in open air. The steel panel for contact angle measurement was also treated in the same manner.

3.6.2 Self-healing anticorrosive epoxy coating

Self-healing anticorrosive epoxy coating was prepared by dispersing 10 wt.% of the synthesized microcapsules with the diameter of about 100 μm into epoxy resin EPOLAM 5015 at ambient temperature, followed by mixing hardener EPOLAM 5014. The mixture was degassed for 20 min and then applied on the pre-treated substrates by an adjustable film applicator (KTQ-II, Pushen Chemical Machinery). The coating was cured at ambient temperature in open air for 24 h. In the coating preparation, the diameter of microcapsules, weight fraction of microcapsules in the coating are changed to study their influence on the self-healing anticorrosive performance of the prepared coating.

3.6.3 Self-healing anticorrosive silicone elastomer

Self-healing anticorrosive silicon elastomer was also prepared in a similar manner by dispersing 10 wt.% of synthesized microcapsules (diameter ~ 100 μm) into silicon resin Sylgard 184 at ambient temperature, followed by mixing hardener. The mixture was then degassed for 20 min and then applied on a pretreated substrate by an adjustable film applicator. The silicone elastomer was cured at ambient temperature in open air for 24 h.

3.7 Evaluation of self-healing anticorrosive performance

3.7.1 Accelerated corrosion test in salt solution

The corrosion protection performance of self-healing coating was evaluated through an accelerated corrosion test in salt solution. On the prepared self-healing coating, cross scratches were applied manually by razor blade following the standard method of ASTM D1654. Scratched specimen was then immersed in 10 wt.% NaCl solution for 48 h. In the meantime, blank coating without microcapsules was prepared with the same thickness as a control and treated in the same manner for comparison.

The different corrosion processes of the steel panels coated with self-healing coating and with neat epoxy control coating were inspected by naked eyes and OM. SEM was also employed to examine the evolution of the scratched area of the coatings to provide detailed information about the corrosion process. Energy-dispersive X-ray spectroscopy (EDX) was employed to reveal the elemental distribution at the scribed area.

3.7.2 Long-term corrosion protection assessment

The prepared anticorrosive silicon elastomer was exposed to 1 M HCl solution for one month, and the exposure area was set at 10 cm^2 using a glass cylinder, which

Figure 3.4 Set-up for long term corrosion protection assessment.

was clamped with a rubber O-ring on the coating surface (Fig. 3.4). The cylinder was covered by a Parafilm to eliminate the evaporation of HCl solution. A neat silicon elastomer without microcapsules was prepared as control and treated in the same manner.

After one month exposure, the silicon elastomer was peeled away from the steel substrate. OM and SEM were both employed to inspect the corroded area on the substrate. EDX was also used to demonstrate the elemental distribution of the corroded substrate surface. As a comparison, prior to the corrosion test, the surface of the steel substrate was characterized by SEM and EDX for both anticorrosive specimen and control specimen.

3.7.3 Salt spray test

Comprehensive salt spray test was performed to evaluate the corrosive protection function of the self-healing anticorrosive coating to metal substrates following standard method ASTM B117. A set of coatings with different formulations were prepared on steel substrates, and the edge and backside of the substrates were covered by water-resistant tape. The coatings were cross scratched following ASTM

D1653 and then placed in salt spray chamber (QC 711, ComeTech). 5 wt.% of sodium chloride solution was used for fogging, and the temperature of the salt spray chamber was set at 35 ± 2 °C. The salt spray test lasted for 2 months.

3.7.4 DC electrochemical test

DC electrochemical test was performed to quantitatively evaluate the self-healing anticorrosive performance of the prepared self-healing coating. The steel panel was coated with self-healing coating. The electrochemical test was performed when the specimen was scribed and immersed 10 wt.% salt solution for 2 days. The test was conducted using a computer controlled potentiostat (Reference 600, Gamry) in a conventional three-electrode electrochemical cell equipped with a Pt counter electrode, a Ag/AgCl in saturated KCl aqueous solution as reference electrode, and the coated steel panel as the working electrode, respectively (Fig. 3.5). Software DC 105 (Gamry) was used for data collection.

Figure 3.5 Schematic diagram of the set-up for DC electrochemical test.

In the measurement, the scribed region on the specimen was exposed to 1 M NaCl aqueous electrolyte solution. The potential was swept from -600 mV to +1100 mV (vs. Ag/AgCl) with a sweep rate of 20 mV/s at ambient temperature, and the current passing through the specimen was recorded. The current was normalized by the area of the steel substrate that contributed in the circuit, which was simply estimated by the product of the crack length and the crack width, while the latter one was the average value of five measurements from SEM image.

3.7.5 EIS measurement

EIS measurement was also performed on the Gamry Reference 600 Potentiostat via a conventional three-electrode system as described in last section. The electrolyte solution was 1 M sodium chloride solution. The frequency range of study was $10^{-2} - 10^5$ Hz with 10 steps per decade, and the AC amplitude was 10 mV. Software EIS 300 (Gamry) was used for data collection, and the obtained impedance plots were fitted with an equivalent circuit by software Echem Analyst (Gamry) as discussed in latter sections.

Chapter 4 Diisocyanate Microcapsule Based Self-healing Anticorrosive Coating

4.1 Motivation

Selection of healing agent is crucial for self-healing coating development. When micro-cracks are formed in a coating, it should be ensured that the healing agents are able to easily flow into the cracks, and in the meantime, they are able to undergo the healing reaction rapidly. Isocyanate monomers are reactive with water or moisture to produce carbamic acid, which is unstable and tends to decompose to an amine which in turn reacts with isocyanate to form urea or biuret or other polymeric products (Fig. 4.1). The moisture-curable property of isocyanate makes it potential to manufacture one-part, catalyst free self-healing system. The one-part self-healing system simplifies the fabrication process, minimizes the impact of microcapsules to the host polymer matrix, and also prevents the use of catalyst, which is of considerable economic importance.

Nevertheless, the high reactivity of isocyanate brings the difficulty for its processing, and its encapsulation is also very challenging. Previous research on the encapsulation of isocyanate has been mainly restricted to its solid state or blocked

Figure 4.1 Mechanism of the reaction of isocyanate with water

form. For example, Yang *et al.* and Rawlins *et al.* reported the encapsulation of a blocked form of polyisocyanate by polystyrene nanocapsules via emulsion polymerization [103-105], and the microencapsulation of a solid state naphthylene-1,5-diisocyanate by protective materials such as polystyrene, chlorinated rubber and polyvinyl butyl ether that were inert to the encapsulated isocyanate was demonstrated by Walther *et al.* [106]. To date, very few public documents have appeared for the encapsulation of liquid state isocyanate monomers. Although the high chemical reactivity of isocyanate monomers makes their microencapsulation rather challenging, their encapsulation is very beneficial for self-healing purpose for two reasons: a) the high reactivity of isocyanate monomers makes instant healing possible when they are used as healing agents; b) the liquid isocyanate monomers can easily flow into cracks where healing is desired.

Yang *et al.* [51] for the first time reported the microencapsulation of liquid state isocyanate monomer. IPDI monomer was encapsulated by PU microcapsules via an interfacial polymerization approach in an oil-in-water emulsion system. TDI prepolymer was synthesized by reacting TDI monomer with 1,4-butanediol, and the obtained prepolymer was mixed with IPDI to form the oil phase, which was then added into surfactant solution to create an emulsion. The following addition of 1,4-butanediol into the aqueous phase initiated its polymerization with the TDI prepolymer at the interface between the water phase and the oil phase, yielding PU microcapsules with IPDI being encapsulated as core materials. Figure 4.2 illustrated the scheme of the polymerization reaction between the TDI prepolymer and 1,4-butanediol.

The procedure described above successfully produced PU microcapsules containing IPDI, and it was proved that the encapsulated IPDI maintained its activity

Figure 4.2 Scheme of the microencapsulation of IPDI by PU microcapsules [51].

during this process. However, the synthesis was based on a self-prepared urethane prepolymer, and thus the preparation is quite tedious. In addition, the reactivity of IPDI is not very high. In our study, more reactive liquid isocyanate monomer, HDI, is facilely encapsulated into PU microcapsules, and the synthesized microcapsules are used to develop a self-healing anticorrosive coating. All of chemicals used in the study are commercially available.

4.2 Microencapsulation of HDI

4.2.1 Overview of synthesis

In the synthesis, commercial MDI prepolymer Suprasec 2644 was dissolved in HDI to yield an oil phase, which was dispersed into gum arabic surfactant solution to create an oil-in-water emulsion. When 1,4-butanediol was introduced, the reaction between hydroxyl functional group from the aqueous phase and isocyanate functional group from the oil phase occurred to create a PU membrane surrounding the oil droplets. The reaction mechanism of PU formation is very similar to that is shown in Figure 4.2, while the only difference is that the TDI prepolymer is replaced by MDI prepolymer. The diol in the aqueous phase diffused across the initial membrane to

further react with the isocyanates and resulted in the membrane increment [107]. MDI prepolymer was much more reactive than HDI, and hence the primary reaction was between 1,4-butanediol and MDI prepolymer to form the shell structure, while the relatively less reactive HDI liquid was encapsulated as core material to produce the final microcapsules. All of the materials used in the synthesis were commercially available, so it was seen that the microencapsulation of HDI was realized in a much more simplified procedure compared with the encapsulation of IPDI as reported before [51]. In a typical run of synthesis, the oil phase was composed of 2.9 g MDI prepolymer and 8.0 g HDI, the concentration of the gum arabic surfactant solution was 3 wt.%, the agitation rate was 500 RPM and the temperature of reaction was 40 °C. At such a condition, the yield of the capsules was about 70 %, and the resultant microcapsules had average diameter of 86.5 µm and shell thickness of about 6.5 µm.

Since the synthesis of the capsule shell wall was not a strict stoichiometric reaction, excess of 1,4-butanediol was used to ensure the Suprasec 2644 was completely consumed, so the yield of the synthesis is calculated simply as below:

$$Yield(\%) = \frac{W_{cap}}{W_{pre-p} + W_{diol} + W_{HDI}} \times 100\%$$

where W_{cap} is the mass of the collected microcapsules after drying, and W_{pre-p} , W_{diol} , W_{HDI} are the masses of MDI prepolymer, 1,4-butanediol, and HDI, respectively. This is a rough method to estimate the yield of the synthesis.

Based on the calculation stated above, at 500 RPM agitation rate, the typical yield was calculated to be 65-74 %, slightly varied with reaction parameters. It was found that the yield was lower at higher agitation rate, and at least two reasons should be responsible for this result. One reason is that more microcapsules will be destroyed by the higher shear force at faster agitation [40]. The other reason is that the yielding

microcapsules will not have the same diameter. Instead, their size nearly follows a normal distribution. During the product collection, a large portion of tiny capsules would be lost in the process of filtration and washing. As discussed below, we can find that finer microcapsule will be produced at higher agitation rate, and accordingly more tiny capsules would escape from our collection, resulting in a lower yield. The yield declined to approximately 54 % when the agitation rate was raised to 2000 RPM.

The formation of microcapsules is quite fast in the synthesis due to the high reactivity of MDI prepolymer. OM examination during the reaction course showed that microcapsules formed within 15 min after the addition of 1,4-butanediol. However, a minimum reaction time (MRT) was necessary to ensure the shell of the capsules was mechanically strong enough to withstand following filtration and further processing. Finding the MRT of the synthesis is very important for both time saving and quality control of the microcapsules shell. To determine the MRT, products were sampled from the emulsion solution at 10 min intervals until dispersed dry microcapsules could be collected by filtration. Although microcapsules were observed at quite an early stage, the capsules formed before MRT were found to collapse to yield viscous bulk polymer during the filtration. As shown in the Table 4.1, the required MRT reduced steadily with the increase of reaction temperature. It meant that the capsule shell growth was more rapid at higher temperature, and this is consistent with the fact that the rate of polymerization reaction for polyurethane

Table 4.1 Minimum reaction time (MRT) and fill content of microcapsules prepared at different temperature.

Temperature (°C)	30	40	50	60
MRT (min)	150	60	45	30
HDI Content (wt.%)	65	62	35	18

formation is positively dependent on temperature.

4.2.2 Chemical constituent of microcapsules

The chemical constituent of the resultant microcapsules was characterized by FTIR. As a comparison, complete capsules together with pure grades of HDI, MDI prepolymer, shell and core materials were investigated. As illustrated in Figure 4.3, the characteristic signals at 2267.6 cm^{-1} (-NCO stretch) and 2929.5 cm^{-1} (CH_2 stretch) from the full microcapsule reveal that the resultant capsules contained large amount HDI. Meanwhile, the NCO signal (2267.6 cm^{-1}) is not observed from the spectrum of capsule shell. It means that the HDI was not absorbed on the microcapsule shell. In addition, it is seen that the spectrum of core materials is almost the same as that of pure HDI, indicating that the core material was mainly composed of pure HDI. Therefore, it can be concluded that the HDI was successfully encapsulated into the PU microcapsules. In addition, the absence of the NCO signal in the spectrum of the pure shell indicates that the prepolymer chains were extended to form PU bulk shell. Based

Figure 4.3 FTIR spectra of HDI, Suprasec 2644, prepared PU microcapsule, capsule shell and capsule core material.

on these observations, it is logical to conclude that polymerization of MDI prepolymer produced the PU microcapsules shell, and HDI was encapsulated as core materials in the synthesis.

However, it is hard to determine the precise chemical structure of the microcapsules because as a commercial product, the composition of Suprasec 2644 is unknown, and many side reactions of isocyanates may occur during the capsule formation process.

4.2.3 Reactivity of core material

When the obtained microcapsules were crushed between two microscope slides, liquid was immediately observed to be released with the generation of irritating smell that is the same as the smell of HDI, implying the successful encapsulation of HDI in the capsules. When a few droplets of ethylenediamine were added into the released liquid, the liquid hardened rapidly accompanied by the production of heat, indicating that the encapsulated HDI was still reactive. When the core material was released on wet glass slide, a whitish solid polymer layer appeared after 24 hours, revealing the potential for self-healing application especially at humid environment.

4.2.4 Morphology and diameter of microcapsules

The synthesized microcapsules have spherical shape with smooth surface as shown in Figure 4.4. The diameters of microcapsules prepared at different agitation rate were summarized in Table 4.2. It can be seen that microcapsules with average diameter in the range of 5 – 350 μm were obtained by adjusting the agitation rate between 300 – 2000 RPM.

In the development of self-healing materials through microencapsulation, control of capsule diameter is critical because the diameter greatly influences the self-

healing performance [34], and in some conditions, only the capsules with a certain range of diameter are suitable. For example, capsules with too large size will not be suitable for self-healing coating because their diameter may even exceed the thickness

Figure 4.4 Morphology of microcapsules. (a) Spherical shaped microcapsules; (b) zoomed in image showing smooth outer surface.

Table 4.2 Diameter and shell thickness of capsules prepared at different agitation rates.

Agitation Rate (RPM)	300	500	800	1000	1500	2000
Diameter (μm)	353.24 ± 144.9	86.54 ± 30.4	38.92 ± 14.5	27.40 ± 9.5	8.17 ± 2.9	5.1 ± 1.3
Shell Thickness (μm)	12.48 ± 2.9	6.68 ± 1.3	5.39 ± 0.9	3.25 ± 0.7	1.76 ± 0.3	1.1 ± 0.2

Figure 4.5 Average diameter and shell thickness of prepared microcapsules prepared at different agitation rate ($n_1=2.18$; $n_2=1.25$).

of the host coating. The microcapsules diameter is influenced by a combination of several factors including the geometry of the mixing device, viscosity of the reaction media, surfactant concentration, agitation rate, temperature, *etc.* Also, in our work the average diameter of microcapsules was primarily controlled by agitation rate. As illustrated in Figure 4.5, when all other variables remained the same during microcapsules synthesis, higher agitation speed resulted in smaller microcapsule size, and this result is in line with previous studies [40, 51]. In an interfacial polymerization, the diameter of produced microcapsules is dependent on the size of droplet in the emulsion. At higher agitation rate, finer oil droplets will form in the emulsion system due to higher shear force, and the final microcapsules will accordingly be smaller. In addition, as revealed in Figure 4.5, the average diameter possessed a linear relationship with the agitation rate in double logarithm coordinates. Although the mechanism for such a relationship is still unknown, the same observation was also reported in previous research [40].

At a set condition, the diameter of the collected microcapsules was located in a broad range, and the size distribution approximately followed a normal distribution as

Figure 4.6 Size distribution of microcapsule prepared at different agitation rates.

demonstrated in the Figure 4.6. Meanwhile, it was found that the distribution of the microcapsules diameter was narrower when the agitation rate was higher. This is reasonable because faster agitation is more favorable for the homogenization of an emulsion, and the droplets accordingly have more uniform size. In the synthesis, the microcapsules were initially formed surrounding the oil droplets, and therefore the diameter of capsules was significantly dependent on that of the oil droplets. Hence, the size of the produced microcapsules was more uniform at higher agitation rate.

Another factor that significantly influenced the capsules diameter was the surfactant concentration. As shown in Figure 4.7, the mean microcapsule diameter decreased significantly when the gum arabic concentration increased in the range of 1.5 - 3 wt.%, followed by a plateau with constant diameter around 85 μm when the surfactant concentration was above 3 wt.%. The exact mechanism by which surfactant concentration influences the capsules formation is still not clear, but it is widely accepted that the surfactant concentration is a dominant factor influencing the interfacial tension of the emulsion media before the critical micelle concentration

Figure 4.7 Average microcapsules diameter as a function of gum arabic concentration.

(CMC) is reached [108, 109]. It is believed that higher surfactant concentration yields smaller oil droplet in an oil-in-water emulsion, and as a result, the microcapsules produced via interfacial reaction will have smaller diameter [109]. Beyond the CMC, a further increase in surfactant concentration will not change the interfacial tension nor the size of dispersed droplets in emulsion system, and therefore the diameter of final microcapsules will approximately remain at a constant value. Based on the variation of the microcapsules diameter, the CMC of this surfactant was estimated to be near 3 wt.% in our study, but the exact CMC value is yet to be identified.

4.2.5 Shell wall

The morphology of the microcapsules wall is shown in Figure 4.8. It was found that the inner surface of the capsules was not as smooth as the outer surface. Meanwhile, the coarse cross section of the capsules indicates that the capsules shell may contain some voids. This is reasonable because the PU shell was mainly composed by the product of the polymerization of MDI prepolymer and 1,4-butanediol, but MDI prepolymer may also react with water to generate CO₂. The

Figure 4.8 Morphology of PU microcapsules shell.

evaporation of CO₂ will leave voids in the capsule shell. It is also possible that the relatively coarser inner surface is due to the different increment rate of the PU shell during the microcapsules formation. The average shell thickness of the resultant microcapsules as a function of agitation rate is plotted in Figure 4.5, which clearly illustrates a linear relationship with the agitation rate in double logarithm coordinate. The average shell thickness of capsules was in the range of 1.1 – 12.48 μm when the agitation rate varied in the range of 300 – 2000 RPM.

4.2.6 Thermal property and core fraction of microcapsules

The TGA weight loss curves of microcapsules synthesized at 500 RPM along with pure HDI and capsule shell materials as a function of temperature are shown in Figure 4.9. It can be observed that microcapsules experienced significant weight loss by 180 °C. This weight loss is in good agreement with that of HDI and reveals the successful encapsulation of HDI within the microcapsules. The decomposition of shell materials started from about 240 °C. Figure 4.9 also illustrated the derivative of the weight loss curve of microcapsule. The evaporation process of HDI in the first

Figure 4.9 TGA weight loss of pure HDI, full microcapsule and microcapsule shell, and the derivative of TGA curve of microcapsules.

peak and decomposition process of shell in the peaks after 240 °C are apparent on the curve of the full microcapsules.

The HDI content or the core fraction in the prepared microcapsules was determined from the peak width of the derivative curve of full microcapsules. From Figure 4.9 it is seen that the HDI content of the microcapsules was about 62 wt.% at 500 RPM based on the weight loss of HDI.

The core material content of microcapsules can be tuned by adjusting the amount of HDI in the recipe. As illustrated in Figure 4.10, a higher fill content in the final capsules was achieved when more HDI was used, and this is a natural consequence because more HDI would be encapsulated. However, a stronger aggregation tendency was observed for the resultant microcapsules with a higher fill content, and this observation was in accordance with previous investigation [110]. The agglomeration may be caused by the residual amount of HDI that is not completely encapsulated into the microcapsules.

Figure 4.10 Core fraction of microcapsule as a function of the amount of HDI in the recipe.

The effects of other parameters in the synthesis on the fill content were also studied. The slight effect of agitation rate on the HDI content in the microcapsules is demonstrated in Figure 4.11. It is seen that a higher agitation rate leads to lower a fill content. The reason may be that the diffusion of 1,4-butanediol across thinner capsules shell was easier. The discussion above has shown that capsules prepared at higher agitation had thinner shell. Therefore, more 1,4-butanediol would penetrate the

Figure 4.11 Core fractions of microcapsules prepared at different agitation rate.

Figure 4.12 Core fractions of microcapsules as a function of gum arabic concentration.

thinner shell to react with encapsulated HDI. As a result, the fill content in the final capsules was lower at higher agitation rate.

The effect of the concentration of surfactant on the core fraction of the microcapsules was also investigated. Although the concentration of gum arabic solution significantly influenced the capsules diameter, as suggested in Figure 4.12, its effects on the fill content was negligible if there was. The HDI content in the final microcapsules remained at approximately 60 wt.% when the gum arabic concentration varied in the range of 1.5 – 10 wt.%.

4.2.7 Optimal reaction temperature

The reaction temperature had considerable influence on the synthesis of microcapsules. From the discussion of the MRT as described above, it is known that that a longer MRT is required to produce microcapsules with sufficient mechanical strength at lower temperature. As shown in Figure 4.13, the MRT is as long as about 150 min when the reaction temperature was 30 °C.

On the other hand, the reaction temperature also greatly influenced the HDI content of the produced microcapsules. As demonstrated in Figure 4.13, the HDI content increased from about 15 wt.% to 60 wt.% when the reaction temperature was reduced from 60 °C to 30 °C during the capsules synthesis. This variation in the core fraction is probably due to the side reactions between 1,4-butanediol and HDI, and water and NCO groups. As discussed above, the shell materials were mainly based on the reaction of 1,4-butanediol with more reactive MDI prepolymer, but the reaction with relatively less reactive HDI was also unavoidable, especially at elevated temperature. In addition, 1,4-butanediol preferably reacted with MDI prepolymer

Figure 4.13 MRT for the synthesis and core fraction of prepared microcapsules as a function of reaction temperature.

during the polymerization process, but the reaction would not stop immediately when the MDI prepolymer was exhausted, and the extra 1,4-butanediol would then continue to react with HDI. Consider that the reaction between hydroxyl group and isocyanate group was very rapid and temperature dependent, at higher temperature more HDI would accordingly be consumed, and as a result, the HDI content in the final microcapsules would be lower.

For the microencapsulation, it was desirable that the reaction is completed in a shorter time, at lower reaction temperature and at the same time, the HDI content of the resultant microcapsules is higher since it is more time and energy saving. From the discussion above, it was seen that the when the reaction temperature was high, the MRT would be shorter but the core fraction of the produced microcapsules would be lower; on the other hand, when the temperature was lower, the core fraction would be higher but the MRT would be longer. By consideration of all these concerns, it was reasonable to choose 40 °C as the optimal reaction temperature for our study. In this condition, the MRT and fill content of the capsules were optimally balanced.

4.3 Environmental stability of HDI microcapsules

4.3.1 Shelf life

When the microcapsules were exposed to open air at room temperature for one month, following TGA analysis revealed that the fill content dropped from 60 wt.% to 45 wt.%. These observations suggest the high permeability of the prepared microcapsules, and the encapsulated HDI liquid will slowly solidify during storage. Further optimization is still required to enhance the barrier property of the microcapsules in order to better protect the encapsulated core materials.

4.3.2 Stability in aqueous solution

To investigate the stability of the prepared capsules in wet environment, the capsules were immersed in water for a period of time and then analyzed by TGA. As a reference, microcapsules without immersion were also characterized by TGA and SEM, and the immersion time is defined as 0 h. As revealed in Figure 4.14, the fill content reduced steadily with the time that the capsules were immersed. After 48 h of

Figure 4.14 Core fractions of microcapsules after immersion in water.

Figure 4.15 Microcapsules after immersion in water for (a) 0 h; (b) 24 h; (c-d) 48 h.

immersion, the core fraction of the capsules reduced to zero. The probable reason is that during the immersion, water would diffuse across the microcapsule wall and react with the encapsulated HDI. As a result, the content of HDI would reduce with time, and finally all of the encapsulated HDI was solidified to afford the core fraction of zero.

This hypothesis could be proved by the SEM images of the capsules that were exposed to water. Figure 4.15a-c show the SEM images of the core part of the microcapsules after immersion in water for different period of time. It could be seen HDI within the capsules was consumed to produce some product with immersion time, and finally liquid core part was completely solidified. In the meantime, it was also found from Figure 4.15d that some product formed on the outer surface of the capsules after 28 h immersion in water. It might imply that in addition to the diffusion of external water into the capsule, encapsulated HDI also

simultaneously diffused out of the capsules and reacted with surrounding water to form polymer depositing on the surface of microcapsules.

4.3.3 Stability in organic solvents

Consider that the microcapsules may be applied in organic environment such as solvent-based paint, the stability of microcapsules in organic solvents was also investigated. If the microcapsules are stable and maintain the good protection to the encapsulated HDI liquid, the content of the NCO groups in the organic solvent after immersion will be low. Otherwise, the encapsulated HDI will leach out from the capsules during immersion and the NCO content in the solution will be high. Hexane, acetone, toluene and *o*-xylene were used in the present study.

The quantity of HDI leached out from a certain amount of microcapsules when the capsules were exposed to organic solvents was determined by titration. 0.5 g of HDI microcapsules was immersed in 25 mL of organic solvents for 30 s, 2 h, 4 h, 8 h, 12 h and 24 h, respectively. After immersion, the mixture was filtered and the collected filtrate was titrated. The quantity of NCO in the organic solvents and the

Figure 4.16 Fraction of HDI leached out as a function of immersion time.

equivalent weight of HDI leached out during the immersion were then determined by titration as described in Chapter 3. In addition, in order to determine the total weight of HDI contained in microcapsules, 0.5 g of microcapsules was crushed in a beaker, and 25 mL of toluene was then added to create a suspension. The NCO in the suspension was titrated, based on which the weight of HDI was calculated. It was found that 0.5 g of microcapsules contained 0.306 g of HDI.

Based on the equivalent weight of HDI in the filtrate, the weight fraction of HDI leached out of the microcapsules during the immersion process can be obtained. As demonstrated in Figure 4.16, when the microcapsules were immersed in acetone, toluene or *o*-xylene, about 80 % of HDI has leached out even though the immersion time was as short as 30 s. When the capsules were immersed in hexane, initially slightly less of HDI has leached out, but the fraction also increased to about 80 % after 2 h. Meanwhile, it was observed that generally the fraction slightly declined after 12 h immersion time. This might be due to the reaction between the dissolved NCO functional group and moisture from environment, and therefore the amount of NCO in the filtrate was underestimated.

Although the titration shows that only about 80 % of HDI leached out when the capsules were exposed to the organic solvents, it is believed that the fraction of HDI lost during the immersion may be even higher. First of all, some of HDI may be absorbed on the filter paper when the capsule/solvent suspension was filtrated, and hence the quantity of NCO in the filtrate may be underestimated. In addition, when the total weight of HDI was determined, some of NCO may be from the MDI prepolymer of the shell, but this part was also counted into HDI in the calculation, and hence the total HDI weight may be overestimated. Consider that more than 80 % of

Figure 4.17 (a) TGA weight loss curve and (b) SEM image of HDI microcapsule after immersion in toluene for 30 s (c) SEM images of HDI microcapsules after immersion in water for 2 days and then in toluene for 1 min.

the core materials was lost during the immersion, actually the results has revealed that the barrier property of the PU microcapsules is very poor in organic solvents.

The fill content of the microcapsules after immersion in organic solvent was characterized by TGA. As revealed in Figure 4.17a, the weight loss of HDI of the fresh microcapsules was not observed in the TGA curve of the microcapsules after they were immersed in toluene for 30 s, indicating that actually no HDI was left once the capsules were exposed to toluene. This result further confirmed the weak resistance of the HDI-filled PU microcapsules to toluene, and in the meantime

consolidated the conclusion that the fraction of the HDI leached out during the immersion process determined by titration as discussed above was underestimated.

Figure 4.17b shows the morphology of the microcapsules that were immersed in toluene for 30 s. It is clearly seen that the initially smooth outer surface of the capsules was completely distorted. This result confirms that the microcapsules are unable to resist toluene, and also explains the observation that no HDI was left once the capsules were exposed to toluene. Such a distortion may be because the encapsulated HDI was rapidly extracted out by toluene, the microcapsules therefore shrank inwards due to the pressure from external solvent. Alternatively, it may be simply that the organic solvent was able to soften and swell the capsules shell and resulted in the distortion. In order to identify the cause, HDI microcapsules were soaked in water for two days. As revealed in last section, the core part of the capsules would solidify. After that, the capsules were immersed in toluene. After 1 min, several droplet of the dispersion was put on a carbon tape for SEM examination. From Figure 4.17c it is seen that the initial spherical HDI microcapsules also became distorted. The first possibility is therefore ruled out since now there is not liquid HDI that could be extracted out by toluene, and the distortion of the microcapsules should be because the organic solvent softened or swelled the capsule shell. Actually when the microcapsules were exposed to the other three organic solvents, the TGA curve and SEM images showed the same feature.

There might be other causes accounting for the distortion of the microcapsules, but the observations described above has undoubtedly revealed that the HDI microcapsules were not stable in organic solvents, and the barrier property of the microcapsules was yet to be improved.

The poor barrier property may be an intrinsic problem for the PU microcapsules synthesized from interfacial polymerization. In an interfacial polymerization reaction, an initial membrane is produced at the interface between two phases, and increment of the membrane results in the final capsule shell. But the increment of requires that the reactants diffuse through the initial membrane to contact with each other. In other words, the formed membrane must be permeable; otherwise, the shell growth will not happen [107]. As a result, the produced microcapsule shell is also permeable, which means the barrier property may not be good enough. In addition, as stated in previous section, some voids were contained in the capsules shell due to the generation of CO₂. When the capsules were immersed in solvents, the solvent may enter the voids, swelling and softening the shell materials. Furthermore, the chemical component of the shell also influences the permeability. For example, it has been reported that the microcapsule made from MDI is more porous than that prepared from TDI [111]. In our synthesis, MDI prepolymer was used to construct the microcapsules, and therefore the capsules will be more permeable.

4.4 Wetting property of HDI on metal substrate

Intact coating provides excellent corrosion protection to metal. But the underlying substrate will be exposed to external corrosive environment when micro-crack formed within the coating. Self-healing anticorrosive coating is able to restore the corrosion protection function by autonomously generate a new film to cover the exposed substrate. Such a self-healing function is realized by the healing reaction of healing species that are stored in the coating system. In order that the newly formed film can cover the exposed area of the substrate, it is desirable that the healing species exhibits hydrophilic property on the metal substrate.

Figure 4.18 Static contact angle of HDI on steel substrate.

The wetting property of HDI liquid on steel substrate was characterized by contact angle. As shown in Figure 4.18, the contact angle was measured to be 26.17° . It indicates that HDI liquid is hydrophilic on the steel substrate used, which implies that once HDI is released from ruptured microcapsules, it will spread to cover the exposed steel substrate.

4.5 Self-healing anticorrosive performances of HDI microcapsules based coatings under various testing methods

Self-healing anticorrosive epoxy coatings were prepared by dispersing synthesized HDI-filled PU microcapsules into epoxy resin. During the synthesis, the agitation rate was carefully tuned so that the produced microcapsules had expected diameter. When the microcapsules integrated epoxy resin was applied on pre-treated steel panels and cured at ambient temperature for 24 h, the afforded coating had a smooth surface.

4.5.1 Accelerated salt immersion corrosion test

An accelerated salt immersion test was performed to the HDI microcapsules based epoxy coating. The prepared HDI based coating was manually scribed and then exposed to 10 wt.% NaCl aqueous solution for 48 h. As shown in Figure 4.19, when

Figure 4.19 Coated steel panel after immersion in 10 wt.% NaCl solution for 48 h. (a) coated with HDI-based self-healing coating; (b) coated with blank coating.

the scribed specimen coated with the neat epoxy coating was immersed in salt solution, severe corrosion was observed at the scribed area. On the contrary, the specimen coated with the self-healing coating was free of corrosion after immersion. Such a difference clearly demonstrates that the epoxy coating modified by HDI filled microcapsules exhibited excellent anti-corrosion property.

4.5.2 Salt spray test

In order to better assess the anticorrosive performance of the HDI microcapsules incorporated epoxy coating, a comprehensive long term salt spray test was performed following standard test method ASTM B117.

The HDI microcapsules based epoxy coatings were manually scribed and placed in a salt spray chamber, while the corrosion behavior of the specimens was monitored. The influences of the three parameters, the average diameter of HDI microcapsules, weight fraction of microcapsules in coating and the thickness of final coating, to the corrosion protection ability of the coatings were investigated. For each parameter three values were taken, so overall 27 formulations of coatings were

Table 4.3 Formulations of HDI microcapsules based epoxy coating.

D (μm)	Φ (wt.%)	H (μm)	Name of samples
100 ± 31.6	10	400, 300, 200	SP-100-10-400; SP-100-10-300; SP-100-10-200
	5		SP-100-5-400; SP-100-5-300; SP-100-5-200
	2		SP-100-2-400; SP-100-2-300; SP-100-2-200
50 ± 17.2	10		SP-50-10-400; SP-50-10-300; SP-50-10-200
	5		SP-50-5-400; SP-50-5-300; SP-50-5-200
	2		SP-50-2-400; SP-50-2-300; SP-50-2-200
30 ± 9.4	10		SP-30-10-400; SP-30-10-300; SP-30-10-200
	5		SP-30-5-400; SP-30-5-300; SP-30-5-200
	2		SP-30-2-400; SP-30-2-300; SP-30-2-200
Control (pure epoxy)	0		SP-Blk-400; SP-Blk-300; SP-Blk-200

Note: Naming policy of samples is used as SP-D- Φ -H where SP means salt spray test, D is average diameter of microcapsules, Φ is weight fraction of microcapsules in coating, and H is thickness of coating.

prepared for the test. In addition, three blank epoxy coatings were prepared at different coating thickness as control. All the formulations of the coatings for the salt spray test are summarized in Table 4.3, and they are labeled in the format of SP-D- Φ -H, while the three control samples were labeled as SP-Blk-H.

The specimens were exposed to salt fog for 2 months in a monitored salt spray chamber. As shown in Figure 4.20, it is seen that after exposure, the blank epoxy coatings (SP-Blk-400, SP-Blk-300, SP-Blk-200) with three different thicknesses developed corrosion along the scribes. Among the other 27 microcapsules modified coatings, coatings SP-100-10-400 and SP-100-10-300 showed no corrosion, indicating their excellent corrosion protection property. In the meantime, slight corrosion was also observed on coatings SP-100-10-200, SP-100-5-400, SP-100-5-300 and SP-100-5-200. It means that these four formulations could provide some corrosion protection, but the performance was slightly worse compared with formulations SP-100-10-400 and SP-

Figure 4.20 HDI based self-healing coatings after exposure to salt spray for 2 months.

100-10-300. For the other formulations, severe corrosion was observed along the scribes, indicating that the protection of these coatings to steel substrates was quite poor. The results reveal that the HDI microcapsules based epoxy coatings exhibit good corrosion protection function to metal substrate if they are properly formulated.

It was found from the salt spray test that the growth of corrosion was related to

exposure time. Figure 4.21 demonstrated the process that corrosion developed on three coatings (SP-100-10-400, SP-50-10-400 and SP-30-10-400) when the salt spray test proceeded. It is seen that corrosion started to appear on SP-50-10-400 and SP-30-10-400 from the first week, and more and more rust was observed when the exposure time of the specimens in salt fog increased. This is a reasonable result because corrosion is an electrochemical process, and it proceeds with time.

Figure 4.21 also revealed the influence of microcapsules size on the corrosion protection ability of the microcapsules based coating. The three formulations, SP-100-10-400, SP-50-10-400 and SP-30-10-400, differed only in the average

Formulations	Exposure Time in Salt Fog			
	0 week	1 week	1 month	2 months
SP-100-10-400: $D = 100 \pm 31.6 \mu\text{m}$ $\Phi = 10 \text{ wt.}\%$ $H = 400 \mu\text{m}$
SP-50-10-400: $D = 50 \pm 17.2 \mu\text{m}$ $\Phi = 10 \text{ wt.}\%$ $H = 400 \mu\text{m}$
SP-30-10-400: $D = 30 \pm 9.4 \mu\text{m}$ $\Phi = 10 \text{ wt.}\%$ $H = 400 \mu\text{m}$

Figure 4.21 Influence of exposure time and capsules diameter on the anticorrosive performance of HDI based self-healing coatings.

diameter of the HDI microcapsules, while the other two parameters of self-healing coatings remained the same. It is seen that specimen SP-100-10-400, in which the diameter of HDI microcapsules was 100 μm , was almost free from rust, while specimen SP-30-10-400, in which the diameter of microcapsules was 30 μm , showed most serious corrosion. The extent of corrosion of specimen SP-50-10-400 was between that of these two specimens. Actually the comparison of other specimens also showed a similar trend, in which the coatings exhibited best corrosion resistance performance when the diameter of incorporated microcapsules was 100 μm , followed by the 50 μm specimens and the 30 μm specimens showed worst corrosion protection. This results indicate that the HDI microcapsules based epoxy coating afforded better corrosion protection towards a steel substrate when the diameter of microcapsules was bigger, given other parameters of the coating remained. This result is in good agreement with that reported in a previous publication [34].

The corrosion protection performance of the HDI based coating was also affected by the weight fraction of microcapsules in the coating and the coating thickness. Figure 4.22 shows nine specimens after exposed to salt fog for two months. The diameter of the HDI microcapsules was at 100 μm for the 9 specimens, while the weight fraction of microcapsules and coating thickness varied for each formulation. If we compare the specimens in each row, in which the weight fraction of microcapsules was constant, it is seen that, generally, more rust was observed on the specimens with smaller coating thickness. If the specimens in each column, in which the coating thickness was the same, were compared, it could be found that the corrosion was more severe when the weight fraction of capsules declined. Similar trend can also be found from other specimens. The results imply that higher microcapsule content in the coating as well as larger coating thickness is favorable for the HDI based self-healing

$D = 100 \pm 31.6 \mu\text{m}$	$H = 400 \mu\text{m}$	$H = 300 \mu\text{m}$	$H = 200 \mu\text{m}$
$\Phi = 10 \text{ wt.}\%$	SP-100-10-400	SP-100-10-300	SP-100-10-200
$\Phi = 5 \text{ wt.}\%$	SP-100-5-400	SP-100-5-300	SP-100-5-200
$\Phi = 2 \text{ wt.}\%$	SP-100-2-400	SP-100-2-300	SP-100-2-200

Figure 4.22 Influence of weight fraction of microcapsules (Φ) and coating thickness (H) on the anticorrosive performance of HDI based self-healing coatings.

anticorrosive coating. It should be pointed out that although the edge and backside of the substrate was protected by water resistant tape during the salt spray test, some corrosion still occurred at the non-coated part. That is why much of yellowish rust was seen on the specimen although the real corrosion was much less as for specimen SP-100-5-200 in Figure 4.22.

As discussed above, the salt spray test of the HDI based self-healing anticorrosive coating reveals that the microcapsules size, weight fraction of microcapsules in coating and the coating thickness all significantly influenced the anticorrosion performance of the prepared coating. Generally, larger microcapsules

size, higher microcapsules content and thicker coating would afford better corrosion protection. The mechanisms of these variances will be discussed in Chapter 6. In addition, from the salt spray test, it is indicated that for the HDI based self-healing coating, in order to achieve a good corrosion protection performance, the diameter of HDI microcapsules should be larger than 100 μm , the weight fraction of capsules should be higher than 5 wt.% and the coating thickness should be larger than 300 μm .

The standard salt spray test provided comprehensive information about the anticorrosive performance of the HDI based self-healing coating. Nevertheless, it is noteworthy that there are also some shortcomings for this test. For example, this test affords only qualitative results, so if the corrosion protection abilities of two specimens are only slightly different, this test will be unable to differentiate them. In addition, there are also several systematic errors with the test. For example, the specimens were manually scratched before exposure to salt fogging. Although the standard method ASTM D1654 was obeyed when the scratches were made, it is still impossible to ensure that all the scribes were the same on each specimen, and this will definitely introduce some variation to the test results. Some other factors influencing the test results include the quality of prepared microcapsules, distribution of microcapsules in coating, the position of specimen in the salt spray chamber and so on. However, despite of these shortcomings, salt spray test is a valuable method to evaluate the anticorrosive function of coatings. Specifically, in our study it was confirmed from the test that by optimizing the formulation, HDI based self-healing epoxy coating could provide excellent corrosion protection to metal substrates.

4.5.3 DC electrochemical test in salt solution

The self-healing ability of the self-healing coating was elucidated by an established electrochemical test [18, 95]. The test was performed on a conventional

Figure 4.23 Schematic diagram of the electric circuit in the DC electrochemical test.

Figure 4.24 DC electrochemical test results for scribed control and self-healed specimen.

three-electrode system, and a steel panel that was coated with HDI based epoxy coating served as the working electrode. In the measurement, a potential was applied and the current passing through the coating was recorded. An intact coating serves as perfect capacitor, so the current will be extremely low. As illustrated in Figure 4.23, once the coating is scratched, the underlying steel substrate directly contacts with the electrolyte solution to form an electrical circuit, and hence the current will be high. When the scratches of the coating are repaired, it can be imagined that the current will

be greatly reduced again. Therefore, the change of the current in the circuit will indicate the self-healing behavior of a scribed coating.

The DC electrochemical test was performed when the scribed coating had been immersed in 10 wt.% salt solution for 2 days. The recorded current was normalized by the scratched area of the coating. As shown in Figure 4.24, the current passing through the scribed control coating was about 10 mA/cm^2 . By comparison, current passing through the scribed self-healed coating was only about $0.2 \text{ }\mu\text{A/cm}^2$ at a slightly negative bias to the reference electrode. The dramatically reduced current value indicated that the scribes of the self-healing coating were autonomously re-sealed during the immersion process, while the ones of the control specimen were still open.

4.5.4 EIS measurement in salt solution

An electrochemical impedance measurement was taken to estimate the self-healing performance of the HDI based self-healing anticorrosive coating. HDI based self-healing coating was coated on steel substrate and then scratched manually. After that, the scratched specimen was immersed into 1 M of sodium chloride solution to allow for corrosion and self-healing. After a period of immersion, the impedance spectra of the specimen were recorded by EIS.

In order to interpret the collected EIS data, a simplified model was constructed based on a proven model [29]. As shown in Figure 4.25a, when the microcapsules loaded coating is scratched, the substrate is corroded by the corrosive electrolyte solution to form an oxide layer, i.e. rust. The scratch ruptures the embedded microcapsules to release HDI monomer, which will react with water to form a new film to cover the exposed substrate. Based on this simplified model, an equivalent circuit is established as shown in Figure 4.25b. Although it is extremely complicated

Figure 4.25 (a) Schematic diagram of a scratched self-healing coating in electrolyte solution; (b) equivalent circuit of the scratched self-healing coating in EIS measurement.

to assign the impedance spectra to the components of the circuit, the EIS data is able to provide some critical information regarding the self-healing behavior of the coating. If the self-healing behavior occurs at the scratched site, one of the most direct information from the EIS data will be the change of healing resistance (R_{healing}) and healing capacitance (C_{healing}).

Figure 4.26 shows the EIS spectrum of HDI-based self-healing coating after exposure to the salt solution for 8 h. From the spectrum one can find the change of impedance modulus (Z_{mod}) and phase angle as a function of the frequency. The equivalent circuit was used to fit the obtained EIS data by Gamry software, and the fitted curves were plotted in Figure 4.26 as well. Based on the fitted curves, the values

Figure 4.26 Bode plots (impedance module, Z_{mod} , and phase angle) and fitted curves (solid line) of scratched HDI-based coating after 8 h of immersion in 1 M salt solution.

of each component in the equivalent circuit can be obtained: $R_u = 22.01$ ohms; $C_{\text{coating}} = 13.79 \times 10^{-6}$ F; $R_{\text{pore}} = 269.7$ ohms; $C_{\text{healing}} = 7.543 \times 10^{-9}$ F; $C_{\text{oxide}} = 176.2 \times 10^{-6}$ F; $R_{\text{oxide}} = 16.55 \times 10^3$ ohms; $C_{\text{dl}} = 23.64 \times 10^{-6}$ F; $R_p = 21.09$ ohms; $R_{\text{healing}} = 2.377 \times 10^3$ ohms. These values stand for the properties of the equivalent circuit when the HDI microcapsules based coating was scribed and exposed to salt solution for 8 h.

The values of each component of the equivalent circuit can be hence similarly

Figure 4.27 Healing resistances (R_{healing}) of HDI-based self-healing coating when the coating was immersed in 1 M salt solution for different time.

obtained when the specimen was immersed in salt solution for different time, and the R_{healing} of the HDI-based self-healing coating as a function of immersion time was plotted in Figure 4.27. It could be seen that generally the R_{healing} of the self-healing coating exhibited a trend of increase with immersion time. When the immersion increased from 2 h to 24 h, the R_{healing} increased from 1.90×10^3 ohms to 4.65×10^3 ohms. Such an increase of the R_{healing} is originated from the formation and increment of the new film, and it implies that the scribes of the coating were self-healed during the immersion.

The new film generated in the scribes also served as a capacitor. The capacitance of a capacitor in an electric circuit is calculated as:

$$C = \varepsilon_r \varepsilon_0 \frac{A}{d} \quad (4.3)$$

where A is the area of overlap of two plates, d is the distance between the plates, ε_0 is electric constant (about 8.854×10^{-12} F/m) and ε_r is the dielectric constant of the materials between the plates. In the present measurement, A was basically determined by the width of scribes and almost constant, and d is the thickness of the formed film. If the ε_r of the film within the scribes was constant, C_{healing} should reduce with immersion since d was increasing due to the increment of the film. Unfortunately, the change of C_{healing} did not show a clear trend in the whole process. This is reasonable since the compactness, content of moisture and other properties of the newly formed film might vary when the healing process proceeded, and hence the change of ε_r also became very complicated. As a result, the change of the C_{healing} during the immersion process was complicated and hard to predict.

The DC electrochemical test and EIS measurement both revealed the excellent self-healing property of the HDI-based coating. The self-healing behavior of the prepared coating is based on the polymerization of HDI monomer, and the detailed

self-healing mechanism will be discussed in Chapter 6. The healing process does not require any manual intervention. In addition, it is seen that the self-healing coating contains only one set of microcapsules, and it does not use any catalyst. Therefore, this is a one-part, catalyst free self-healing coating.

4.6 Summary

PU microcapsules containing HDI as core materials were facilely synthesized via an interfacial polymerization in an oil-in-water emulsion. The synthesis afforded spherical microcapsules with the yield of about 70 %, and the yield was dependent on reaction parameters. The diameter of the microcapsules was in the range of 5 – 350 μm , and the shell thickness was in the range of 1 - 15 μm when the agitation rate varied from 300 to 2000 RPM. The average diameter and shell thickness of the microcapsules reduced with the increase of agitation rate following a linear relationship in double logarithm coordinates. HDI content of the resultant capsules was around 60 wt.%, and it declined with the increase of the reaction temperature. By investigating the influence of the reaction temperature on the synthesis, it was found that the optimal temperature was 40 °C for the reaction. The reactivity of HDI was maintained during the microencapsulation process. The stability of HDI microcapsules in different environments was studied, and the barrier property in organic solvents was still to be improved.

A self-healing anticorrosion coating was prepared by incorporating the synthesized HDI microcapsules into epoxy coating. The prepared coating showed excellent corrosion protection ability to steel substrate under an accelerated corrosion process. A comprehensive salt spray test was carried out following industrial standard, and the results demonstrated that the corrosion protection performance of the coating was influenced by the coating variables including the diameter of capsules, weight

fraction of capsules in coating and the coating thickness. In addition, it was found from the salt spray test that in order to achieve satisfied corrosion protection performance, the diameter of the microcapsules should be larger than 100 μm , the content of the microcapsules in the coating matrix should be higher than 5 wt.% and the coating thickness should be larger than 300 μm . The self-healing ability of the prepared coating was demonstrated by a DC electrochemical test and EIS measurements. The HDI-based coating is a real one-part, catalyst free self-healing anticorrosive coating since the healing process did not involve any manual intervention, and only one set of microcapsules was used to in the self-healing coating.

Chapter 5 Organic Silane Microcapsule Based Self-healing Anticorrosive Coatings

5.1 Motivation

Many healing species such as DCPD [40, 41], linseed oil [62], amines [52] and epoxy resins [58] have been encapsulated for self-healing purposes, and in the previous chapter, microencapsulation of HDI for self-healing was explored [112].

Inorganic silicates have been used for self-healing and corrosion protection applications for many years [113-115]. For example, Aramaki *et al.* used sodium silicate in the preparation of a highly protective and self-healing film, which displayed good corrosion suppression effect to zinc surface [114]. The inorganic silicate based corrosion resistant coating mainly takes use of the deposition of silicates to realize the corrosion suppression function. But inorganic silicates are usually directly mixed into coating matrix, and hence they may be susceptible to interaction with environment, leading to problems in corrosion protection during long term service. Organic silane molecules tend to hydrolyze in wet environment and crosslink to form a solid film, and such a property indicates their potential as novel healing agent for one-part and catalyst free self-healing additive to corrosion resistant coating. To date, the research on organic silanes for self-healing materials remains largely unexplored, and only a few publications have appeared [18, 19, 96]. Braun and co-workers reported the polydimethylsiloxane-based microcapsules applied for self-healing coatings [18, 19]. A mixture of hydroxyl end-functionalized polydimethylsiloxane and polydiethoxysiloxane was directly phase-separated, or encapsulated and then dispersed in epoxy matrix, and the yielding coating exhibited good self-healing ability for corrosion protection. However, organo-tin catalyst was necessary for such self-

healing systems. Another study was microencapsulation of self-synthesized silyl ester for self-healing coatings [96]. Octyldimethylsilyloleate, a silyl ester, was synthesized and encapsulated into PUF microcapsules, which were then incorporated into epoxy to produce a self-healing coating, and the excellent corrosion-resistant property of the prepared coating was demonstrated via self-healing. But the synthesis of silyl ester increased the complexity and cost to the procedure.

In the present study, a novel self-healing anticorrosive polymer coating is fabricated based on the microencapsulated novel organic silane, i.e. *1H,1H',2H,2H'*-perfluorooctyl triethoxysilane (POTS). There are several advantages of this coating system over the existing self-healing materials: a) POTS is able to hydrolyze in wet environment to form a silane-based film and as mentioned, such ability indicates that the use of catalyst can be avoided in the end self-healing product. b) The newly formed film from hydrolysis and poly-condensation of POTS and water is hydrophobic [116]. Such a special wetting property will serve to repel aqueous electrolyte solution away from metal and hence provides further corrosion protection to metal substrate [96]. c) POTS is commercially available and hence the preparation of self-healing coating will be more convenient and time efficient for mass production.

5.2 Microencapsulation of POTS

5.2.1 Overview of synthesis

PUF microcapsules containing POTS as core materials were synthesized through an *in situ* polymerization in an oil-in-water emulsion. In the synthesis, ethylene maleic anhydride copolymer was surfactant, urea and formaldehyde were the monomers contributing to the microcapsule shell, and POTS was the encapsulated core material, as illustrated in Fig. 5.1. Ammonium chloride behaved as hardener and resorcinol acted as brancher for the polymerization reaction [60]. When the oil phase

Figure 5.1 Mechanism of the PUF microcapsules synthesis

comprised of POTS and toluene was added into the aqueous solution containing surfactant, urea, ammonium chloride and resorcinol, an oil-in-water emulsion was created. After the addition of formaldehyde solution, polymerization reaction between urea and formaldehyde occurred in the acidic aqueous phase to form a PUF membrane surrounding the oil phase. Further polymerization reaction produced PUF nanoparticles depositing on the initial membrane, leading to the shell increment to form the final microcapsules shell. The encapsulation was achieved at elevated temperature, and therefore most of toluene will evaporate away during the synthesis, leaving POTS as the main component of core materials in the final microcapsules, which will be illustrated by FTIR analysis in latter section.

5.2.2 Yield of synthesis

The synthesis of the capsule was not a strict stoichiometric reaction, and most of the toluene would evaporate during the heated reaction process. The yield of the synthesis is therefore simply calculated by the ratio of the mass of collected microcapsules to the total mass of POTS, urea, ammonium chloride and resorcinol, while the mass of toluene was ignored.

Based on the calculation above, the yield was around 67 % in a typical synthesis, in which the agitation rate was 800 RPM. The yield is relevant to agitation rate during the synthesis. Generally, higher agitation rate results in lower yield of synthesis. Based on our observations, such a correlation may be explained by the disturbance of emulsion solution. The emulsion solution was disturbed due to mechanical agitation during the synthesis, and part of starting materials was observed to stick on the wall of the container, forming bulk PUF polymeric materials. This part of materials would not contribute to the final PUF microcapsules. Under higher agitation, the disturbance of the solution was more serious, and a larger portion of materials would stick on the wall, and hence the yield of microcapsules was accordingly lower. In addition, the shear force of the emulsion solution under agitation may also account for the yield variation. Higher agitation rate creates higher shear force, and therefore a larger portion of produced microcapsules may be destroyed [40], resulting in lower yield for the synthesis. The yield of the synthesis reduced to about 52 % when the agitation rate was increased to 1500 RPM.

5.2.3 Chemical constituent of microcapsules

The chemical composition of prepared microcapsules was determined from FTIR analysis. The FTIR spectra of complete capsules together with pure grades of POTS, shell and core materials were shown in Figure 5.2. It is seen that the full capsules contained signals at 3330 cm^{-1} (O-H and N-H stretching), 1620 cm^{-1} (C=O stretching) and 1540 cm^{-1} (N-H bending) [58, 117], indicating the formation of PUF from the polymerization reaction between urea and formaldehyde. In addition, the signals at 1240 cm^{-1} and 1190 cm^{-1} (C-F stretching) as well as the signals at 1100 cm^{-1} and 1080 cm^{-1} (Si-O-C stretching) implies the presence of POTS within the synthesized microcapsules. A simple comparison between the spectrum of full

Figure 5.2 FTIR spectra of POTS, capsule core, capsule shell and full PUF microcapsules.

Figure 5.3 SEM images of (a) microcapsules; (b) broken microcapsule; (c) cross section of microcapsule shell.

microcapsule and capsule shell clear shows that the POTS was absent in the shell part. In the meantime, it can be seen that the spectrum of capsule core is identical to that of pure POTS. Therefore, it is logical to conclude that POTS is not absorbed on the PUF microcapsules; instead, it is indeed encapsulated into the microcapsules as core materials. In other words, the synthesis successfully produced PUF microcapsules containing POTS liquid as the core material.

5.2.4 Morphology and diameter of microcapsules

The synthesized microcapsules were analyzed under SEM. As shown in Figure 5.3a, the produced microcapsules have a spherical shape. In addition, it is seen from Figure 5.3b that the microcapsule is composed of a rough outer surface and a relatively smooth inner surface. The inner surface is an impervious PUF shell, and the outer surface is the deposition of a large number of PUF nanoparticles [40]. The cross section of capsules wall as shown in Figure 5.3c reveals that the thickness of the smooth inner shell is around 218 nm. The shell structure of the synthesized microcapsules is in good agreement with previous results [40, 91].

5.2.5 Thermal property and core fraction of microcapsules

The thermal property and core fraction of microcapsules were characterized by TGA analysis. The TGA weight loss curves of microcapsules synthesized at 800 RPM along with pure POTS and capsule shell material as a function of temperature are shown in Figure 5.4. It can be seen that microcapsules experienced significant weight loss from approximately 100 °C, which is in good agreement with that of pure POTS, revealing the successful encapsulation of POTS within the microcapsules. The decomposition of shell materials started from about 200 °C.

Figure 5.4 TGA weight loss curve of pure POTS, prepared microcapsules and capsule shell, and the derivative of these TGA curves.

The derivative of the weight loss curve of microcapsules was also plotted in Figure 5.4. It clearly shows the evaporation process of POTS in the first peak and decomposition process of capsules shell in the peaks after 200 °C. From the peak width of the derivative curve, the core fraction of the microcapsules was determined to be around 60 wt.% at 800 RPM. The core fraction of the produced microcapsules could be increased by raising the content of POTS in the oil phase, but as will be discussed in latter section, the quality of microcapsules would be compromised.

5.2.6 Influence of agitation rate on microencapsulation

From discussion above it is clear that the agitation rate greatly influenced the yield of the synthesis. It was found that the agitation rate also imposed considerable effect on the diameter of the resultant microcapsules. As a matter of fact, in an emulsion polymerization process, the microcapsules diameter is influenced by a combination of several factors including the geometry of the mixing device, viscosity of the reaction media, surfactant concentration, agitation rate, temperature, *etc.* Among the variety of factors, agitation rate is the most important one in determining average diameter of microcapsules.

Figure 5.5 Diameter and core fraction of microcapsules as a function of agitation rate.

In this study, the influence of agitation rate on the diameter of produced microcapsules was investigated. It was found from Figure 5.5 that the average diameter of microcapsules would reduce from about 400 μm to about 40 μm when the agitation rate was raised from 300 RPM to 1500 RPM. This observation demonstrates that the increase of agitation rate will result in smaller microcapsules. The main reason for such a correlation is that at higher agitation rate, finer oil droplets would form in the emulsion system due to the stronger shear force. Because the diameter of the final microcapsules was highly dependent on the oil droplet size in an *in situ* polymerization [118], in this case, the final microcapsules were accordingly smaller. Actually, as shown in Figure 5.5, the mean diameter of resultant microcapsules exhibits linear relationship to the agitation rate in double logarithm coordinates, and this result is in agreement with previous research [40, 51].

Although the agitation rate exhibited significant effect on the diameter of microcapsule as discussed above, its influence on core fraction was almost negligible. As shown in Figure 5.5, the core fraction approximately remained at about 60 wt.% when the agitation rate was increased from 300 RPM to 1500 RPM.

5.3 Role of toluene in the synthesis

As mentioned above, the POTS content of the synthesized PUF microcapsules could be increased by raising the POTS content in the oil phase when the emulsion solution was created. Unfortunately, it was found that the increase of POTS content in the oil phase would compromise the quality of the final microcapsules. When the oil phase was composed of POTS and toluene with the weight ratio of about 2:1, the produced microcapsules had regular and spherical shape as shown in Figure 5.3a. However, when the weight ratio was increased to 4:1, as shown in Figure 5.6, the prepared microcapsules appeared irregular in shape. It was even found that if the oil phase was composed of pure POTS, the expected microcapsules would not be produced since no stable emulsion was formed. Hence it can be tentatively concluded that toluene served as a necessary auxiliary agent for emulsion although it would evaporate away when the synthesis proceeded. In our study, the ratio of 2: 1 between POTS and toluene was adopted to synthesize POTS microcapsules, because at this ratio, the POTS content and quality of resultant microcapsules were best balanced.

Figure 5.6 SEM image of PUF microcapsules when POTS : toluene = 4 : 1.

5.4 Environmental stability of microcapsules

PUF microcapsules are well known for their excellent stability and barrier properties [40, 72], and these properties were also confirmed in the present study. When the synthesized POTS-filled microcapsules were exposed to open air for one month, it was found that the core fraction only slightly reduced from about 60 wt.% to about 57 wt.% based on TGA analysis. It means that the PUF microcapsules shell is impervious and provides good protection to the encapsulated POTS.

The stability of the POTS filled PUF microcapsules in different solvents was investigated. The synthesized microcapsules were immersed into water, hexane, toluene, ethanol and methanol for a period of time. After immersion, the suspension was vacuum filtered and the weight fraction of POTS in the collected microcapsules was determined by TGA analysis. The variation of the core fraction when the capsules were exposed to these solvents for different time is plotted in Figure 5.7. It is seen that the core fraction only slightly reduced when the microcapsules are exposed to water, hexane, methanol and toluene for up to 24 h, indicating that the microcapsules were stable in these solvents, and the excellent barrier property of the capsules remained. However, when the microcapsules were immersed in ethanol, dramatic drop of the POTS content of the microcapsules was observed, and after 24 h there was almost no POTS left in the capsules. It indicates that the PUF microcapsules were unable to resist ethanol.

In order to identify the reason for the poor barrier property of the PUF microcapsules in ethanol, the collected microcapsules were further examined using SEM. As revealed in Figure 5.8, the microcapsules have been completely out of their initial shape after exposed to ethanol for 24 h. It confirms that the PUF microcapsules are unable to resist ethanol and also explains why the core fraction of the capsules

Figure 5.7 Core fraction of PUF microcapsule after immersion in solvents.

Figure 5.8 SEM image of PUF microcapsule after immersion in ethanol for 24 h.

dropped to zero after immersion in ethanol.

The interior surface of the microcapsules was inspected using SEM after the capsules were immersed in the different solvents, as shown in Figure 5.9. For comparison the interior surface of fresh POTS-filled microcapsules was also examined. It has been known that the synthesized PUF microcapsules shell is composed of an impervious and smooth inner membrane, on which a large number of PUF nanoparticles were deposited. Therefore, it can be seen that the excellent barrier

property should be mainly from the impervious inner membrane, because the agglomeration of PUF nanoparticles is highly permeable. Compare Figure 5.9(b-e) with Figure 5.9a, it is seen that after immersion in water, hexane, methanol and toluene for 24 h, the smooth interior surface of the microcapsules basically remained. On the contrary, as revealed in Figure 5.9f, the smooth surface was destroyed when the capsules were exposed to ethanol. Without the support of the inner shell, naturally the microcapsules will be unable to preserve the morphology of the microcapsules, as shown in Figure 5.8.

The different stability of the capsules in different solvents might be explained

Figure 5.9 Interior surfaces of (a) fresh PUF microcapsule and of microcapsules after immersion in (b) water, (c) toluene, (d) hexane, (e) methanol and (f) ethanol for 24 h.

by the solubility of PUF microcapsule shell materials. During the synthesis of PUF microcapsules, the inner PUF membrane contained some polar groups, so it might be partially soluble in polar organic solvent such as ethanol [62]. Unfortunately, it was found that the microcapsules were still stable in methanol, which has the same polarity with ethanol. So the reason by which the inner shell was destroyed by ethanol but remained intact in other solvents may be more complicated.

5.5 Self-healing anticorrosive performances of POTS microcapsules based coatings under various testing methods

POTS based self-healing anticorrosive epoxy coatings were prepared by dispersing synthesized POTS-filled PUF microcapsules into epoxy resin. During the synthesis, the agitation rate was carefully tuned so that the produced microcapsules had expected diameter. When the microcapsules integrated epoxy resin was applied on pre-treated steel panels and cured at ambient temperature for 24 h, the final coating was obtained with smooth surface.

Similarly the synthesized POTS microcapsules were integrated into silicone resin to prepare a corrosion resistant silicone elastomer. The prepared elastomer has much weaker adhesion to metal substrate than epoxy, and this is favorable for long term corrosion test as discussed below since the coating has to be peeled off to inspect the corrosion on the underneath substrate.

5.5.1 Accelerated salt immersion corrosion test

An accelerated salt immersion test was performed to the POTS microcapsules based epoxy coating to demonstrate the self-healing anticorrosive property. The prepared coating was manually scratched and then immersed into 10 wt.% NaCl aqueous solution to evaluate the anti-corrosion performance. It can be seen from

Figure 5.10 Coated steel panel after immersion in 10 wt.% NaCl solution for 48 h. (a) coated with POTS-based self-healing coating; (b) coated with blank coating.

Figure 5.10 that the scratched area of the steel panel coated with self-healing coating was nearly fully free of corrosion after 48 h immersion in salt solution, while severe corrosion was seen in the control specimen. This considerable difference clearly demonstrates the excellent corrosion protection of the prepared coating towards steel panel. As will be discussed in latter chapter, the anticorrosion function of the scratched coating is realized through a self-healing mechanism.

5.5.2 Corrosion protection performance of intact coating in HCl solution

The anticorrosion property of an intact POTS based coating was demonstrated by a long time corrosion test. POTS microcapsules based silicone elastomer was coated on pre-treated steel substrate and then exposed to 1 M hydrochloric acid solution for one month. As shown in Figure 5.11, apparently the POTS based anticorrosive silicon elastomer shows much less corrosion than the control specimen after exposure.

When the coating was peeled off, the underlying steel substrate was examined

Figure 5.11 Anticorrosive silicon elastomer and control elastomer after exposure to 1 M HCl solution for 1 month.

Figure 5.12 SEM images of steel substrate of (a) anticorrosive specimen before exposure; (b) anticorrosive specimen after exposure; (c) control specimen before exposure and (d) control specimen after exposure.

under SEM, as shown in Figure 5.12. It is seen that prior to exposure to the HCl solution, both steel substrates have smooth surface (Fig. 5.12a and Figure 5.12c). Nevertheless, after exposure, the surface of the anticorrosive specimen (Fig. 5.12b) was much smoother than the control sample (Fig. 5.12d). Since corrosion of metal

will create rust and destroy the smooth substrate surface, this considerable difference indicates that the steel substrate coated with POTS-based anticorrosive coating was much less corroded during the exposure to corrosive HCl acid solution.

The corrosion resistant property of the POTS based coating was also demonstrated by EDX analysis. It is known that corrosion of steel will convert iron (Fe) into rust (Fe_2O_3). Hence, for a steel panel, within a given area, the ratio of element O to Fe (O/Fe) will increase when corrosion occurs, and a higher O/Fe value in turn implies more corrosion. To compare the extent of corrosion on the steel substrate that was coated with POTS-based anticorrosive elastomer or control elastomer during exposure to 1 M HCl solution, the steel substrates were analyzed by EDX to determine the O/Fe ratio of the substrate. As shown in Fig. 5.13, prior to exposure to HCl solution, the steel substrates of both anticorrosive specimen and control specimen afforded only element Fe. It means that the substrates were nearly totally free of corrosion. After exposure, elements O, Fe and Si were detected on both specimens, but it can be seen that the O/Fe value was dramatically different between two specimens. The O/Fe of the substrate coated with anticorrosive elastomer is 0.425 while that of the control sample is 1.148. Admitted that the O/Fe difference between these two specimens alone is not very conclusive since the corrosion product may be quite complicated, and in the meantime, element O may come from other sources such as open air and silicone elastomer. Nevertheless, if the influence of other factors is assumed to be at the same level for the two specimens in the test, which is a reasonable assumption, the apparently smaller O/Fe value of the anticorrosive specimen from another aspect supports the conclusion above that the corrosion of substrate coated with the POTS-based anticorrosive coating is less compared with that of the control specimen. From the SEM and EDX analysis, it can be concluded that

Figure 5.13 EDX analysis of POTS-based anticorrosive coating and control coating. The specimen and analyzed area are the same as those shown in Fig. 5.12.

the integration of POTS microcapsules enhanced the corrosion protection performance of the silicon elastomer coating.

5.5.3 DC electrochemical measurement in salt solution

Similar to the HDI based self-healing coating as discussed in Chapter 4, the self-healing ability of the POTS based coating was also characterized by a DC electrochemical test following an established method as described in previous publications [18, 95]. The electrochemical test was performed when the scribed coating had been immersed in 10 wt.% salt solution for 2 days. Potential was swept and the current passing through the coating was recorded. The current was normalized by the area of the scratches.

As shown in Figure 5.14, for the control coatings, the current passing through the coating was about 10 mA/cm². By comparison, the current passing through the scribed POTS based self-healed coating was only about 2.2 μ A/cm². The dramatic difference implied that the scribes of the self-healing coating were autonomously re-

Figure 5.14 DC Electrochemical test results for scribed control and self-healed specimen.

sealed during the immersion process, while the ones of the control specimen were still open.

5.5.4 EIS measurement in salt solution

EIS measurement was also carried out to characterize the POTS based self-healing coating. Identical to the characterization for HDI based self-healing coating as described in Chapter 4, the scribed POTS coating was exposure to 1 M of sodium chloride solution, and EIS measurement was performed to evaluate the self-healing behavior during the immersion.

The interpretation of EIS spectra was also based on the equivalent circuit as described in Figure 4.25, and again the resistance of the newly formed film, R_{healing} , was used to assess the self-healing performance of the coating during the immersion process.

Figure 5.15 shows the EIS spectrum of POTS-based self-healing coating after exposed to salt solution for 8 h, and the fitted curve was plotted as well. Based on the fitted curves, the values of each component in the equivalent circuit can be obtained:

$R_u = 46.00$ ohms; $C_{\text{coating}} = 15.68 \times 10^{-6}$ F; $R_{\text{pore}} = 237.3$ ohms; $C_{\text{healing}} = 4.786 \times 10^{-9}$ F; $C_{\text{oxide}} = 12.56 \times 10^{-6}$ F; $R_{\text{oxide}} = 3.099 \times 10^3$ ohms; $C_{\text{dl}} = 62.99 \times 10^{-6}$ F; $R_p = 31.29$ ohms; $R_{\text{healing}} = 1.365 \times 10^3$ ohms. These values stand for the properties of the equivalent circuit when the POTS microcapsules based coating was scribed and exposed to salt solution for 8 h.

The values of each component of the equivalent circuit were similarly

Figure 5.15 Bode plots (impedance module, Z_{mod} , and phase angle) and fitted curves (solid line) of scratched POTS-based coating after 8 h of immersion in 1 M salt solution.

Figure 5.16 Healing resistances (R_{healing}) of POTS-based self-healing coating and control when the specimens were immersed in 1 M salt solution for different time.

obtained when the specimen was immersed in salt solution for different time, and the change of R_{healing} of the POTS-based self-healing coating as a function of immersion time was plotted. As demonstrated in Figure 5.16, R_{healing} of the POTS-based self-healing coating showed an increasing trend with the immersion time. The R_{healing} increased from about 1.0×10^3 ohms to 2.2×10^3 ohms when the immersion time increased from 2 h to 24 h. The increase of the R_{healing} implied that self-healing behavior indeed occurred for the POTS-based coating when the scribed coating was immersed in salt solution.

However, similar to that for HDI-based coating as discussed in Chapter 4, the change of the healing capacitance (C_{healing}) is very complicated and hard to predict for the POTS-based coating.

The DC electrochemical test and EIS measurement as discussed above both confirmed the self-healing property of the POTS-based coating. The self-healing behavior of the prepared coating is based on the hydrolysis and poly-condensation of POTS, and the detailed self-healing mechanism will be covered in Chapter 6. The healing process does not require any manual intervention. In addition, it is seen that the self-healing coating contain only one set of microcapsules, and it does not use any catalyst. Therefore, this is a one-part, catalyst free self-healing coating. Furthermore, the organic silane healing agent, POTS, is commercially available, simplifying the synthesis process and also making it possible for mass production.

5.6 Summary

PUF microcapsules containing POTS as core materials were synthesized through an *in situ* polymerization reaction in an oil-in-water emulsion. The yield of the synthesis was about 67 % and dependent on reaction parameters. The synthesized microcapsules had spherical shape, and the capsule shell was composed of a rough

outer surface and a smooth inner surface. The outer surface was the deposition of a large number of PUF nanoparticles. The diameter of the prepared microcapsules varied in the range of 40 – 400 μm when the agitation rate was increased from 300 to 1500 RPM. The average diameter of the microcapsules possessed a linear relationship with agitation rate in double logarithm coordinates. POTS content of the resultant capsules was about 60 wt.%, and it approximately remained at a constant value when the agitation rate varied from 300 to 1500 RPM. The core fraction could be improved by increasing the quantity of POTS in the feeding recipe, but it would compromise the quality of resultant capsules. The POTS microcapsules showed excellent stability for storage within at least one month, and their excellent barrier property was maintained in water and most of solvents used in our study. However, the POTS microcapsules were unable to resist ethanol

The synthesized POTS microcapsules were incorporated into epoxy resin or silicone resin to fabricate self-healing coatings. Scratched POTS-based epoxy coating exhibited excellent corrosion protection to steel substrate under an accelerated salt immersion test, and the intact POTS-based silicon elastomer showed excellent corrosion resistance to HCl in a long time corrosion test. In addition, the good self-healing performance of the POTS-based coating was demonstrated via a DC electrochemical test and EIS measurements.

Chapter 6 Anticorrosive Mechanisms of One-part-microcapsule-based Coatings

6.1 Motivation

The excellent corrosion protection functions of both HDI-based and POTS-based anti-corrosive coatings have been demonstrated in an accelerated salt immersion corrosion test as discussed in Chapters 4 and 5, respectively. It is necessary to discuss and understand the mechanisms by which the excellent anticorrosion ability of the prepared coating was realized. In addition, it has been revealed by the salt spray testing results that several factors exhibited considerable influences on the anticorrosion performance of the prepared coatings. Some of the influences are quite apparent. For example, it is reasonable that a higher microcapsules weight fraction in the coating will contribute to better anticorrosion performance since more healing agents will be available. However, the influence of some other variables may be more complicated and needs to be further investigated.

6.2 Anticorrosive mechanism for scratched coatings

6.2.1 Experimental observation of self-sealed scratches

In the accelerated salt immersion test, HDI-based or POTS-based epoxy coating was applied on steel substrate. After scratching, the specimens were exposed to 10 wt.% NaCl solution for two days. It was found that the prepared coatings were nearly free from rust after exposure. On the contrary, the specimen coated with neat epoxy coating showed severe corrosion. In order to reveal the mechanism of the anti-corrosion function of the microcapsules based coating, the scribed area of the coating was examined by SEM after immersion.

Figure 6.1 illustrates the scribed sites of the HDI-based coating and the blank

Figure 6.1 SEM images of the scribed regions of HDI-based epoxy coating (a: before immersion; b: after immersion) and control epoxy coating (c: before immersion; d: after immersion). The coated specimens were immersed in 10 wt.% NaCl solution for 48 h.

epoxy coating when the coatings were immersed in salt solution for two days. After the application of scratches on the coatings, the underlying steel substrate was exposed to corrosive salt solution and would be corroded. Compare Figure 6.1a with Figure 6.1b, it is clearly seen that some new materials were created in the scribes of the HDI-based epoxy coating after immersion. It means that the crack on this coating was healed autonomously. This is self-healing since such a healing process did not involve any manual intervention. Due to such a self-healing activity, the scribes were sealed and the underneath steel was separated again from external corrosive environment to display corrosion protection function. The materials generated in the crack should be the product between HDI, released from ruptured microcapsules, and water from the environment. As a comparison, it could be seen from Figure 6.1c and Figure 6.1d that the crack of the control specimen was not sealed, and therefore the corrosive salt solution can still directly attack the steel.

Similar observations were seen when the POTS-based anticorrosive coatings were treated in the same manner. The scratched areas of both the POTS-based epoxy coating and a control coating were inspected by using SEM after the accelerated salt immersion corrosion test was completed, as shown in Figure 6.2. Compare Figure 6.2a and Figure 6.2b, it is obvious that the crack of the POTS based coating was filled with newly formed materials after the immersion. The crack was in this way re-sealed to retard the diffusion of salt solution and thus protected the substrate from corrosion. On the contrary, from Figure 6.2c and Figure 6.2d, it is seen that the crack of the control specimen was still open. Therefore, it could be concluded that the anti-corrosion function of the coating originated from its sealing/self-healing property. However, as shown in Figure 6.2b, it is also observed that the sealing material of the POTS-based coating is not very dense and even, which may influence the corrosion protection performance of the coating, especially when long term effect is considered.

Figure 6.2 SEM images of the scribed regions of POTS-based epoxy coating (a: before immersion; b: after immersion) and control epoxy coating (c: before immersion; d: after immersion). The coated specimens were immersed in 10 wt.% NaCl solution for 48 h.

In order to further reveal the underlying mechanism of the self-healing behavior occurring at the scribed area of the prepared coating, after the salt solution immersion process, EDX analysis was performed to the coating surface to demonstrate the elements contained in the scribed area, as shown in Figure 6.3. Herein elements silicon (Si) and fluorine (F) were the focus of EDX analysis because POTS was the sole source for them. If the newly formed materials in the scribes as shown in Figure 6.2 were from encapsulated POTS, elements Si and F should be detected in the scribed area of the self-healing coating while absent in control coating.

It is seen from Figure 6.3 that the scribed area of control coating (Full area in Fig. 6.2d) contains O, Na, Cl, Au and Fe. Consider that the epoxy polymeric coating itself contains C, O and H, the coating was covered by a layer of Au prior to the EDX analysis, and the specimen was immersed in NaCl solution, so the presence of these elements is reasonable. On the contrary, for the self-healing coating (Full area in Figure 6.2b), no detectable Fe is found at the scribed area; instead, elements Si and F are detected. It means that the scribe of the self-healing coating was covered by a layer of material that contained elements Si and F. This material should be made of derivative of POTS because POTS is the only source for Si and F. In the meantime, it is observed that Si and F are not detected at the intact area (Area 1 in Fig. 6.2b) of the self-healing coating. It suggests that elements Si and F could not be detected from the self-healing coating if the embedded POTS-filled microcapsules are not ruptured, even though POTS is indeed stored in the coating. From these two aspects, it can be concluded that the elements Si and F within the scribed area were from ruptured microcapsules. As a matter of fact, this conclusion can be further consolidated by a direct analysis to the materials created within the scribed area (Area 2 in Fig. 6.2b) of the self-healing coating. As illustrated in Figure 6.3, the presence of Si and F is

Figure 6.3 EDX analysis of self-healing coating and control coating after immersion in 10 wt.% NaCl solution for 48 hours. The specimen and analyzed area are the same as those shown in Fig. 6.2.

obvious in the newly formed materials within the crack when Area 2 was analyzed. Hence, it can be concluded that the newly generated materials in the scribes were from stored POTS when the distributed microcapsules were ruptured.

From the discussion for the HDI-based and POTS-based anticorrosive coatings as described above, it is seen that the excellent corrosion protection function of the microcapsules based coating was realized through a self-healing/sealing mechanism. The healing mechanism of the anticorrosive coatings is illustrated in Figure 6.4a. When the microcapsules modified coatings were scratched, the healing species, HDI or POTS would flow from the ruptured microcapsules into the cracks. Upon contact with water or moisture, the healing species would then undergo a healing reaction in the form of polymerization, crosslink or condensation to create a film within the scribes, separating the metal substrate from the corrosive external environment. As a result, the corrosion of the substrate was hindered. On the contrary, for the control sample, the underlying metal substrate would be severely corroded

Figure 6.4 (a) Schematic diagram of the self-sealing mechanism of microcapsules based anticorrosive coating; (b) healing reaction of HDI; (c) healing reaction of POTS

since it was directly exposed to corrosive salt solution once the coating was scratched. The healing reactions of the HDI-based and POTS-based self-healing anticorrosive coatings are demonstrated in Figure 6.4b and Figure 6.4c, respectively. HDI monomer will react with water to produce an amine, which further reacts with HDI to form a polyurea film. The POTS monomer will hydrolyze in water, and the following crosslink and poly-condensation finally produce a silane-based film depositing on the substrate surface [119]. However, it is noteworthy that in practical situation, the actual healing reaction and the chemical constituent of the newly formed film may be much more complicated than those proposed here.

From the discussion above, it can be concluded that self-healing occurred to the prepared anticorrosive coating during the corrosion test, and it is such a self-

healing ability that resulted in the favorable anticorrosion protection function when the coatings were scratched. The healing behavior of the microcapsules-embedded epoxy coating was completely autonomous without any external intervention such as heating or UV exposure, and it did not require catalyst or other assisting materials either, making it easier for the development of one-part and catalyst-free self-healing materials, which is of considerable technical and commercial importance. Moreover, herein all of the chemicals used for the synthesis and coating development were commercially available. Therefore, the entire fabrication process is significantly simplified, which is very important for mass production.

6.2.2 Influence of parameters on anticorrosive performance

For microcapsules based self-healing polymer materials, the self-healing performance is influenced by factors such as the content of microcapsules in the polymer and diameter of microcapsules [120]. Rule *et al.* pointed out that for a scratched self-healing material, the self-healing performance was directly related to the amount of healing agents that were available for delivery per unit scratch area [34]. Based on a simplified model, he proposed an equation, from which it was seen that the self-healing performance of a microcapsules-based self-healing material was proportional to the microcapsules weight fraction and diameter. Mookhoek *et al.* [121] also developed a model to predict influences of capsule diameter, aspect ratio and concentration, as well as the crack opening distance on the self-healing performance.

In the salt spray test for the HDI-based self-healing coating as described in Chapter 4, it was revealed that the anticorrosion performance of the coatings was greatly influenced by the diameter of the HDI microcapsules, the weight fraction of microcapsules with respect to the coating and the coating thickness. Generally, the coating would exhibit better anticorrosion property when the microcapsules were

Figure 6.5 Schematic diagram of a scratched microcapsules based coating.

larger, the weight fraction of capsules was higher and the coating was thicker. As discussed in the last section, the anticorrosive function of the scribed HDI-based coating was mainly realized through a self-sealing mechanism. Hence, the influences of these three factors on the anticorrosive property of the coating are discussed in terms of the self-healing behavior.

The discussion below is based on several assumptions: a) the microcapsules with uniform diameter are evenly distributed in the coating matrix; b) the fill content of each microcapsule is the same; c) the shell of the microcapsules is negligible; d) when a scratch forms in the coating, all of the microcapsules located at the scratch plane are ruptured; e) all of the encapsulated healing agent of ruptured microcapsules will freely flow into the scratch; f) the healing species will spread within the scratch.

Consider a rectangle microcapsules-based coating is penetrated by a planar scratch as shown in Figure 6.5. Microcapsules with uniform diameter (d) are randomly distributed in the coating matrix. When a planar scratch penetrates the coating, all of the microcapsules lying in the scratch will be ruptured to release the healing species.

The number of microcapsules that are ruptured (n) is:

$$n = N \times P \quad (6.1)$$

where: N = total number of microcapsules in the coating;

P = probability that the center of a microcapsule lies within the rupture zone of the scratch plane.

Because the microcapsules were assumed to be distributed evenly in the coating, the probability is:

$$P = \frac{Ad}{M/\rho} = \frac{\rho Ad}{M} \quad (6.2)$$

where: A = area of the scratch plane

d = diameter of the microcapsules

M = mass of the coating

ρ = density of the coating

The total number of microcapsules in the coating can be calculated as:

$$N = \frac{\Phi \times M}{m} \quad (6.3)$$

and the area of the scratch plane is:

$$A = H \times L \quad (6.4)$$

where: Φ = weight fraction of microcapsules in the coating;

m = mass of one microcapsule;

H = thickness of coating;

L = length of the scratch.

Combine Equations 6.1 – 6.4, the number of microcapsules ruptured by the scratch is calculated as:

$$n = \frac{\rho \Phi H L d}{m} \quad (6.5)$$

In a typical self-healing material, the amount of the delivered healing agents has to be normalized by the area of the scratch plane since it is expected that the entire scratch plane is reconnected and re-bonded [34]. Nevertheless, for corrosion

protection purpose, the basic requirement is that the exposed substrate is covered by the healing agents in the whole length of the scratch with a certain width, while the agents do not have to completely fill the entire scratch depth. Therefore, the amount of the delivered healing agents is normalized by the scratch projection area as below:

$$m_0 = \frac{n \times m}{t \times L} = \frac{\rho \Phi H d}{t} \quad (6.6)$$

where: t = width of the scratch.

For a given microcapsules based coating, the density of the coating (ρ) is basically determined by the coating matrix itself if the fraction of microcapsules is not too high, and hence it can be considered as a constant. From Equation 6.6, it is seen that the amount of healing species available at the scratched sites is proportional to the weight fraction of microcapsules (Φ), diameter of microcapsules (d) and thickness of coating (H). In addition, according to the discussion in last section, the anticorrosion function is realized through a self-healing mechanism, and better self-healing property indicates better anticorrosion property. Therefore, the corrosion protection performance is accordingly also positively related to the microcapsules diameter, microcapsules weight fraction and coating thickness. This conclusion is in good consistence with the results as observed in the salt spray test. Furthermore, although the effect of the scratch width to the corrosion protection function of the coating was not investigated in our study, it is seen from Equation 6.6 that the corrosion protection function of the microcapsules based coating should be inversely related to the width of the scratch (t). It suggests that a wider scratch is more difficult to be self-repaired by the coating itself.

As discussed above, when a microcapsules based self-healing anticorrosive coating is damaged, the corrosion protection function of the coating will be restored as long as the scratch is covered by the released healing agents, although the agents

may not completely fill the entire scratch depth. Nevertheless, when the long term corrosion protection function is considered, it is desired that the scratch depth is filled as much as possible by the healing agents since external corrosive solution may slowly diffuse through the newly formed materials within the scratch and eventually reach the underlying substrate. The extent to which the released healing agents fill up the scratch can be expressed by the filling efficiency (η), which is defined as the ratio of the height of the healing agents within the scratch to the depth of the scratch when a microcapsules based coating is damaged.

The volume of the healings agents flowing into the scratch is:

$$V = \frac{n \times m}{\rho_{healant}} = \frac{\rho \Phi H L d}{\rho_{healant}} \quad (6.7)$$

where: $\rho_{healant}$ = density of the healing agent.

The height of the agent within the scratch is:

$$h = \frac{V}{t \times L} = \frac{\rho \Phi H d}{t \times \rho_{healant}} \quad (6.8)$$

Therefore, the scratch filling ratio (η) by healant can be calculated as:

$$\eta = \frac{h}{H} = \frac{\rho \Phi d}{t \rho_{healant}} \quad (6.9)$$

For a given microcapsules based coating, the density of the coating (ρ) and the healing agents ($\rho_{healant}$) are known and constant for the fixed formulation. It is seen from Equation 6.9 that the scratch filling ratio is proportional to the diameter of incorporated microcapsules (d) and their weight fraction in the coating (Φ), but reversely related to the width of the scratch (t). Here only healant is considered without further reaction for simplified analysis. In the practical case, healant will react with water to produce the final product to seal scratch. The actual sealing efficiency or equivalent anticorrosive performance will be highly dependent on the properties of

the final product, such as its bonding strength with matrix, density, thickness, water diffusivity, *etc.*, the study on which is beyond the scope of the current work.

6.3 Anticorrosive mechanism for intact coatings

The self-healing mechanism of the microcapsules based anticorrosive coating as discussed above is for scribed coating. It has also been observed that the intact POTS-based coating exhibited better corrosion protection performance than blank coating when the coatings were exposed to corrosive HCl solution. The anticorrosive property of the unscratched microcapsules based coatings can also be explained by the healing reaction of the healing agents, i.e. POTS or HDI in our study, that were pre-stored in the coating systems. Corrosion is an electrochemical process that requires the involvement of water. When metal is protected by a coating layer, although intact coating is able to effectively separate the substrate from corrosive environment, corrosion is still inevitable in terms of long term effect since water may penetrate the coating via diffusion to corrode the substrate. For the HDI-based or POTS-based self-healing coating, the pre-stored healing agents were reactive with water, so the water molecules may be trapped by HDI or POTS molecules during the diffusion process, as illustrated in Figure 6.6. It means that the rate that the water passing through the

Figure 6.6 Schematic diagram of the corrosion retardant effect of microcapsules in an intact microcapsules based coating.

coating layer will be retarded, and as a result, the corrosion of the underlying metal substrate will accordingly be retarded.

6.4 Summary

The excellent anticorrosive properties of both HDI-based and POTS-based coatings are realized through crack self-sealing mechanism under scratched condition and water/moisture trapping-and-reaction mechanism under intact form. The self-sealing behavior of the coating does not require manual intervention. In addition, in both self-sealing coatings only one healing agent is used without catalyst, so they are one-part and catalyst free self-healing coating systems. Based on a simplified model, it is revealed that the anticorrosive performance of the microcapsules based self-healing coating is influenced by the microcapsules diameter, microcapsules weight fraction in coating and the coating thickness. In addition, the mechanism by which the microcapsules enhance the corrosion resistance performance of intact coatings is also discussed.

Chapter 7 Conclusion and Future Work

7.1 Conclusion

Two one-part, catalyst free self-healing anticorrosive coatings have been successfully developed based on the microencapsulation of novel healing species, HDI and POTS. The prepared coatings are characterized by different testing methods, and the results demonstrated that the one-part coatings exhibit excellent self-healing anticorrosive performance, while the self-healing functionality is realized without any manual interventions. In addition, quantitative electrochemical methods are employed to assess the anticorrosive performance of the coatings, and the results revealed the self-healing behavior of the coatings during the test process.

PU microcapsules containing HDI as core materials were synthesized through an interfacial polymerization in oil-in-water emulsion. The yield of the synthesis was about 70%, dependent on reaction parameters. Spherical microcapsules with the diameter in the range of 5 – 350 μm and shell thickness in the range of 1-15 μm were prepared by adjusting agitation rate from 300 to 2000 RPM. The average diameter and shell thickness of the microcapsules reduced with the increase of agitation rate following a linear relationship in double logarithm coordinates. HDI content of the resultant capsules was around 60 wt.%, and it was inversely related to the reaction temperature. The reactivity of the HDI was remained during the microencapsulation process.

PUF microcapsules containing POTS as core materials were synthesized through an *in situ* polymerization reaction in an oil-in-water emulsion. The yield of the synthesis was about 67 % depending on reaction parameters. The synthesized microcapsules had a spherical shape, and the capsule shell was composed of a rough outer surface and a smooth inner surface. The outer surface was the deposition of a

large number of PUF nanoparticles. The diameter of the prepared microcapsules varied in the range of 40 – 400 μm when the agitation rate was increased from 300 to 1500 RPM. The average diameter of the microcapsules possessed linear relationship with agitation rate in double logarithm coordinates. POTS content of the resultant capsules approximately remained at a constant value of around 60 wt.% when the agitation rate varied from 300 to 1500 RPM. The POTS microcapsules showed excellent environmental stability.

Self-healing anticorrosive coatings were prepared by dispersing the synthesized microcapsules into a coating matrix. The excellent corrosion protection function of the created coating was demonstrated by accelerated salt immersion corrosion test and salt spray test. The anticorrosion function was realized through a self-healing mechanism, and the good self-healing performance of the coatings was quantitatively demonstrated by both DC electrochemical test and EIS measurements. The self-healing anticorrosive performance of the prepared coating was found to be related to the microcapsules diameter, microcapsules weight fraction in the coating and the coating thickness. Generally, larger microcapsules size, higher microcapsule weight fraction and larger coating thickness are favorable to achieve better self-healing anticorrosive performance. The influences of the coating variables on the anticorrosive performance of the coating were explained based on a simplified model.

The self-healing anticorrosive coatings we have developed are one-part systems, so the manufacturing process is much more simplified compared with most of existing self-healing coatings. In addition, the self-healing function was realized from the reaction of the encapsulated healing species with environment. Therefore, the use of a catalyst is not necessary in our systems, and this is of considerable economic importance. Furthermore, all of the materials used in the fabrication of the

self-healing anticorrosive coatings are commercially available, which is favorable for mass production and commercialization.

7.2 Future work

Although one-part, catalyst free self-healing anticorrosive coatings have been successfully fabricated by using two novel healing species, further studies are still important and should be performed in future.

1. Microencapsulation of new healing species for self-healing anticorrosive applications. Finding new healing species is always a very important part in the field of self-healing materials.
2. HDI is a good healing agent, but it is toxic and may impose hazard to environment in field application. Liquid polyisocyanate has much lower toxicity, and hence they may be encapsulated for self-healing applications.
3. Although the HDI based coating exhibits excellent self-healing anticorrosive properties, it is also revealed that the prepared microcapsule has a high permeability, and the stability of the microcapsules in organic solvents is still far from satisfactory. Hence, more efforts should be made to improve the barrier property of the microcapsules. PUF microcapsules have shown much better barrier property, so we can try to synthesize two-layer microcapsules to store the healing species. The synthesis may be realized through a two-step procedure [71]. HDI-filled PU microcapsules are prepared first, which are then used as the template to synthesize the second layer of PUF microcapsules. In addition, it has been reported that the barrier property of microcapsules could be improved by adding nanoclays in the wall [122]. We also can try to modify the current PU microcapsules with some nanoclays or other fillers to improve the stability of the microcapsules for field applications. In addition,

the permeability of the PU microcapsules is also determined by the chemical composition of the shell materials itself. For example, it has been reported that the PU microcapsules made from MDI is more permeable than those made from TDI [111]. Hence, we can try to re-design the synthesis by using different starting materials in order to improve the barrier property and stability of the microcapsules.

4. The POTS microcapsules based coating has shown good self-healing and corrosion protection performance. However, POTS is not cheap and therefore more efforts should be made to find other hydrolysable organic silane with lower price for self-healing. In addition, the core fraction of the synthesized POTS-filled PUF microcapsules was only about 60 wt.%, which is not very high compared with core fraction of up to 90 wt. % when other liquid such as DCPD was encapsulated by PUF microcapsules as reported before [40]. Since the core fraction of the microcapsules is directly related to the amount of healing agents available for healing, which considerable influences the self-healing and anticorrosion function of the final microcapsules based coating, more efforts are required to improve the synthesis process in order to achieve higher core fraction of the microcapsules.
5. Different self-healing and corrosion tests have been performed to evaluate the quality of the prepared self-healing coating in the present study. But the conditions under which these tests were conducted are still different from the real environment that the coatings may be exposed to. Hence, larger scale field tests are necessary before the coatings are considered for real applications.

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List of Publications

Book chapter:

J.L. Yang, H. Zhang, **M.X. Huang**. "Chapter 11: Emerging technology in aerospace materials: self-healing composites", in "Aerospace Materials Handbook" edited by S. Zhang & D.L. Zhao, Publisher: Francis & Taylor, New York, 2012.

Journal publications:

1. **M.X. Huang**, J.L. Yang. "Facile microencapsulation of HDI for self-healing anticorrosion coatings". Journal of Materials Chemistry, *inside front cover*, 2011, 21, p11123-11130.
2. **M.X. Huang**, H. Zhang, J.L. Yang. "Synthesis of organic silane microcapsules for self-healing corrosion resistant polymer coatings", Corrosion Science, 2012, 65, 561.
3. **M.X. Huang**, J.L. Yang. "Salt spray and EIS studies of HDI based self-healing anticorrosive coatings", Manuscript in preparation.
4. **M.X. Huang**, H. Zhang, J.L. Yang. "Characterization of POTS based self-healing anticorrosive coatings", Manuscript in preparation.

Patents:

1. J.L. Yang, **M.X. Huang**. "Microencapsulation of diisocyanates and the application to self-healing anticorrosion coatings", Application No. 13/755251.
2. J.L. Yang, **M.X. Huang**. "Microencapsulation of organic silanes and the application to self-healing anticorrosion coatings", NTU TD filed #: PAT/026/12/12/US PRV, US patent application #: 61/610,218, 12 March, 2012.

Conference:

1. **M.X. Huang**, Jinglei Yang, Facile microencapsulation of HDI for anticorrosive coatings, International Conference on Materials for Advanced Technologies (ICMAT2011), Singapore, 26 June – 1 July, 2011, Poster presentation.
2. **M.X. Huang**, Jinglei Yang, Long-term salt-spray testing for HDI-based self-healing coatings, Thin Film Symposium (TFS2012), Singapore, 14 July – 17 July, 2012, Oral presentation.

Resume

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- 2005 – 2008: Master of Science in Chemistry
National University of Singapore, Singapore
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University of Science and Technology of China, China

Experience:

- 01.2013-present Chemist, Optitune International Pte. Ltd.
- 06.2007-12.2009 Research Officer, BASF South East Asia Pte Ltd
- 07.2005-12.2007 Teaching Assistant (Part-time), Dept. of Chemistry, NUS

Awards:

- Teaching Assistant Award, 2007: National University of Singapore;
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