Self-Healing anticorrosive coatings

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Preface

This dissertation summarizes results of 3 years of scientific work on self-healing anticorrosive coatings, which has been carried out within the Ph. D. project. The investigation has been performed at the Combustion and Harmful Emission Control (CHEC) research center of the Department of Chemical and Biochemical Engineering at the Technical University of Denmark in collaboration with Hempel A/S. The project was supervised by Associate Professor Søren Kiil, Professor Kim Dam-Johansen from CHEC and Ph. D. Lars Thorslund Pedersen from Hempel A/S. The work has been financially supported by the Technical University of Denmark and J. C. Hempel’s foundation.

I would like to thank Kim for giving me opportunity to work on this exciting and challenging project and sharing ideas on how it can be improved. I am very grateful to Søren for our numerous meetings and discussions of progress and failures, for supporting me when I was upset and encouraging in persistent development of the project. Søren has also contributed a lot to the articles I have written, thoroughly reviewing them.

At Hempel I am very grateful, firstly, to Lars. Although I was working mainly at DTU, every time when I needed your comment or had a question to you, you answered. Secondly, I am very much thankful to Ph. D. Per A. Sørensen, who was employed at Hempel A/S until recently. Per, you did a lot for me both in terms of support and sharing knowledge. I always appreciated that, thank you. I would also like to thank all the colleagues, whom I work with in the lab at Hempel A/S, as all of them were very friendly and willing to help. Thank you, Fabian, Marta, Karl, Andreas and others.

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Tatyana Nesterova
Kgs. Lyngby, April 2012
Summary

Self-healing anticorrosive coatings are multi-component so-called smart materials, which have been proposed as a way to long-lasting corrosion protection of steel structures. The presently most promising technology route is based on microcapsules, filled with active healing agents, and has been the focus of this work. The microcapsules consist of a solid polymeric shell and a liquid core material. When a microcrack, originating from internal stress or a physical damage, propagates through the coating, the microcapsules rupture and release healing agents, which flow to the fracture plane due to capillary forces. The healing agents then start to react, form a polymer network, and ‘glue’ the crack. The approach has been applied to development of an epoxy-based self-healing anticorrosive coating for above water heavy duty corrosion protection. Emphasis has been on investigation of practical issues associated with development and testing of this type of coating.

A laboratory investigation, to identify the most suitable method for production of mechanically stable (filled with industrially relevant core materials) and forming a free-flowing powder upon drying microcapsules, has been performed. Four different experimental procedures, available in the literature, have been used for encapsulation of six core materials, including epoxy resins, diluent, and linseed oil. Several challenges have been identified during the investigations. Main of them dealt with encapsulation of viscous healing agents and a necessity of a thorough adjustment of the synthesis procedures for a wider use with other than original core materials. Free-flowing powders of two types of microcapsules (filled with linseed oil and alkylglycidylether) have been produced and investigated for solvent stability, stability towards stirring and storage, as well as ease of capsule dispersion. A systematic laboratory study, for reduction of poly(urea-formaldehyde) microcapsule size, filled with linseed oil, has been performed. Several synthesis parameters were varied (temperature, stabilizer content, stirring rate, stirrer geometry) and mechanical means of separation were investigated. Capsules with a mean diameter less than 150 µm were obtained using a steel sieve coated with a fluoropolymer coating. These smaller capsules were used in further investigation as model capsules.

A range of microcapsule-containing coatings was formulated, applied to steel substrates, and subjected to salt spray exposure and reverse impact testing. Neither of the tests revealed any drawbacks from addition of microcapsules to an epoxy coating in a concentration up to 50 vol%.
On the contrary, the results of the impact test has shown that addition of microcapsules reduces the intensity of crack formation (both in number and length) compared to filler-containing coatings and prevents the coating from flaking upon damage. Based on specular gloss measurements, a preliminary critical pigment (microcapsule) concentration (CPVC) value was estimated to about 30 vol %. The number is lower than anticipated and needs to be confirmed.

Finally, a 3-D model, based on Monte-Carlo simulations, has been developed for prediction of healing efficiency of a microcapsule-based anticorrosive coating. Two kinds of cracks were considered: cracks accommodated within the bulk coating and cracks starting from the coating surface. The model takes into account volume of the crack formed, crack geometry and linear dimensions, as well as diameter, volume concentration, and wall thickness of the microcapsules embedded in the coating. Simulations showed that diameter of microcapsules and crack geometry played an important role in the self-healing action of the coating, especially when low concentrations of capsules were used.
**Resumé**


Metoden er anvendt her i udviklingen af en epoxy-baseret selvreparerende antikorrosiv maling til brug for korrosionsbeskyttelse over vand. Fokus har været på undersøgelsen af praktiske forhold i forbindelse med udvikling og test af denne type maling.

En laboratorieundersøgelse er gennemført med henblik på at klarlægge de mest anvendelige metoder til produktion af mekanisk stabile kapsler (indeholdende industrielle relevante kernematerialer) og til dannelse af et fritflydende pulver efter gennemført tørring. Fire forskellige eksperimentelle procedurer fra litteraturen er anvendt til indkapsling af seks kernematerialer bl.a. epoxybindere, reaktive fortyndere og linolie. Forskellige udfordringer dukkede op. Indkapsling af viskose kernematerialer har bekræftet nødvendigheden af at justere på syntesevejene for at kunne indkapse andre end de oprindeligt brugte kernematerialer. Fritflydende pulvere af to typer af mikrokapsler (med linolie og alkylglycidylether som kernematerialer) er blevet syntetiseret og undersøgt for solvent- og lagringsstabilitet samt hvor let dispergeringen forløber. Et systematisk laboratoriestudie for reduktion af kapselstørrelse er også blevet gennemført. Forskellige syntese-parametre blev varieret (temperatur, stabilisatorindhold, omrøringshastighed, omrører geometri) og mekanisk separation blev undersøgt. Kapsler med en middeldiameter under 150 µm kunne opnås ved at bruge en metalsløjfe belagt med en flurbaseret maling. De mindre kapsler blev efterfølgende brugt i malingsformulering som modelkapsler.

En række mikrokapsel-indeholdende malinger blev formuleret, påført stålsubstrater og udsat for salttåge og omvendt slagtest. Ingen af testene afslørede nogen ulemper ved brug af mikrokapsler i en epoxymaling i en koncentration op til 50 vol %. Faktisk viste slagtesten, at mikrokapsler reducerer intensiteten af revnedannelse (både længde og antal) sammenlignet med en fyldstof-indholdende maling. Også tendensen til flaggedannelse nedsettes. Baseret på glansmålninger blev den
kritiske pigment (mikrokapsel) volumen koncentration bestemt til 30 vol. %. Det tal er lavere end forventet og skal bekræftes ved yderligere målinger.

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**Introduction**

Anticorrosive coatings are an efficient and often used mean for protection of steel structures against corrosion. Although a high performance of these materials can be now achieved in terms of adhesion, mechanical properties or durability, various mechanical, chemical, or thermal impacts, experienced by the products during service life, lead to formation of microcracks and premature failure of the coating system [1;2]. Maintenance and repair of the damaged coatings on large and industrially used steel structures like offshore oil rigs, sea ships, etc. are known to be very expensive. Costs of structural failures, subsequent environmental pollution and sometimes even human lives are dramatically higher than that.

Looking for solutions to prolong service life of anticorrosive coatings, scientists referred to intrinsic and the most remarkable ability of biological materials to self-repair [3] and have developed a class of polymeric materials called self-healing. Most often self-repairing or self-healing coatings are understood as the coatings, which have ability to restore their structural integrity once a micro-damage has happened. Healing occurs at the site of the micro-crack and prevents the crack from further propagation and diminishes penetration of water, oxygen and ions down to the substrate and, thereby protecting the metal substrate from corrosion. Meanwhile, another meaning of “self-healing coating” can be found in the relevant literature. Thus, A. Yabuki et al. [4], A. Zheludkevich et al. [5], and G. Galiwoda-Porebska et al. [6] described self-healing efficiency of the fluoro-organic compound, 8-hydroxyquinoline and polypyrrole-containing coatings, in which release of inhibitor restores the protection function of the coatings, although the real healing of the coating fracture does not occur. In this work the methods capable of polymer integrity restoration and developed to be used in thermoset systems are considered. Such limitation to a scope is due to necessity of use of special approaches to healing of densely cross-linked polymer materials, characterised by restricted mobility of the polymeric network segments and hindered diffusion of single molecules through the network [7].

This project is dedicated to investigation of practical issues associated with development of a novel self-healing anticorrosive coating intended for protection of above-water industrial structures. Investigation is divided into parts. It starts with literature survey in the field of self-healing coatings and composites in Chapter 1. Based on the data found, choice of self-healing system, chemistry, and a polymer matrix is to be done. Then synthesis methods need to be chosen, optimized, and
microcapsule produced. Chapter 2 deals with those issues. Chapter 3 describes properties of produced microcapsules, important for microcapsule-containing coating formulation (eg. solvent stability, stability towards mixing). Chapter 4 is dedicated to experimental work on reduction of microcapsule size to make them suitable for use in coatings. Formulation and application of such coatings is also done and described there, as well as subsequent testing. Chapter 5 addresses development of the model for prediction of various parameters of microcapsule-based self-healing coatings, such as concentration of microcapsules, needed for healing of a crack of certain dimensions or maximum size of a crack, which can be healed. Finally, in Chapter 6 conclusions and suggestions for further work are given.

References
Chapter 1. Literature survey

List of abbreviations
BGE – 1-butyl glycidyl ether
CA – 3,4-epoxycyclohexylmethyl- 3,4-epoxy cyclohexanecarboxylate
DA – Diels-Adler reaction
DBA – N,N-dimethylbenzylamine
DBTL - di-n-butyldilaurate
DCPD – Dicyclopentadiene
DGEBA – diglycidyl ether of bisphenol A
DMDT - dimethyldecanedioate
DSC – Differential Scanning Calorimetry
EG – ethylene glycol
ENB – ethylideneborborenone
ESEM – Environmental Scanning Electron Microscopy
EPA – ethyl phenylacetate
FTIR – Fourier transform infrared spectroscopy
HHPA – hexahydro-4-methylphtalic anhydride
HOPDMS – hydroxyl end-functionalized polydimethylsiloxane
IUPAC – Interantional Union of Pure and Applied Chemistry
m-PDA – m-phenylenediamine
NMR – nuclear magnetic resonance
OM – optical microscopy
PDES - polydiethilsiloxane
PUF - polyureaformaldehyde
ROMP – ring opening metathesis polymerization
SH – self-healing
TDCB - tapered double-cantilever beam
TGA - thermo gravimetric analysis
TKAS – tetrakis(acetoxydibutyltinoxy) silane
UF - ureaformaldehyde
UV – ultra violet
XPS – X-ray photoelectron spectra
1.1 Introduction

While a “complete infancy” of the field of self-healing materials was noted by P. Fratzl in 2007 [1], a number of journal articles [2;3] and books [4;5], published on self-healing coatings and composites since the early 2000s, illustrate fast development of the field. A great interest to self-healing materials has also been demonstrated at the International Conferences on Self-Healing Materials, held in the Netherlands, USA and UK. In 2007, Sottos et al. claimed “a critical mass of scientific activities has been achieved throughout the world” and “the future of self-healing is quite strong and it holds great promise across a broad spectrum of technologies” [6] (Sottos et al. 2007, p. 348). In addition to many recent developments of new approaches to self-healing there are sporadic reports available on commercialization of very simple self-healing coatings. However, publications with critical assessment of the already developed methods and investigation of practical issues of their implementation have recently started to appear [7;8;9]. In this literature survey, a brief introduction to the various approaches to self-healing polymeric materials that have appeared over the years is given.

1.2 Classification of self-healing approaches

Carolyn Dry was mentioned as the pioneer of self-healing composites by S. Hayes et al. [10], R. Wool [11], and also D. Wu et al. [2]. In 1996 she, in collaboration with N. Sottos, developed a system of hollow fibers containing a reactive fluid which released into the damage sites upon fracture, reacted, and healed the crack [12]. Since that time various approaches to the thermoset polymers healing have been proposed and tested and the presence of a healing agent is the only common thing for all of them whereas the triggering mechanism is of a principal difference. Among the healing systems, those based on temperature stimulus, UV-light, and pH change, as well as mechanical action, are mostly studied [13]. In this chapter, the heating/light-triggered systems will be discussed in section 1, pH-triggered in section 2, and mechanically triggered systems in section 3.

1.2.1. Temperature/UV-light – triggered self-healing systems

1. Thermally reversible polymers. A new class of highly cross-linked polymeric materials with mechanical properties similar to epoxy has been developed [2]. These materials can be added to thermoset systems for healing and do not require solvents or catalysts to begin their work.
The approach is based on retro Diels-Adler (DA) reaction: it was found that the energy to break DA adduct is much lower than to break covalent bonds of the matrix and that means the retro-DA reaction will be the main pathway for crack propagation [14]. Being reheated up to 120 °C, furan and maleimide moieties, contained in the system, will reconnect again healing the crack. The capability of multiple healing with retaining of 60% of the material’s original strength was reported by X. Chen and co-authors.

However, the healing process could not be considered as truly autonomous as the external trigger – temperature or UV-light – is needed [15]. This is the main disadvantage of the proposed system.

2. Inclusion of thermoplastic additives. D. Wu reported that the first self-healing system based on inclusion of thermoplastics into the thermoset matrix was developed in 1999 by Zako and Takano [2]. Thermoplastic epoxy particles, incorporated into epoxy matrix, melt under the heating, flew into internal cracks and healed them.

“Solid-state” self-healing system was patented by Jones and Hayes in 2005 [2]. In their approach, a linear polymer is dissolved into the thermosetting epoxy matrix and bonding to the matrix through hydrogen bonds. Under heating the added polymer becomes mobile and can diffuse through the matrix bridging the cracks. When diglycidyl ether of bisphenol-A was added as a healing polymer to bisphenol-A-based epoxy matrix, 43-50% healing efficiency was identified [10]. The systems are capable of healing small or not very open cracks.

3. Chain rearrangement. Polymer molecules at the crack surface possess enhanced mobility due to higher degree of freedom [11]. The chain rearrangement that may occur at ambient or elevated temperature simply due micro-Brownian motion heals the cracks in the matrix through interdiffusion of dangling chains or chain slippage [2]. “These ends and segments penetrate like (bent) prongs of a fork into the opposite matrix. Through kinks in the main chain and through the sidegroups each prong forms a number of physical cross-links with the matrix” [16]. The modifying of the chain ends with suitable reactive groups can lead to improved healing performance of such systems [15].

1.2.2. pH change-triggered self-healing systems

Polyelectrolyte species are deposited on the surface of containers as the films – layer by layer. The containers could be complexated organic molecules, or hyperbranched polymers, or oxide
particles, or naturally occurring halloysites filled with corrosion inhibitor. The degree of
dissociation of the polyelectrolyte shell changes with pH of the medium. In case of a coating
damage, the corrosion begins and the accompanying alkalinity causes release of the inhibitor from
the nanocontainer. Once pH returns to initial value, the release of the inhibitor stops [17]. The
authors reported the absence of corrosion products when 2-(benzothiazol-2-ylsulfanyl)-succinic
acid was used as inhibitor. They also noted the capability of migration of the polyelectrolyte shell
and of subsequent healing of the coating defect.

1.2.3. Mechanically triggered microcapsule-based self-healing systems

Based on the approach originally proposed by S. White [18], different kinds of self-healing
systems, utilizing a chemical reaction of species embedded into the polymer matrix for healing of
microcracks, have been developed. All of them use a liquid healing agent that needs to be
encapsulated into a polymeric shell in order to prevent its spontaneous mixing with the matrix
material during proceeding or storage.

The overall concept of the approach is illustrated by Fig. 1. Microcapsules filled with healing
agent as well as the catalyst are embedded into the polymer matrix. Once a damage-induced crack
propagates a capsule, release of the healing agent occurs through the capillary action. The healing
agent dissolves the catalyst which initiates reaction in the fracture plane, and the forming polymeric
material binds the faces of the plane together repairing the matrix’s structural integrity. The
approaches differ by organization of healing process (e.g. number of reagents involved, their
condition in matrix) and healing chemistry and will be considered in this review, based on the latter.

Irrespective of their particular characteristics, every proposed microcapsule-based self-healing
system should meet the following requirements. All the reagents and newly formed polymeric
materials should be compatible with the polymer matrix and exhibit good adhesion. Both the
reagents and the capsule shell should survive for a long time being stable to degradation and various
chemical reactions including self-polymerization. The chemical reaction between a healing agent
and a catalyst or a hardener leading to formation of the healing film is to be completed in a -10 – 35
°C temperature range at a reasonably short time. The degree of compliance of considered
microcapsule-based self-healing approaches with these requirements will be further evaluated.
1.3. Microencapsulation techniques and properties of the capsules

Microencapsulation of a healing agent is a process where the agent’s droplets are covered with a thin film of a shell material. A number of microencapsulation processes have been developed and according to S. Kumar Gosh they can be classified as chemical, physico-chemical and physico-mechanical processes [19]. Although the main approach to the chemical encapsulation is to drive reactions to interfaces or to produce polymers that precipitate at the interface. Thies marked 5 types of processes within interfacial polymerization, and in situ encapsulation can be chosen as the most relevant to the discussed topic among them [20].

In situ polymerization requires that the monomers for the shell creation are soluble in continuous, often water phase, whereas the core material is immiscible with water and presents in the form of emulsion. In many cases, copolymers are used in order to stabilize emulsion and enhance deposition of the shell material.
The first step in this process is to prepare an aqueous solution of one of the monomers, which will participate in the shell wall creation, also containing a stabilizer and a substance adjusting pH to 3.5, usually that is sodium hydroxide solution. Then, always under agitation, the core material is poured slowly into the system. The agitation rate depends on the desired microcapsule size. Several minutes are needed to stabilize core material-in-water emulsion, after that the second shell monomer can be added.

Once two shell-forming reagents present at the acidified water phase, the reaction begins. In case of urea-formaldehyde shell formation, the nucleophilic addition starts first giving pre-polymer-methylolurea product, which undergoes polycondensation reaction forming a linear polymer (Fig. 2).

Fig. 2. Chemical reaction of urea with formaldehyde pre-polymer formation.

Oligocondensate molecules deposit on the surface of the core material droplets where polycondensation continues. Ultimately, under heating, the highly cross-linked and water insoluble polymer shell is produced, Fig. 3.

Fig. 3. Chemical formula of the cross-linked polyurea-formaldehyde capsule’s shell.
The electron microscopy investigation of the capsules surface morphology that was performed by E. Brown and co-authors has revealed “smooth inner membrane free of voids or inclusions and a rough porous morphology on the outer surface” [21]. It is believed, that the inner shell surface is formed through the deposition of low molecular weight pre-polymer at the Dicyclopentadiene (DCPD)-water interface while the pre-polymer remains soluble. The rough outer surface seems to be the result of aggregation of higher molecular weight molecules in aqueous phase and then deposition of ureaformaldehyde (UF) nanoparticles on the capsule’s surface, Fig. 4. The authors also found that the rough capsules’ surface enhanced adhesion of the microcapsules to the polymer matrix and, consequently, improved self-healing performance.

![Fig.4. UF microcapsule’s morphology ([21], p. 724)](image)

The generalized scheme of in-situ encapsulation process can be seen from Fig. 5 as example of dicyclopentadiene capsule creation.

Although the process does not look very complex, it should always be held with a great care as the obtained capsules need to meet many requirements, and many parameters of the synthesis process can affect their yield and eventual properties. The ability to keep capsulated material for a long time without its leakage or diffusion and although to rupture readily when the polymer is damaged can be called as the most important microcapsules characteristics. It is also necessary for capsules to remain intact during coating formulation and application and possess a high adhesion to the polymer matrix.
Shelf-life of the UF-microcapsules fabricated by *in-situ* polycondensation was evaluated by E. Brown and co-authors. They reported that after 30 days of the capsules exposure to the laboratory conditions the average fill content decreased by 2.3 wt % [21]. However, for similar microcapsules but with different core content A. Kumar reported 4 weeks as a period after which capsules began to collapse in the wet paint. The author also pointed out that UF microcapsules, being pre-mixed with the polymer matrix, could not be applied to the protected surface using a spray gun [22].

Among the factors affecting shell wall thickness and mechanical strength are low initial pH, smaller amount of DCPD added, and contaminated glassware, unbalanced mixer were enumerated by Brown [21].

The very high loading of active agent is the main advantage of *in-situ* polymerization approach [23].

1.4. Ring opening metathesis polymerization – based self-healing systems

A literature survey on the microcapsule self-healing approach has revealed that the systems based on ring opening metathesis polymerization (ROMP) are the most developed and extensively studied ones. 25 journal articles published on this topic in 2001-2008 period were chosen for further consideration, and around 85% of them came from Scott White’s group working at the University of Illinois at Urbana-Champaign. The research conducted was mainly focused on epoxy polymers
and composites with some exceptions for polyurethanes and vinyl ester. Although deep studies of these self-healing systems have been expanded at the lab-scale there was no information found on the industrial implementation of the approach.

In a case of ROMP, the polymer chain is known to be “living” [18] that means that it starts to grow on the active centers of the catalyst as in any other case, but the end of the chain remains active and capable of further extend if the monomer is supplied [24]. Thus, the multiple healing effects can be achieved. The reaction scheme is illustrated by Fig. 7.

![Fig. 7. Structure of cross-linked polydicyclopentadiene ([25], p.68)](image)

**1.4.1. Healing efficiency estimation**

For evaluation of the results obtained by the authors a way of healing efficiency estimation has to be first described.

Crack healing efficiency ($\eta$) was assessed as ability to recover fracture toughness at the monotonic conditions and defined as the ratio of the fracture toughness of healed $K_{I\text{healed}}$ and virgin $K_{I\text{virgin}}$ materials [26]:

$$\eta = \frac{K_{I\text{healed}}}{K_{I\text{virgin}}}$$
\[ \eta = \frac{K_{\text{healed}}}{K_{\text{virgin}}} \quad (1). \]

A tapered double-cantilever beam (TDCB) test was used in order to find the fracture toughness values. The geometry of TDCB specimen, developed by Mostovoy, Fig. 8, ensures a controlled crack growth across the centre of a brittle sample and makes the fracture toughness to be independent of the crack length. Thus, in order to calculate fracture toughness of TDCB specimen only the critical fracture load \( (P_c) \) needs to be measured and geometric terms need to be known [26]. The healing efficiency in that case can easily be found as

\[ \eta = \frac{P_{\text{healed}}}{P_{\text{virgin}}} \quad (2). \]

Fig. 8. Tapered double-cantilever beam geometry (in millimeters) ([27], p. 1704.)

Fig. 9. Tapered double-cantilever beam testing in operation ([28], p. 3292).

Capability of the self-healing system to retard fatigue crack growth was assessed under cyclic loading conditions as the fatigue life-extension:

\[ \lambda = \frac{N_{\text{healed}} - N_{\text{control}}}{N_{\text{control}}} \quad (3) \]

where \( N_{\text{healed}} \) is the total number of cycles to failure for the self-healing sample and \( N_{\text{control}} \) is the total number of cycles to failure for a similar sample without healing [29].
1.4.2 Materials evaluation

1. Healing agents. Being a cheap and commercially available endo-DCPD (Fig. 10) was the first healing agent utilized in ROMP self-healing system [30;31]. According to [18] it possesses the whole range of desirable properties among which are low monomer volatility and viscosity, long shelf life (although stabilizer is needed [32]), rapid polymerization at ambient conditions and low shrinkage upon polymerization, as well as formation of highly cross-linked and tough polymer material [33]. Lee and co-authors also emphasized high modulus, excellent impact resistance as well as a good surface appearance and corrosion resistance of DCPD-polymer [34].

![Figure 10. Chemical structures of the healing agents.](image)

It was, however, reported that no measurable healing was observed in the DCPD-healing system within 30 minutes after crack propagation [32], figure 11, and the full recovery of mechanical toughness required 10 hours at ambient temperature [26]. It can be also expected that decrease in the operation temperature will result in even lower value of the polymerization rate that along with a high melting point of endo-DCPD (32.5 °C) reduce dramatically the interval of efficient applicability of the system [35]. All this encouraged researchers to develop more effective healing agents for ROMP-based self-healing systems which would possess fast curing time at ambient temperature, high rigidity after curing, low catalyst consumption and altogether - superior self-healing efficiency.

Exo-dicyclopentadiene and ethylidenenorbornene (fig. 10) were introduced for the study as it was previously reported that they might react faster in ROMP [36]. Additionally, exo-DCPD was known as having a gel time approximately 150 times faster than endo-DCPD and being in liquid state down to -50 °C [35]. During studies the special emphasis was placed on the reaction kinetics, mechanical and thermal properties of the resulting polymers and on the healing efficiency of the system obtained.
Based on the experimental results, Mauldin and co-authors confirmed that \textit{exo}-DCPD had faster polymerization kinetics compared to that of \textit{endo}-stereoisomer. Evaluating the origin of that difference, J. Rule and J. Moore concluded that it was mainly caused by the sterical interactions specific to the monomer and were entropic in nature [36].

Although fast polymerization kinetics of \textit{endo}-DCPD gives invaluable advantage of the rapid retardation of the quickly propagating cracks, this monomer’s feature did not result in increased healing efficiency since agents’ short gelation time was not sufficient to dissolve enough quantity of the catalyst [36]. However, the blend of these isomers, combining benefits of both, demonstrated high healing efficiency, fast kinetics and extended temperature range of the healing effect.

Sheng and co-authors, exploring differential scanning calorimetry, have found that ENB has even higher ROMP reactivity than \textit{exo}-DCPD [37]. However, that leads to a linear polymer which cannot be effective in microcracks healing due to its physical and mechanical properties [38]. Nevertheless, ENB cross-linking density can be increased by blending it with the cross-linkers. As it was shown by Sheng, CL-3 (Fig. 12) is the most effective agent for enhancement of the polymer
network. That is probably due to the separation of two norbornene rings by a benzene ring that gives an additional opportunity to one ring to move and react while another is already kept by the polymer chain.

Fig. 12. Chemical structures of the norbornene–based cross-linking agents investigated by Sheng et al., [37].

Another promising approach of blending slowly-reactive but forming cross-linked polymer endo-DCPD with very active ENB was evaluated by Liu and co-authors. It has been demonstrated that such system reacts faster than pure endo-DCPD at lower catalyst loading and, at the same time, has a high rigidity after curing [33].

Although a number of attempts were made in order to improve healing agent performance no sufficient data on fracture behaviour and healing efficiency of those systems were found in literature and the further discussion will be focused on endo-DCPD containing self-healing systems.

2. Catalysts. Three variations of expensive ruthenium-based Grubbs’ catalyst were considered to be used in self-healing system: the commonly used for ROMP and highly tolerant to moisture and oxygen 1st generation Grubbs’ catalyst, having improved thermal stability and catalytic efficiency 2nd generation Grubbs’ catalyst, and stable and recyclable Hoveyda-Grubbs’ second generation catalyst [28].

The first generation Grubbs’ catalyst was originally employed at the DCPD self-healing systems as it capable of performing ROMP of dicyclopentadiene with formation of cross-linked polymer network, is tolerant to moisture, oxygen and other foreign species in the polymer matrix and compatible with a wide range of solvents [18]. The IUPAC name of the catalyst is benzylidene-bis(tricyclohexylphosphine)dichlororuthenium and the chemical structure can be seen in fig 13.
The 90% healing efficiency was achieved using this catalyst [26]; however, some important issues were also reported. First of all, the 1st generation Grubbs’ catalyst tends to agglomerate that consequently leads to 1) lowered toughness [32], and 2) irregular catalyst distribution. That means that the amount of catalyst incorporated into the matrix must far exceed the actual needed quantity as only the part of it is available for healing [39]. Indeed, the stated above healing efficiency was achieved with a quite large loading of the catalyst – 2.5 wt % (relative to epoxy/amine cured matrix) [40]. Since the Grubb’s catalyst is relatively expensive, this “overload” makes the material prohibitively costly [41].

Secondly, all researchers investigating the DCPD- Grubbs’ catalyst self-healing system observed degradation of the catalyst by curing agent [42] Thus, Brown and co-authors [26] studied the different orders of the catalyst incorporation into the matrix and when they mixed the catalyst directly with diethylenetriamine curing agent no healing efficiency was observed. That was the direct evidence of the catalyst degradation.

As one of the approaches mitigating this issue, M. Kessler suggested to use tertiary amine as a curing agent instead of primary one since it had little chemical interaction with the catalyst [32]. Although good results of fracture toughness recovery were obtained by the author – 45% at room temperature for in situ healing; and 73 % - when only catalyst was embedded into the matrix whereas DCPD was manually injected – other solutions still need to be found. That is clear that self-healing system must possess a certain degree of versatility and to work efficiently in various matrices.
Another approach to the catalyst protection has been developed by Joseph Rule and co-authors who adopted the idea of Taber and Frankowski to protect the Grubbs’ catalyst from air creating a paraffin wax shell [39]. The results obtained were more than positive. In their experiment the wax shell saved 69% of the catalyst reactivity during its exposure to diethylenetriamine, whereas activity of unprotected catalyst was lost completely. Moreover, it was shown that the maximum healing efficiency – 93% could be achieved even with 0.75% wt of the catalyst load. The authors interpreted this data as the evidence of both wax ability to protect the catalyst from the curing agent and more uniform distribution of the encapsulated catalyst within a matrix [39]. Among disadvantages of the catalyst encapsulation is thermal instability of the wax shell, and plasticization of polyDCPD in the crack plane [28].

Although the amount of catalyst available for healing in the fracture plane is of great importance, the influence of catalyst dissolution rate highly affects the effective catalyst concentration and the overall system performance [43]. “If the catalyst does not dissolve fast enough, then heterogeneous polymerization occurs in locations where catalyst particles are exposed”, - Jones wrote. That means that no continuous poly-DCPD layer will form in the fracture plane, and even if the crack kept close by this partially polymerized DCPD the much lower fracture toughness value will be obtained. By him and many other authors [38;42] it was shown that the dissolution rate of the catalyst is mainly dependent on the catalyst’s morphology. It was also reported that the 1st generation Grubbs’ catalyst can exist in several different crystal polymorphs, Fig. 14, which differ by crystal shape, thermal stability and, of course, dissolution rate even between batches from the same supplier. Obviously, that makes it difficult to design material with reproducible properties [28].

![Fig. 14. ESEM picture of the 1st generation Grubbs’ catalyst polymorphs purchased from 2 different suppliers ([43], p. 1313)](image)
In order to overcome this issue several attempts were made. The as-received Grubbs’ catalyst underwent recrystallization by solvent evaporation, recrystallization by addition of acetone and freeze-drying from benzene. Although the smallest particles that were obtained in the latter case showed the fastest dissolution kinetics they were more susceptible to deterioration by the curing agent than polymorphs with larger crystals [43], even being protected by a wax shell [42]. So, the balance between fast dissolution rate of the catalyst in monomer and its survival during application should be tuned for the improved self-healing performance.

On this stage of the catalyst investigation 2nd generation Grubbs’ and Hoveyda-Grubbs’ 2nd generation catalysts were added to the study. The IUPAC names corresponding to these substances are benzylidene[1,3-bis(2,4,6-trimethylphenyl)-2-imidazolidinylidene]-dichloro(tricyclohexylphosphine)ruthenium and (1,3-Bis-(2,4,6-trimethylphenyl)-2-imidazolidinylidene)dichloro(o-isoproxy-phenylmethylene)ruthenium, Fig 15.

![Chemical structures of the 2nd generation Grubbs catalyst and Hoveyda-Grubbs’ 2nd generation catalyst](image)

Figure 15. Chemical structures of the 2nd generation Grubbs catalyst and Hoveyda-Grubbs’ 2nd generation catalyst.

Both catalysts showed significantly faster initial polymerization rate compared to the 1st generation Grubbs’ catalyst, however that did not result in the improved self-healing ability [28]. In case of the second generation Grubbs’ catalyst it could be due to its granular and clumped together shape, illustrated at Fig 16. [38], which limited distribution of the catalyst within matrix and its dissolution rate.

The Hoveyda-Grubbs’ catalyst exhibited high ROMP activity but that led to self-limiting polymerization and inefficient use of the catalyst [28]. It is important, that DETA curing agents
caused formation of new active complexes in situ with both catalysts whereas the 1st generation catalyst was deactivated. The authors also observed the best thermal stability of the 2nd generation Grubbs’ catalyst and its capability to polymerize all the studied healing agents. Thus, this catalyst exhibited the best overall performance while all the catalysts had different dissolution rates, chemical and thermal stabilities and the certain one needs to be chosen for the every system with desired properties.

Fig. 16. Scanning electron microscopy image of the 2nd generation Grubbs’ catalyst [38].

The system utilised the 1st generation Grubbs’ catalyst will be discussed further in this report as the most commonly used and deeply studied one.

1.4.3 Effect of the particle size and reagents loading on self-healing performance

1. Healing agent. The ultimate aim of the microcapsules incorporation is delivery of a sufficient quantity of the healing agent for maximum self-healing to occur. Logically, the minimum amount of healing agent needed to fill the crack can be found multiplying volume of the crack by healing agent density [42]. There are two ways to deliver this quantity of healing agent – 1) high microcapsule loading, or 2) bigger microcapsule size. A fair advantage of the former approach was pointed out by A. Kumar who wrote that the larger microcapsules could contain and deliver more healant once they had been ruptured than could be delivered by smaller microcapsules. He also noted that the probability of rupture of smaller number of large microcapsules was higher than of rupture a larger number of small microcapsules capable to deliver the same amount of healing agent and suggested to use capsules with 63 – 150 µm in diameter [22]. Results of the Rule’s and his co-authors’ study have also demonstrated superior performance of larger microcapsules at a given weight fraction, Fig. 17 [42]. For instance, as it was shown by E. Brown, the maximum healing
efficiency for 180 µm microcapsules occurs near 5 vol. %, whereas for 50 µm the high healing efficiency was reached only at 20 vol. % capsule loading level [27].

The character of the fracture toughness dependence on microcapsule concentration is another factor encouraging the use of larger-sized capsules. Fracture toughness rises with increase in microcapsule concentration until reaching a maximum value after which starts to decrease. The microcapsule loading at which this maximum occurs depends on microcapsule diameters [27]. The plot, Fig. 18, constructed by Brown and co-authors shows clearly that larger capsules exhibit maximum toughening at higher concentration (and may cause decrease in elastic modulus though). That means that more healing agent can be delivered into the system without weakening of the mechanical strength of the matrix when larger capsules are used.

Fig. 17. Dependence of healing efficiency of the system on microcapsules concentration and diameter

Fig. 18. Influence of microcapsule size and diameter on fracture toughness of epoxy matrix ([27], p. 1705)
On practice, however, where the thickness of each of the layers of anti-corrosion coating usually does not exceed 100 µm, the microcapsule size has to be limited. That also has to be done if the healing of smaller forms of damage like microcracks is desired as it is required for self-healing to occur that both microcapsule and catalyst are intersected by the same crack path [42].

Blaiszik and co-authors made it possible to start healing process at such a small scale which could not be reached earlier – they produced UF-shell capsules with mean diameters as small as 220 nm and as large as 1.65 µm utilized sonication technique, Fig. 19 [44]. The capsules exhibited good thermal stability, did not cause any significant reduction in elastic modulus, and increased significantly fracture toughness of the composite.

![Fig. 19. Sonicated UF-DCPD nanocapsules (44, p. 981)](image)

It should be noted, however, that even in case of microcapsule with excellent performance the combination of two factors – capsule diameter and capsule loading – must be always considered in order to reach the maximum self-healing efficiency.

2. **Catalyst.** The multiple studies that were carried out on ROMP-based self-healing systems have shown significant influence of the catalyst concentration in polymer matrix on self-healing ability of the system. Thus, Bruce Bernstein quoted the data obtained at S. White’s group, at which with increase of the catalyst to healing agent ratio from 2:1 (g/l of epoxy) to 10:1 healing efficiency went up from 84 to a hundred percent [45]. Among the factors limiting catalyst concentration is its cost and lowering of the specimen fracture toughness with increase in concentration loading [26]. Although the optimal catalyst loading was found to be 2.5 wt % of the catalyst from chemical degradation, regular distribution within matrix and the catalyst’s dissolution rate continue to be the
key issues of the catalyst usage. The importance of those factors and their relationship with self-healing efficiency were discussed above.

**1.4.4 General conclusion**

ROMP-based self-healing approach has been extensively studied as having a high potential to be used in self-healing composites and coatings. As much as 90% healing efficiency was reached and as little as 0.25 wt% of catalyst was required. The system exhibited thermal stability up to boiling point of the healing agent and had a long shelf life.

Implementing this approach, a high attention should always be paid to the catalyst morphology and distribution as well as protection from the curing agent. The catalyst itself is quite expensive and all the procedures that have to be performed to keep it in working condition also add to the cost of the polymer product. Self-polymerization of the encapsulated healing agent and toxicity aspects are not very clear. Another point which should be considered is the difference of materials formed polymer matrix and healing wedge as it represents danger of these layers separation under repeated stress.

**1.5 Solvent-based self-healing systems**

Self-healing system utilizing encapsulated solvent was considered by S. White’s group as perspective for healing of the structural integrity of epoxy matrix at room temperature without involvement of any additional chemistry. The system seemed to be less complex in material processing as only one reagent was intended for encapsulation, and also cheaper and more robust than the ROMP-based approach [46].

The idea of the approach is in following, Fig. 20. Incoming crack propagates microcapsule filled with the solvent. Flowing out of the capsule, the solvent locally swells the matrix that facilitate to residual amines to go to the fracture plane and react with residual epoxy functionality. It seems to be too simple to be effective but it works. 82 % of the healing efficiency was achieved by incorporation of 20 wt % of the UF - chlorobenzene capsules into EPON 828 : DETA matrix. Microcapsules of average diameter 160 μm exhibited good stability – no leakage through the shell wall was detected.
It should be mentioned that healing ability of 17 solvents was primarily studied by the authors, Fig. 21. It was revealed that aprotic solvents worked well as healing agent whereas protic did not. The possible reason for that is formation of hydrogen bond by aprotic solvent and a large amount of hydroxyl groups of the reacted epoxy.

![Diagram of solvent-based autonomic healing](image)

Fig. 20. The concept of solvent-based autonomic healing ([47], p.1899).

Unfortunately, the solvents showing the best performance such as N-methyl pyrrolidone, dimethylformamide, dimethylacetamide could not be encapsulated in UF shell due to their high polarity while chlorobenzene could and therefore was chosen for initial trials.

![Graph of self-healing performance of different solvents](image)

Fig. 21. Self-healing performance of different solvents ([46], p. 8831).
Interesting observations were made by the authors during experiment: the fracture surface became more textured with additions of microcapsules as it earlier occurred with UF-DCPD capsules; and the most important that the self-healing efficiency increased with increase of concentration of amine curing agent and decreased with increase in the cross-link density. The latter confirmed the suggested by author mechanism of self-healing promotion by solvent.

One but significant drawback of that system is a high toxicity of encapsulated chlorobenzene. To avoid this issue authors investigated phenylacetate and ethyl phenylacetate as the “greener” healing agents [47]. For further improvement of the autonomically self-healing system epoxy-monomer was co-encapsulated with a solvent that enabled additional epoxy delivery to the crack plane increasing the chance of further cross-linking. A new material deposited at the crack plane consisted of the same epoxy as the matrix and could be distinguished only by use of brominated epoxy as a marker. At Fig. 22 new epoxy film is shown in yellow.

The results obtained at this study were rather noticeable. A full recovery of fracture toughness was achieved with 15 wt % loading of the microcapsules containing 5 wt% solution of epoxy in chlorobenzene. A 100 % healing efficiency was also reported for epoxy - ethyl phenylacetate microcapsules. Relationship between healing efficiency of that system and amount of delivered epoxy can be seen from the Fig. 23. That is clear that a healing decrease after 0.1 mg/cm² of delivered epoxy is due to excess of epoxy compared to residual amine content that demonstrates “that only a small amount of epoxy is required to react with residual amine functionality in the matrix” ([47] p. 1901).

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Fig. 22. SEM-EDS image of the fracture surface ([47], p. 1901).
Fig. 23. Healing efficiency of the epoxy-EPA system ([47], p. 1902)
It was also found that epoxy-solvent self-healing system could undergo 3 – 5 subsequent healing events. Decrease of healing efficiency with every additional healing cycle, according to the authors, was attributed with a local depletion of healing agent and reduction of residual amine content.

Testing of stability of the system’s self-healing effect was carried out during a month at room temperature. Although epoxy-chlorobenzene capsules performed better, healing efficiency of epoxy-EPA system decreased at 10-15% that was considered by authors as good result due to high experimental scatter.

Incorporation of UF capsules filled with solution of epoxy in solvent into epoxy matrix looks as attractive and promising approach to autonomic healing. Nevertheless, some issues as toxicity caused by excess of amine curing agent or ability of the solvent to react either with matrix or curing agent or decompose should be thoroughly considered prior to approach implementation.

S. Mookhoek and co-authors continued investigation of a solvent-based healing, placing an emphasis on procedure of incorporation of solvent-containing microcapsules into amorphous polymer matrix [48]. Four different solvents were successfully encapsulated into poly(urea-formaldehyde) shell and then dispersed through the resin system via addition of them at the polymerization stage. The authors have shown that the concept is capable of healing thermoplastic materials but the cracks were only healed partly and a maximum strength related healing efficiency of 30 % was obtained for 15 wt % of capsule concentration and 14 days healing.

1.6 Epoxy-containing self-healing systems

When an epoxy composite or coating needs to be protected from microcracking it seems to be a better way to do that also using epoxy. The performed investigations showed that epoxy monomers could be efficiently employed both as core material and as a shell.

High compatibility of epoxy material with the matrix is a main advantage possessed by such systems and resulting in good adhesion of the newly formed film with the matrix or of the capsule shell with the matrix if epoxy is used as an encapsulation agent [49]. In both cases, the improved repair effect can be expected [50].

Li Yuan with co-authors from the Northwestern University of China have prepared polyureaformaldehyde capsules filled with diglycidyl ether of bisphenol A (DGEBA) with 1-butyl
glycidyl ether (BGE). The latter was used as the diluent to decrease epoxy’s viscosity and to allow healing agent to release readily from the capsule through the capillary effect when its rupture occurs. The article contains very detailed description of encapsulation process and epoxy’s self-reaction chemistry, and results of a large number of laboratory experiments that were performed to determine influence of formulation conditions on microcapsules characteristics [51]. The interesting finding is a high stability of microcapsules – only 0.23 wt% of the weight loss was detected for the capsules exposed to room temperature for 50 days, Fig. 24.

![Graph showing weight loss vs. storage time](image)

**Fig. 24.** Microcapsules storage stability ([51], p. 5347).

During the further study of the same group the microcapsules long service time was confirmed. Fig. 25 illustrates that there were no morphological changes at the capsules surface after being exposed to the air at room temperature for half a year [52].

![SEM images of microcapsules](image)

**Fig. 25.** SEM images of epoxy-containing UF-microcapsules ([52], p.422).
The authors have also found very good solvent resistance of microcapsules – they remained intact after 24 hours acetone-treated time, and high mechanical strength. Thermal stability was also investigated and it was shown that intactness of microcapsules can be maintained up to 180 °C and decomposition of shell and core materials became predominant only above 251 °C. Below this temperature diffusion of the core material through the shell wall occurred that made capsules with higher shell wall thickness more suitable for high temperature applications [53].

Fig. 26. Self-healing concept of epoxy – 2-imidazole approach ([54], p. 202).

Another approach to the use of epoxy as a healing agent was introduced by Tao Yin and co-authors from Zhongsham University of China. They created two-component healing system consisting of UF-shell microcapsules filled with bisphenol-A epoxy resin and the latent curing agent that was the complex of CuBr2 and 2-methylimidazole, dissolved in the matrix. It was believed that the hardener’s dissolution in the matrix might increase its availability for healing. The overall concept of the suggested self-healing system is shown at Fig. 26. The important thing that is not shown at the figure is a need of manual intervention: the hardener will be only reactive when the complex is dissociated into copper bromide and 2-methylimidazole. In order to achieve that site-specific heating up to 130 - 170°C should be conducted. That means, for the time being this particular approach could not be implemented for heavy-duty anticorrosion protection.
At the same university several other studies have been performed on encapsulation of epoxy resins and hardeners to be used in a microcapsule-containing self-healing coating. As there is a difficulty with encapsulation of amines by conventional methods due to their high activity and amphotericity, the authors proposed procedures for encapsulation of polythiol [55] and mercaptan [56] as hardeners for epoxy.

Amine was later successfully encapsulated by D. McIlroy and co-authors at the University of Illinois at Urbana-Campaign (USA). The core material has been prepared by interfacial polymerization of an isocyanate and amine stabilized by an inverse Pickering emulsion. Capsules released the core material when ruptured and were able to cure epoxy resin to form a polymer film [57].

A group of French authors – V. Sauvant-Moynot, S. Gonzalez and J. Kittel - have developed a novel self-healing system for metal under cathodic protection [58]. Epoxidised phenol-novolac polyepoxide resin was mixed with diethanol amine and transformed into a water-soluble acetate adduct with 30±10 µm grains that could be easily incorporated into a polymer matrix as fillers avoiding encapsulation step. As the result of the grain contact with water hydration was expected to occur enabling migration of the acetate adduct to the cathode, its deposition and self-cure. Figure 26 shows steel panels that were used for the trial film deposition during experiment. Evaluation of the adhesion properties of the deposited films by the cross-hatched test showed 100 % adhesion in both cases that was probably due to the high amount of hydroxyl groups in the adduct. That, in turn,
meant that developed adduct was capable of electrodeposition under cathodic polarization. However, authors noted that the barrier properties were only slightly improved and the further optimization of the system geometry and composition was needed.

An attempt to use epoxy as a capsule shell forming agent was made by O. Pascu and co-authors, who prepared epoxy microcapsules enclosing oily core. The shell of the capsules was formed by interfacial polymerization of diglycidyl ether of bisphenol A and multifunctional carboxylic acids – either decandeoic or 1,3,5-benzenetricarboxylic acids. It was important to find out that use of the decandeoic acid led to linear and soluble polymer whereas the use of the trifunctional acid resulted in crosslinked polymer with high mechanical resistance and very rough surface that can be seen at Fig. 27. The authors also investigated reaction conditions and their influence on microcapsules performance.

![Fig. 27. SEM micrograph of microcapsule surface, formed by epoxy and trifunctional acid interfacial polymerization ([49], p. 1005)](image)

1.7 Silyl-based self-healing systems

An idea of non-capsulated healing agent whereas catalyst is encapsulated was implemented by Soo H. Cho within Scott White’s group in USA [59]. They presented a system, utilizing a mixture of hydroxyl end-functionalized polydimethylsiloxane (HOPDMS) and polydiethylsiloxane (PDES) as a healing agent that was phase separated in the vinyl ester matrix and di-n-butylin dilaurate as a catalyst, encapsulated in polyurethane shell. The concept of the system is illustrated by Fig. 28, where the catalyst containing microcapsules are yellow and the healing agent droplets are white.
Siloxane-based polymers forming the healing agent cannot react with each other without the catalyst, so the mechanical damage of the catalyst capsules is required for reaction to occur.

One of the challenges during system implementation was the poor adhesion of the HOPDMS-PDES that was later mitigated by addition to the matrix of methylacyloxypropyl triethoxysilane as the adhesion promoter.

The healing efficiency of the developed system was determined using a tapered double cantilever beam as it was described above. The achieved values of healing efficiency were lower in that case than those obtained for DCPD-based systems of the same research group and did not exceed 46%. It was expected to be due to the lower stiffness and fracture toughness of the new siloxane polymer than of the surrounding its matrix.

Nevertheless, the system possesses a range of benefits to be used in anti-corrosive coatings in harsh environments: the chemistry is stable in humid and wet environments and elevated temperatures; the components are widely available for low cost; phase separation of the healing agent greatly simplifies processing. That is even more important that the authors tested corrosion
resistance of the formulated self-healing epoxy vinyl ester coatings, coating steel samples, scribing them, allowing healing and then immersing them into salt water. No evidence of corrosion was found at the self-healing samples after 120 hours of being in water. The addition of the top coat made from the same material but excluding microcapsules improved the appearance of the coating system and did not reduce self-healing ability [60].

The most recent concept utilizing healing of microcracks, based on silyl compounds, have been developed by S. Garcia et al. in 2011 [61]. The authors incorporate a new water-reactive healing agent based on a silyl ester into poly(urea-formaldehyde) shell, which releases upon damage of the coating and reacts with moisture in the environment, forming adhered to the metal barrier film for preventing the substrate from a further corrosion attack. Use of one component system for healing of the coating without a need for a catalyst or cross-linker and formation of a film, directly adhered to the surface of the substrate, are the clear advantages of the approach, which now needs to be optimized for being used.

1.8 Miscellaneous

An interesting approach to the capsule shell preparation has been developed by researchers of Tianjin University of China [62]. They fabricates double layered microcapsules consisted of inner poly-urea and outer poly-ureaformaldehyde layers in order to retain all the advantageous properties of polyurea such as flexibility, optical transparence, and leaktightness and, at the same time, to overcome agglomeration and cross-linking of the adjacent capsules .The comparative micrographs of single-layered (a) and two-layered capsules (b) can be seen from the Fig. 29 illustrating the agglomeration tendency of the former and the hard and stable protective shell of the latter.

![Fig. 29. Optical micrographs of single- (a) and double- (b) layered microcapsules ([62], p. 728).](image-url)
The developed approach allowed fabrication of capsules with ultra-thick capsule wall with extra protection to core material and improved thermal stability. Although the special benefit of the system is easy-handling of microcapsules, the influence of thick shell wall on the capsules’ rupture behaviour and core agent release should be considered prior to this approach implementation.

Recently, the method of UF capsules’ surface modification has been proposed by Haiyan Li and co-authors [63]. Their study aimed to improve self-healing efficiency of the composites making stronger interfacial adhesion between microcapsules and epoxy polymer matrix. The authors found that modification of the surface characteristics of the UF microcapsules could be performed with 3-aminopropyltriethoxy silane-coupling agent. The silane coupling agent underwent some chemical reactions and then reacted with hydroxyl groups of poly-UF shell. The amino-silane derivative, formed on the capsule’s surface, while embedded into the resin matrix, reacted with epoxy function group forming the strong chemical bond and greatly improving interfacial performance, Fig. 30.

![Mechanism of action for amino-silane modified PUF microcapsules and epoxy matrix](image)

**Fig. 30.** Mechanism of action for amino-silane modified PUF microcapsules and epoxy matrix ([63], p.3)

A novel capsule architecture design has been developed by S. Mookhoek et al in 2009 [64], which allows storage of both isolated healing materials within 1 capsule. Although some sophisticated techniques are used to produce such binary capsules, the method possess a great potential as overcomes healing agent mixing issues of a standard microcapsule-based system, where healing and catalyst or cross-linker stay separately within the matrix.
1.9 Conclusions

Design of self-healing anticorrosive coatings is a very attractive approach to long-lasting and efficient anticorrosion protection. Great attention is now paid to polymers and composites with a self-ability for healing of microcracks. Many different studies that were performed in this area in the years 1998 – 2012 are or can be relevant to self-healing coatings and have been described in this chapter. However, the majority of the studies were held in laboratory conditions, often with expensive or toxic chemicals, and mostly dedicated to the self-healing chemistry. Other issues investigated are the effects of reaction conditions on the size of microcapsules formed and the thickness obtained for the capsule shell. Only one article focusing on the anticorrosion behavior of a self-healing coating was found. Meanwhile, a lot of practical issues are expected to appear during coating development and several of these can affect both the formulation and application procedures as well as properties of the resulting product. The ultimate aim is to design and develop an efficient, environmentally friendly, long-lasting, and yet still competitive coating. The remaining of this thesis will deal with various issues of relevance for the practical realization of a self-healing anticorrosive coating.

References


Chapter 2. Synthesis of durable microcapsules: a comparison of selected methods

Different approaches are available in the literature for preparation of microcapsules for use in a microcapsule-based self-healing coating. In this chapter a comparative study of 4 different encapsulation procedures in application to 6 different core materials is described.

The chapter has been published with a title “Synthesis of durable microcapsules for self-healing anticorrosive coatings: A comparison of selected methods” in Progress in. Organic Coatings 70, 342-352 (authors Tatyana Nesterova, Kim Dam-Johansen and Søren Kiil).

List of abbreviations

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
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<tbody>
<tr>
<td>DCPD</td>
<td>dicyclopentadiene</td>
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<tr>
<td>EMA</td>
<td>poly(ethylene-alt-maleic anhydride)</td>
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<tr>
<td>ENB</td>
<td>5-ethylidene-2-norbornene</td>
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<tr>
<td>MUF</td>
<td>poly(melamine-urea-formaldehyde)</td>
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<tr>
<td>PUF</td>
<td>poly(urea-formaldehyde)</td>
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<td>PVA</td>
<td>poly(vinyl alcohol)</td>
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<tr>
<td>SDBS</td>
<td>sodium dodecylbenzenesulphonate</td>
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<tr>
<td>SDS</td>
<td>sodium dodecylsulphate</td>
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<td>SEM</td>
<td>scanning electron microscope</td>
</tr>
<tr>
<td>UF</td>
<td>urea-formaldehyde</td>
</tr>
</tbody>
</table>

Abstract

Self-healing materials have the ability to ‘repair’ themselves upon exposure to an external stimulus. In the field of coatings, extensive laboratory research has been conducted on these so-called smart materials in the last decade. In the present work, a self-healing concept for epoxy-based anticorrosive coatings, based on incorporation of microcapsules, filled with reactive agents, into the coating matrix, is investigated. Upon small damages to the coating, the reagents are released from the capsules and react, thereby forming a cross-linked network, which heals the crack. However, for the concept to work, microcapsules have to be strong enough to remain intact.
during storage and coating formulation and application. Furthermore, the capsules must remain stable for many years in the dry coating. Laboratory experiments, using four out of several encapsulation methods available in the literature, have been conducted to investigate the challenges associated with the synthesis of stable microcapsules. It was found that the nature of the core material strongly affects the microcapsule stability and performance. Furthermore, it was evident that experimental procedures developed for certain core materials were not suitable for encapsulation of other compounds without modifications. This is a severe limitation as not many of the encapsulation procedures have been developed for industrially relevant core materials such as epoxy resin. Results of experiments, aiming at finding optimal conditions for robust microcapsule production, are discussed.

2.1 Introduction

Self-healing materials have become an intense field of research in the last decade. The aim is to develop materials with a built in capability to retain functionalities and restore their structural integrity autonomically after the damage. The ability to self-heal should result in prolonged material service life, less maintenance, and therefore potential cost reductions. A large number of scientific papers, several review articles [1–5], and two textbooks [6;7], focusing on the different aspects of self-healing phenomena, have been published recently. Additionally, two international conferences on self-healing materials have been held in 2007 and 2009 [8]. Different triggering mechanisms, that can impose self-healing processes in thermoset polymeric systems, have been proposed. These complex systems can be based on mechanical, thermal, photo, electrical or other external stimuli [1,2], capable of initiating a healing process. Presently, judging from the number of publications [2], self-healing systems utilizing mechanical stimulus, seem to be the most realistic approach to truly autonomous self-healing polymeric coatings. The approach is based on incorporation of microcapsules, filled with reactive chemicals, into the polymer matrix. The microcapsules, one of which is schematically shown in Fig. 1, are spherical particles with a typical diameter of 10–200 μm, consisting of a solid polymeric shell and a liquid core material. When a microcrack, originating from internal stress or a physical damage, propagates through the coating, the microcapsules are supposed to rupture and release healing agents, which flow to the fracture plane due to capillary
forces. The healing agents then start to react, form a polymer network, and ‘glue’ the crack.

![Image: A simplified illustration of a microcapsule.](image)

**Fig. 1. A simplified illustration of a microcapsule.**

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

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

In addition, due to their particulate nature, microcapsules should be regarded as pigments or fillers and therefore put a limit to the amount of other pigments (particles) that can be added to the coating, because properties change rapidly at or near the critical pigment volume concentration.

It is clear that only microcapsules having mechanically strong walls (but not too strong, otherwise they will not rupture on demand) and possessing a high durability can preserve materials and keep them isolated for years until there is a demand to release them. However, recently it has been indicated that stability of the capsules is very sensitive to the parameters of the encapsulation process, which suggests that the preparation of durable microcapsules presents some difficulties. Brown et al. [9] noted that only the thickness of the outer porous layer of the urea–formaldehyde
microcapsule shell was severely affected by variations in shell and core material quantities, cleanness of glassware, and use of an unbalanced mixer. Liu et al. [10], on the other hand, have subsequently reported that urea–formaldehyde microcapsules, depending on the synthesis conditions, can have thin and rubbery walls leading to low storage stability and synthesis difficulties. Another group of researchers, Li et al. [11], have developed microcapsules with a double-layered wall to prevent agglomeration and inter-capsule cross-linking.

The overall aim of our research is to develop an experimental procedure for making stable microcapsules containing epoxy resin for future use in epoxy-based anticorrosive coatings. Epoxy resins are used in many thermoset coatings for corrosion protection [12], and are therefore an obvious material choice also for healing chemistry. At a later stage the possibilities of encapsulating a suitable crosslinker will also be investigated. In the present work, four procedures, proposed in the literature and relevant for making microcapsules, which can be used in a coating, have been investigated. Each method is evaluated and compared to the alternatives. The important parameters considered are stability of microcapsules and ease and time of their preparation. The microcapsules synthesized have diameters of 80–100 m. This is larger than the ideal size range of 10–50 m, but still relevant for anticorrosive coatings in the heavy duty industry, where individual coating layers of a full coating system can be 100–200 m. Future work will aim at reducing microcapsule size.

2.2 General procedure of in situ microencapsulation

An in situ microencapsulation process is typically conducted in an aqueous environment [13]. The core material is hydrophobic and forms an oil-in-water-emulsion; the shell material monomers are hydrophilic and dissolved in the continuous aqueous phase. When the shell forming reactants are present simultaneously, catalyst has been added and heating applied, polymerization starts in solution. The process continues on the surface of the core material droplets leading to formation of a solid polymeric shell.

In this work, procedures using urea–formaldehyde and melamine–formaldehyde as capsule shell materials were chosen. Many studies [2] have indicated that capsules with cross-linked and insoluble shell can be formed using this chemistry. Furthermore, the chemicals are reasonably safe to work with and inexpensive. This makes them potentially suitable for use in high-performance
anticorrosive coatings and a subsequent potential scale-up of production.

Polymerization of urea–formaldehyde and melamine–formaldehyde can be both acid- and base-catalysed and, conventionally, is carried out in two stages, where the first one is basic and the second acidic. Under basic conditions, series of addition reactions of formaldehyde to amino groups of urea or melamine lead to formation of pre-polymers [14]. Mono-, di- and trimethylolureas are formed at this stage and tetramethylolurea is not produced in detectable quantity. In case of melamine, pre-polymers with one to six methylol groups are formed. A generalised scheme of pre-polymers formation reaction is illustrated in Fig. 2a. Process duration, amine to formaldehyde ratio, and alkalinity of the medium determine chemical composition and structure of the pre-polymers and are of crucial importance for stability of the microcapsules. If the process lasts too long or if pH is too high, polymerization of methylolureas or melamine pre-polymers starts and leads to formation of cured pre-polymers, which cannot be used for the capsule shell formation [15].

As soon as the pre-polymer solution is added to the stabilized emulsion of core material and the medium is acidified, the second stage, polycondensation, starts rapidly. Surfactants, protecting the core material droplets from coagulation both through electrostatic repulsion and steric interactions, are used in the polymerization processes. Additionally, as it was pointed out by Thies [13], the use of anionic polymers or copolymers as surfactants can enhance deposition of the urea–formaldehyde capsule shell. The polycondensation reaction goes through formation of methylene ether bridges by reaction of two methylols groups and formation of stronger and therefore more favourable methylene linkages through the several possible reactions of methylol and amino groups, Fig. 2B. Condensation products deposit on the surface of the core material droplets and, upon continued reaction, give a cross-linked and water-insoluble capsule shell. Due to the higher functionality, melamine–formaldehyde networks are harder than urea–formaldehyde networks and more resistant towards hydrolysis [16].
Fig. 2. Reaction schemes of (a) urea–formaldehyde and melamine–formaldehyde pre-polymers formation in an alkaline environment; (b) polycondensation process, taking place under acidic conditions and leading to formation of a polymer network [14]. Note that in two-stage synthesis reaction (b) takes place only when emulsion is present.

Some researchers (e.g. [17]) use the above chemistry in a one-stage interfacial urea–formaldehyde polymerization under acidic conditions. The key difference of this approach is that polymerization of urea with formaldehyde starts in the presence of already formed and stabilized core material emulsion. From a practical point of view, this means that urea, ammonium and resorcinol are first dissolved in surfactant solution, and then core material is added and stabilized under vigorous agitation. After emulsion stabilization formaldehyde is added and pH and temperature adjustments start.

2.3 Microcapsule properties

Stability of the final microcapsules is mainly determined by the chemical structure and mechanical properties of the crosslinked shell material. In turn, the shell properties are critically
dependent upon kinetics of polymerization reactions, which is pH- and temperature-dependent [15,18]. It was shown by Yuan et al. [19], that a too fast polycondensation reaction leads to formation of a significant amount of urea–formaldehyde (UF) nano-particles in the solution, which does not contribute to the shell growth and adhesion to core material. On the contrary, it was found that the most stable capsules were formed at high reaction rates [20]. Thus, in order to make stable capsules, a compromise in experimental conditions has to be found. In addition to the factors influencing kinetics, microcapsule performance can be severely affected by the nature of the core material used and initial reagent ratios, agitation rate and type of a stirrer, cleanliness of glassware.

2.4. Microcapsule preparation methods

Several methods for microcapsule preparation have been developed [2,3]. The following four procedures have been chosen for investigation because they were either specifically developed for encapsulation of epoxy resins, or showing a high performance, supported by the results of the extensive studies provided.

The first method (Yuan et al.) was specially created for encapsulation of bisphenol A epoxidized resin into a poly(urea–formaldehyde) (PUF) shell and is based on a two-stage conventional polymerization process. Extensive study on the microcapsule properties and effect of experimental conditions on microcapsule performance was conducted by the authors of the method. Mean diameter and chemical composition of the capsules were estimated and morphology, storage stability and thermal properties were studied [19,21,22].

The second method (Brown et al.) is dedicated to dicyclopentadiene microencapsulation into a poly(urea–formaldehyde) shell [9]. This approach, in addition to another core material, differs from that of Yuan et al. by the use of a one-stage urea–formaldehyde polymerization procedure and another stabilization mechanism. The procedure of [9] has overcome some weak points of the earlier method by Yuan et al. [19].

The third method (Suryanarayana et al.) of microcapsule preparation is also based on a one-stage formation of a poly(urea–formaldehyde) shell in acidic medium, but the core material in this case is linseed oil. The procedure is very similar to that of Brown et al. [14] and the article includes an
extensive characterization of the microcapsules [23].

In the fourth method (Liu et al.), the microcapsule wall material is melamine–urea–formaldehyde (MUF) and the core material is 2-ethylidene-5-norbornene (ENB) or ENB with 10 wt% of a norbornene-based crosslinking agent [10]. The encapsulation utilizes a two-stage polymerization process. According to the authors, MUF microcapsules exhibit superior properties compared to poly(urea–formaldehyde) microcapsules.

An overview of the four methods is provided in Table 1.

### 2.5 Experimental

This section provides concise details on the experimental procedures used to synthesize microcapsules following the four chosen encapsulation methods. Some modifications or elaborations to the original procedures were required and these are also described.

**Method 1 [19,21,22]:** urea and formaldehyde served as shell materials; sodium dodecylbenzenesulphate worked as emulsion stabilizer; the mixture of bisphenol A epoxidized resin and alkylglycidyl ether was used as a core material. pH of the medium was adjusted by 1–2 wt% sulphuric acid solution and tri-ethanolamine.

**Method 2 [9]:** urea, formaldehyde, resorcinol and ammonium chloride were the shell forming compounds; dicyclopentadiene, alkylglycidyl ether, and bisphenol A epoxidized resin were used as core substances; poly(ethylene-alt-maleic anhydride) was used as stabilizer; 2 wt% hydrochloric acid and 10 wt% sodium hydrox-ide solutions were utilised for pH adjustments and maintenance; 1-octanol was used to eliminate surface bubbles.
Table 1
Details of the four studied microencapsulation methods. The following abbreviations are used in the table: U = urea, F = formaldehyde, AC = ammonium chloride, R = resorcinol, DGEBPA = diglycidyl ether of bisphenol A, BGE = 1-butylglycidyl ether, DCPD = dicyclopentadiene, EMA = poly(ethylene-alt-maleic)anhydride, PVA = poly(vinyl alcohol), M = melamine, ENB = 5-ethylenedine-2-norbornene, SDS = sodium dodecyl sulphate, and SDBS = sodium dodecylbenzenesulphonate.

<table>
<thead>
<tr>
<th>Method</th>
<th>Authors (year)</th>
<th>Intended application</th>
<th>Shell material</th>
<th>Core material</th>
<th>Surfactant/stabilizer</th>
<th>Stages</th>
<th>pH range</th>
<th>Temperature range, °C</th>
<th>Time, h</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Yuan et al. (2006–2008)</td>
<td>Self-healing composites</td>
<td>U, F</td>
<td>DGEBPA, BGE</td>
<td>SDBS</td>
<td>(1) Alkaline; (2) acidic</td>
<td>(1) 8–9; (2) 3–4</td>
<td>(1) 60–70; (2) 60–65</td>
<td>7</td>
<td>[19,21,22]</td>
</tr>
<tr>
<td></td>
<td>Suryanarayana et al. (2008)</td>
<td>Self-healing anticorrosive coatings</td>
<td>U, F, AC, R</td>
<td>Linseed oil</td>
<td></td>
<td>Acidic</td>
<td>3.5</td>
<td>55</td>
<td>5</td>
<td>[23]</td>
</tr>
<tr>
<td></td>
<td>Liu et al. (2009)</td>
<td>Self-healing composites</td>
<td>M, U, F</td>
<td>ENB</td>
<td>SDS, PVA</td>
<td>(1) Uncatalysed; (2) uncatalysed</td>
<td>–</td>
<td>(1) 70; (2) 86</td>
<td>6.5–7</td>
<td>[10]</td>
</tr>
</tbody>
</table>

Method 3 [23]: urea, formaldehyde, resorcinol and ammonium chloride were the shell forming compounds; poly(vinyl alcohol) and sodium dodecyl sulphate were emulsion stabilizers; linseed oil and alkylglycidyl ether were the core materials. pH of the medium was adjusted by the use of 5 wt% hydrochloric acid solution; 1-octanol was used to eliminate surface bubbles.
Method 4 [10]: urea, melamine and formaldehyde worked as shell materials; sodium dodecylsulphate and poly(vinyl alcohol) were used for emulsion stabilization; bisphenol A epoxidized resin, alkylglycidyl ether, triglycidyl ether of polyoxypropylene glycol and bisphenol F epoxidized resin were the core agents.

Data on purity of the substances used in this work and supplier information are provided below. Urea (99–100.5 wt%), sodium dodecylsulphate (>98.5 wt%), 1-octanol (99+ wt%) and resorcinol (99 wt%) were purchased from Sigma–Aldrich. Heloxy modifier 8 (alkylglycidyl ether C12–C14), Epicote 828 (bisphenol A epoxidized resin, epoxy equivalent weight 175–210), Epicote 862 (bisphenol F epoxidized resin, epoxy equivalent weight 175) were purchased from Hexion. Araldite DYL (triglycidyl ether of polyoxypropylene glycol) was purchased from Hunstman Advanced Materials. Formaldehyde (36.5 wt% aqueous solution), ammonium chloride (≥99.5 wt%), sulphuric acid (95–97 wt%) and sodium hydroxide were purchased from Fluka. Thriethanolamine (≥99 wt%) was purchased from Sigma, and poly(ethylene-alt-maleic anhydride) with Mw 100,000–500,000 g/mol, sodium dodecylbenzenesulphate, dicyclopentadiene (3a,4,7,7a-tetrahydro-4,7-methanoindene), Mowiol (poly(vinyl alcohol) with Mw 61,000 g/mol), melamine (99.9 wt%) were purchased from Aldrich. 25 wt% solution of hydrochloric acid was purchased from Riedel-de Haen. Linseed oil was an ordinary food oil. All the materials were used without additional purification.

Chemical structures of the two epoxy resins (bisphenol A and bisphenol F epoxidized resins), as well as of the two reactive diluents (alkylglycidyl ether and triglycidyl ether of polyoxypropylene glycol), which were encapsulated separately or added to the epoxy resins to lower their viscosity, are given in Fig. 3. Viscosities of the selected core materials were determined using a paddle viscosimeter. The viscosity of bisphenol A and bisphenol F epoxidized resins at room temperature was 1.5 and 1.3 kg/(m s), respectively. The viscosity of the remaining core materials was much lower (below the accuracy of the paddle viscosimeter).
Fig. 3. Chemical structures of the core agents containing epoxide functionalities. n is typically low (0.11–0.15) for liquid epoxy resins for anticorrosive coating.

2.5.2 Methods

Key data of the four chosen microcapsule preparation methods are summarised in Table 1. The detailed descriptions of the original procedures can be found in the corresponding references. Only modifications, made during experiments, are summarised below.

In this work, the following apparatus were used for all the methods: Metroholm 780 pH-meter, Eurostar digital IKA Labortech mechanical stirrer and IKA RCT basic heating plate. All the reactors were immersed in a silicon oil bath for a proper temperature control. Agitation rates were chosen in order to obtain microcapsules with a mean diameter within 80–120 m.

Method 1 [19,21,22]. Encapsulation was performed in a 500 ml three-neck round bottom flask (250 ml flask was used in [18]) at 500 rpm mixing rate, assuring sufficient agitation with the use of crescent-shaped Teflon head stirrer. In agreement with a recommendation of the authors regarding optimal stability of microcapsules, the chosen core–shell materials weight ratio was 1.2:1. The
initial amount of shell material was 30 g with 1:2 weight ratio of urea to formaldehyde.

In methods 2–4 a four-bladed metal head stirrer was used.

Method 2 [9]. In addition to dicyclopentadiene, a mixture of bisphenol A-(epichlorhydrin) epoxy resin and alkylglycidyl ether, and linseed oil were used as the core materials at a quantity of 30 ml (instead of 60 ml from the recipe) for stability reason. Agitation rates used were 600, 800, and 1200 rpm.

Method 3 [23]. The amount of the core material (linseed oil, alkyl- glycidyl ether) was reduced from 60 to 30 ml in further syntheses and 30 ml of 0.5 wt% of SDS aqueous solution was added for better emulsion stabilization. Dryers (cobalt naphtenate and lead octoate) were not added to the core materials. Agitation rates were 800 and 1000 rpm.

Method 4 [10]. A mixture of bisphenol A epoxidized resin with 30 wt% of alkylglycidyl ether and of bisphenol F diglycidyl ether with 50 wt% alkylglycidyl ether, alkylglycidyl ether and triglycidyl ether of polyoxypropyleneglycol were used as the core materials. 500 rpm agitation rate was used in accordance with the recommendation of the authors.

2.5.3. Microscopic characterization of microcapsules

A preliminary investigation of microcapsules synthesized was performed using an optical microscope (Nikon eclipse ME600). During microcapsule syntheses and right after, a drop of a reaction mass was spread over an examination glass and observed under the microscope with a magnification up to 50×. If the concentration of microcapsules or the amount of nanoparticles was too high to create a thin layer on the examination glass, the aliquots were diluted with sufficient amount of water (approximately 15 ml of water to 1 ml of reaction suspension). In the same way, to achieve a mono-layer of microcapsules, aliquots of the filtered products (both wet and dry) were first dispersed in water and then analysed.

A more detailed examination of microcapsule surfaces was carried out by means of an Inspect “S” scanning electron microscope (company name FEI) operating in both high vacuum and environ- mental modes. Specimens were prepared by placing a small amount of a dry powder, a
drop of a reaction mass, or a drop of a prepared aqueous dispersion of filtered microcapsules on a carbon tape. All the samples were allowed to dry at least for 24 h and sputtered with gold.

2.6. Results and discussion

Syntheses of microcapsules have been performed in accordance with the four chosen procedures. In this section results of the studies will be evaluated in terms of ease of synthesis, stability of microcapsules and specific relevant observations. Optimization procedures applied will also be mentioned. Subsequently, the four methods are compared and discussed.

2.6.1. Method 1: poly(urea–formaldehyde) capsules filled with epoxy resin [19,21,22]

2.6.1.1. Stability of microcapsules

The stability of the epoxy-filled poly(urea–formaldehyde) microcapsules obtained was not satisfactory. Three hours after addition of core material to the reaction medium, only emulsion droplets, no capsules, were present. While viewing the sample using optical microscopy, see Fig. 4A, initial droplets agglomerated into a few large droplets in less than 1 min. After 5 h of reaction, capsules could remain intact for a few minutes in wet condition, but their tendency to agglomerate was still pronounced and could be clearly observed under the microscope. Moreover, the amount of urea–formaldehyde (UF) nano-particles formed in solution increased significantly with time, Fig. 4B, and abundant depositions of this material were formed on the stirrer and walls of the reactor. This means, that a large amount of urea–formaldehyde did not participate in the capsule shell wall formation, affecting its strength and stability. The vacuum-filtered product looked like a white wet paste turning beige and waxy after a couple of days.

To optimise the procedure, a few changes have been introduced. To avoid the excess formation of nano-particles and increase the number of stable methylene linkages at the capsule shells, the alkaline stage was simply left out of the synthesis. In addition, the core–shell material weight ratio was changed to 2:1 and the quantity of shell monomers decreased from 30 to 15 g. A 1 wt% sulphuric acid solution, supplied by means of peristaltic pump, was used to keep the pH at 3.5. The capsules obtained by this synthesis are shown in Fig. 4C. Owing to the clear shell material
observation under the optical microscope, there were no doubts in this case that microcapsules, as opposed to emulsion droplets, were formed in the synthesis. Microcapsules were stable on a microscope examination glass until all water had evaporated. At this point, the walls of a majority of capsules started to crack simultaneously and microcapsules opened as nut shells. Once wall shells broke, droplets of viscous epoxy resin appeared as can be seen in a couple of places in Fig. 4D.

![Fig. 4. Optical microscopy images of bisphenol A epoxidized resin encapsulation into poly(urea–formaldehyde) shell obtained by method 1 (Yuan et al. [18]). (A) Emulsion obtained 3 h after addition of core material; (B) rise in nano-particle quantity, 5 h after addition of core material; (C) one stage acidic experiment, 5 h after addition of core material; (D) destruction of microcapsules upon drying on a microscope examination glass. Drops of epoxy resin are visible.](image)

To further increase the thickness of the shell, the synthesis was repeated with a weight ratio of shell to core materials of 1:1. Capsules obtained had, as previously, nice shells, were stable and did not break upon drying. However, the capsules were smaller and had a tendency to form clusters together with nano-particles. Approaching each other, capsules were deformed, but breakage did not occur and epoxy resin did not come out. The use of alkylglycidyl ether as a core agent in a proportion of 2:1 by weight to the shell material did not improve stability of the capsules and drops of non-encapsulated material were observed on the solution surface.

2.6.1.2. Ease of capsule preparation

The entire encapsulation process took 7 h and was made up of pre-polymer formation time (1 h), the period of pH and temperature adjustment (2–3 h) and the polycondensation stage (3 h). The very slow pH and temperature adjustment were challenging to conduct.


The attempt to reproduce results of the synthesis was successful and proper dicyclopentadiene (DCPD)-filled PUF microcapsules were obtained. The capsules did not tend to agglomerate and the solution was clear and free from UF nano-particles as long as the reaction was performed at a pH level of 2.2–2.4. Details (apart from the supplier and the fact that it was purified) of the DCPD used in the original article were not reported, but in another article by some of the same authors it was stated that endo-DCPD with a depressed melting point of 15 °C was used. In our reproduction we used a commercial grade DCPD with a melting point of 33 °C [24], and therefore the storage stability of microcapsules at room temperature cannot be evaluated because of the DCPD crystals formed as shown in Fig. 5. Subsequent this initial investigation with DCPD, it was of interest to try the method for encapsulation of epoxy resin as core material. Results of this study are presented below.
Fig. 5. Optical micrograph (50×) of poly(urea–formaldehyde) microcapsules filled with DCPD, method 2 [9]. Crystals within the microcapsules are visible.

2.6.2.1. Stability of microcapsules with epoxy resin as core material

The core material applied was a bisphenol A epoxidized resin with 30 wt % of an alkylglycidyl diluent. The original recipe was followed using 60 ml of the core material and 18.7 g of the shell material. The capsules obtained did not tend to agglomerate and some of the capsules with an undamaged shell remained intact after drying. However, the capsules in general suffered from low shell strength. To optimise capsule performance, variations of the recipe were tried and the most promising result was obtained by reducing the amount of core material by a factor of 2. This change should increase the wall thickness of the microcapsules. In this case, optical microscopy on a sample, taken from the reaction medium after only 1 h of synthesis, revealed capsules having intact shells and surviving much longer time compared to both the 60 ml encapsulation process and results of encapsulation method 1. Summarizing, microcapsules with epoxy resin as core material survived drying of the ‘film’ on the microscope examination glass, vacuum filtration, and drying of the filter cake. However, the material synthesized was a dense mass and not the desired free flowing powder. On the third day after the synthesis, oily traces of epoxy resin appeared on the filter paper as can be seen (beige colour) in Fig. 6A. A similar result was reported by Brown et al. [9] for unstable
capsules sampled from the reaction mass after 75 min of synthesis using DCPD as core material.

Fig. 6. Vacuum filtered poly(urea–formaldehyde) microcapsules filled with epoxy resin, method 2 [9]. (A) 3 days after the synthesis and (B) 50 days after the synthesis.

One reason for the dense structure of the resultant product can be proposed based on optical microscopy observations. A large quantity of capsules with ruptured shells was present in the reaction medium and product. This indicates that the rate of the polymer formation on a droplet surface was slower than deterioration of the shell by mechanical stirring. The positive side of a slow reaction rate is a complete deposition of UF pre-polymer on the droplet surface and, as a result, stronger wall shells, more stable capsules and more efficient filtration, not hindered by urea–formaldehyde nano-particles.

2.6.2.2. Ease of capsule preparation

Duration of the synthesis was considerably shorter than in Yuan et al. procedure and took 4.5 h plus time needed for the preparation of stabilizer solution. However, a very high sensitivity of the capsule performance to the rate of pH adjustment required thorough attention to the synthesis. Although the amount of nano-particles formed was significantly lower than in method 1, filtration of the epoxy resin-containing microcapsules was still problematic. On the contrary, linseed oil-filled microcapsules were easily filtered. In this latter case, due to the density difference between oil-filled microcapsules and urea–formaldehyde particles the former were first decanted and then filtered.
Decantation was not performed with epoxy resin-containing microcapsules because they were at the bottom of the reactor together with UF nano-particles.

**2.6.2.3. Specific observations**

An important and unexpected phenomenon has been observed during epoxy resin encapsulation. Right after addition of formaldehyde to the emulsion of epoxy resin in aqueous solution of urea, ammonium chloride and resorcinol, pH of the medium dropped from above 3.5 to values as low as 1.5, whereby the PUF formed precipitated from the solution. To maintain the pH level above 2, a constant supply of NaOH solution had to be secured during 40 min of the synthesis. The unexpected pH drop led to a reduction in the microcapsule yield by 50% and oily spots floating on the aqueous solution. Aiming at finding the cause of this phenomenon several experiments have been performed. The results, illustrating presence or absence of a drastic pH drop, are summarised in Table 2. It can be seen that only epoxy resin plus ammonium chloride in combination with formaldehyde resulted in the pH drop. This means that epoxy resin participates in a side reaction, and consequently the epoxy functionalities need to be protected. One way to do this is to isolate the epoxy core material from ammonium chloride by a layer of pure PUF (no additives). This was done by formation of a double wall shell adding urea and formaldehyde amount in two steps (50% of material in each step). The first part was added at the beginning of the synthesis, whereas the second part was introduced into the system 2 h later together with ammonium chloride and resorcinol. The pH drop did not occur this time and capsules at least as stable as having mono-layered shell were obtained. Even after a week of storage on a dried filter paper many of them remained intact. Another observation was that the material synthesised turned reddish upon storage (Fig. 6B), most probably because of oxidation of resorcinol.

**2.6.3. Method 3: poly(urea–formaldehyde) capsules filled with linseed oil [23]**

**2.6.3.1. Stability of microcapsules**

The original procedure with linseed oil as core material was first tried. The product obtained was easily filtered although it appeared a bit sticky. No traces of oil appeared during filtration. To optimize mechanical strength of the capsules shells, the amount of core material was reduced to 30
ml compared to 60 ml in the procedure. Furthermore, 30 ml of a 0.5 wt% SDS aqueous solution was added to enhance stabilization of droplets in the emulsion. A dry free flowing powder, with adequate mechanical strength was obtained after the procedure modification. The optical micrograph of the capsules obtained is shown in Fig. 7A. Following this initial investigation with linseed oil, it was of interest to try the encapsulation method with another core agent. A reactive diluent, alkylglycidyl ether, was chosen for encapsulation, as having both epoxy functionality and a low viscosity. The result was not as satisfactory as with linseed oil although microcapsules were formed, Fig. 7B. Only a small portion of microcapsules, subjected to direct vacuum filtration, was a flowing powder. The rest of the product, according to the procedure for increasing the rate of filtration, was first decanted and then filtered. This resulted in a somewhat sticky material, indicating that some capsules had broken during the filtration process. Due to the insufficient stability of the alkylglycidyl ether filled microcapsules, the study was not continued with epoxy resin.

![Micrographs](Image)

Fig. 7. Optical micrograph of poly(urea–formaldehyde) microcapsules containing (A) linseed oil and (B) alkylglycidyl ether, prepared with method 3 [23].
Table 2

Results of an experimental study performed to identify a source of a drastic pH drop observed during epoxy resin encapsulation using the method 2. “+” and “−” means presence and absence of a certain core or shell material in the reaction medium, respectively.

<table>
<thead>
<tr>
<th>Core material</th>
<th>Urea</th>
<th>Formaldehyde</th>
<th>Ammonium chloride</th>
<th>Resorcinol</th>
<th>pH drop</th>
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<tbody>
<tr>
<td>Epoxy resin</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>Yes</td>
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<tr>
<td></td>
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</tr>
<tr>
<td>Dicyclopentadiene</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>No</td>
</tr>
<tr>
<td>Linseed oil</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>No</td>
</tr>
</tbody>
</table>

2.6.3.2. Ease of capsule preparation

The procedure of linseed oil encapsulation was easy. It consisted of only one stage and required pH control only during pH and temperature adjustment (initial 45 min). However, the total synthesis time was about 5 h. In most cases filtration was straightforward and easy.

2.6.3.3. Specific observations

After three months of storage under ambient conditions, capsules, initially yellow, became slightly reddish in colour. This could be due to oxidation of resorcinol, as in method 2. After 6 months of storage, glue-like transparent material was observed at the bottom of a storage container, although microcapsules had still liquid cores. This means that linseed oil was partially released from the microcapsules and polymerized by reaction with oxygen.


The original procedure was followed except for the core material, ENB, which was considered irrelevant to the purpose of the present investigation. Instead the following core materials were used: bisphenol A and bisphenol F epoxidized resins, linseed oil, alkylglycidyl ether and triglycidyl ether of polyoxypropylene glycol.
2.6.4.1. Stability of microcapsules

Encapsulation of epoxy resin by this method worked out quite well. Microcapsules filled with bisphenol A and F epoxidized resins survived vacuum filtration and could be identified as capsules in the dry reaction product, using optical microscopy, one week after preparation. However, the resultant material was not really a powder. Fig. 8 shows SEM pictures of microcapsules filled with bisphenol A epoxidized resin taken for analysis from the reaction mass right after the synthesis (A) and from the filtered and dry material (B). Liquid epoxy can be seen in the right hand picture and few microcapsules have retained their shape. Some of them have probably released their core material. Wet powder with a smell of core agent has been obtained as a result of triglycidyl ether of polyoxypropylene glycol encapsulation. The smell and wet appearance were the evidence of the presence of destroyed capsules in the material. The effect of the prolonged time of the synthesis on durability of microcapsules could not be estimated as nano-particle growth took place in solution and made it almost impossible to filter. On the other hand, the results of alkylglycidyl ether encapsulation were perfect. A free flowing dry powder was obtained and can be seen in Fig. 9. Encapsulation of linseed oil was unsuccessful and the core material came out of the capsules during the vacuum filtration.

Fig. 8. SEM micrograph of poly(melamine–urea–formaldehyde) microcapsules filled with bisphenol A epoxidized resin, method 4 [10]. (A) Specimen taken from the reaction mass right after the synthesis; (B) specimen taken from filtered and dry material.
2.6.4.2. Ease of capsule preparation

According to the procedure used, synthesis of microcapsules required few steps: preparation of aqueous solutions of stabilizers, preparation of melamine–formaldehyde pre-polymer solution, and a final encapsulation stage. Leaving out preparation of stabilizers solutions, which can be done beforehand, the synthesis of microcapsules took about 6.5–7 h. Meanwhile, as pH control was not required at all during any of the steps, the synthesis was easy to perform. It was important, however, to make pre-polymer solution right before the polycondensation step due to MUF precipitation upon cooling. The ease of filtration, following the synthesis, was greatly dependent on microcapsule stability and synthesis duration. So, filtration was straightforward for the freshly prepared epoxy resins-filled microcapsules and for durable alkylglycidyl ether-filled microcapsules. When epoxy resins-filled microcapsules were left overnight in solution and subsequently filtered, the filtration process was considerably slower. When the pre-polymer formation stage was prolonged from 20–25 min (recommended by the authors) to 30 min or when 100 min longer encapsulation of triglycidyl ether of polyoxypropylene glycol was performed to improve capsules wall thickness, the vacuum filtration rate became much slower. Finally, it should be mentioned that the one-stage procedure is not applicable to melamine–urea–formaldehyde polymerization due to low solubility of melamine in water [25].
2.6.4.3. Specific observations

Microcapsules filled with alkylglycidyl ether had almost perfect spherical shape, whereas microcapsules filled with more viscous epoxy resins had many dents on the surface. The microcapsules filled with bisphenol F epoxidized resin had both dents and wrinkles on the shells as shown in Fig. 10.

Fig. 10. Optical microscopy images of poly(melamine–urea–formaldehyde) microcapsules filled with bisphenol F epoxidized resin (method 4 [10]), illustrating (A) dents and (B) wrinkles on the capsules shell surface.

2.6.5. Comparison of the methods

The four encapsulation methods studied in this work were developed for different chemistries both in terms of materials and the processes used. The shell materials were urea–formaldehyde with and without additives and melamine–urea–formaldehyde, and the syntheses were carried out as a one- or a two-stage polymerization. The core materials of the proposed procedures were also different: epoxy resin, linseed oil, dicyclopentadiene, or 5-ethylidene-2-norbornene. Additionally, the methods varied in stabilizers used, temperature, pH, agitation rate and the process duration.

In this work the methods were all tested using the original core material (except method 4) and subsequently using other materials, relevant to the purposes of the study. The materials of interest were alkylglycidyl ether, bisphenol A and F epoxidized resins and triglycidyl ether of polyoxypropylene glycol. When comparing the four methods, the following key challenges were identified:
• Excessive agglomeration of microcapsules.
• Microcapsule stability is core material-dependent.
• Undesirable formation of nano-particles in bulk solution.
• Long synthesis time.

To use microcapsules in a coating, it is essential to obtain a free-flowing powder and to avoid a dense sticky mass. While conventional agglomeration may be handled using traditional dispersion techniques, a sticky material will be tedious and perhaps impossible to use in a formulation. Based on a microscopic investigation, it was found that the tendency of capsules to agglomerate decreased in the following order of the surfactants used: ionic surfactant (SDBS, method 1), polymer (EMA, method 2), combination of ionic surfactant with polymer (SDS, PVA, modified method 3 and method 4).

Microcapsules stability was found to be very dependent on the core material used. As an example, method 3 worked perfectly well for encapsulation of linseed oil, but encapsulation of alkyldiglycidyl ether did not result in a free-flowing powder. On the other hand, method 4 provided stable capsules with alkylglycidyl ether as a core material, whereas capsules filled with linseed oil were instable. Another observation, common for all of the procedures used, was that weaker capsules were formed with more viscous core agents. A scientific explanation for this observation is not yet available, but one possibility is that the higher elasticity of more viscous compounds can put more stress on the shell material during handling of the capsules. Another relevant and unexplored issue is the potential solubility of core agent in the shell material, which may affect properties of the shell.

Undesirable formation of polymeric nano-particles in the bulk solution, which prevents proper shell formation and complicates the filtration process, was another challenge and one, which was, indeed, difficult to control. Ranking the methods from the lowest to highest degree of nano-particles formation, the following sequence is obtained: method 3 < method 4 < method 2 < method 1. Overall, one-stage polymerization of urea and formaldehyde performs better than the two-stage approach in terms of driving reactions to the interface, as opposed to bulk solution reaction, and ease of control. To perform well, the two-stage urea–formaldehyde polymerization process requires a very fine adjustment of temperature and pH of the medium. This is best handled using a programmable thermo-stat and auto pH regulator. A decrease of the ratio of shell to core materials can also lead to reduction in the amount of nano-particles formed, as it was found using methods 1
and 2. Consequently, a compromise between shell thickness and the quantity of nano-particles formed has to be identified.

Synthesis time and temperature are other important issues when evaluating the potential of a microencapsulation technique for a large scale production. In all cases the synthesis time was rather long (4.5–7 h) and temperature varied from 55 to 86 °C.

Summarizing, taking into account both stability of microcapsules and time and ease of their preparation, methods 3 and 4 seem to be the best of the methods tested. The procedures, however, require additional tuning for every specific core material used.

2.7. Conclusions

Four different in situ microencapsulation procedures were studied. The aim was to identify a ‘simple’ and robust technique allowing formation of stable microcapsules with an industrially relevant core material. It was found that microcapsule synthesis based on urea–formaldehyde as shell material in some cases was extremely sensitive to experimental conditions and therefore the methods were difficult to use. Capsules having poly(urea–melamine–formaldehyde) shells, on the other hand, were more robust, and the procedure of their synthesis was easier to perform. Furthermore, encapsulation of viscous liquids (viscosity of about 1.3–1.5 kg/(m s)) was found to be difficult in all the methods and it was not possible to synthesize a free-flowing powder of microcapsules containing either bisphenol A or bisphenol F epoxidized resins. Additionally, a transfer to the industrial relevant core material was accompanied with an acid producing side reaction of bisphenol A epoxidized resin, ammonium chloride and formaldehyde. Protection of epoxy functionality has been established by formation of a double wall shell using the first pure PUF layer. To reach the desired stability of epoxy-filled microcapsules, several options can be considered. The main one is adjustment of parameters of the microencapsulation process, as shown in this work.

Acknowledgments

Financial support by J.C. Hempel’s Foundation and The TechnicalUniversity of Denmark is gratefully acknowledged.
References


Chapter 3. Investigation of microcapsule stability

Stability of microcapsules to solvent exposure, mechanical stirring and storage is of high relevance and importance for use of capsules in a coating formulation. Stability has been investigated and described in this chapter for two kinds of synthesized microcapsules.

The chapter has been submitted for publication in a special issue of the Chemical Engineering and Processing: Process Intensification journal with the title “Microcapsule-containing anticorrosive coatings: investigation of microcapsule stability” (authors Tatyana Nesterova, Kim Dam-Johansen and Søren Kiil).

Abstract

This work addresses the development of an epoxy-based self-healing anticorrosive coating. The self-healing concept utilizes poly(urea-formaldehyde) and poly(urea-melamine-formaldehyde) microcapsules, filled with linseed oil or alkylglycidylether, as prototypes for active capsules containing a healing agent. Capsules synthesized are analysed for storage, solvent, and mixing stability and ease of dispersion. Results of the experimental investigation have shown that both kinds of microcapsules remained intact after 1 month storage in xylene. Linseed oil-filled microcapsules on the other hand were damaged during 1 month storage in polar solvents and artificial seawater. Poly(urea-formaldehyde) microcapsules filled with linseed oil degraded during long term storage in a closed jar under ambient conditions, while poly(urea-melamine-formaldehyde) capsules were unaffected. Both kinds of microcapsules were easily dispersed and remained intact in diluted epoxy binder under 550 rpm stirring rate, while poly(urea-melamine-formaldehyde) microcapsules could remain intact also during dispersion in pure epoxy, without any addition of solvent. In summary, microcapsules show different degrees of stability depending on core and shell materials and that has to be considered in formulation of microcapsule-containing anticorrosive coatings.

3.1. Introduction

The idea of thermoset self-healing materials first appeared in the beginning of the 1990s, when Carolyn Dry proposed the use of hollow fibers filled with a reactive fluid in self-healing composites [1]. In 2001 results of an investigation by Scott White and his research group at the University of Illinois at Urbana-Champaign on a new microcapsule-based approach to autonomous healing was
first published [2]. Since then, being inspired by a remarkable potential ability of materials to repair microcracks autonomously and thereby restore functionality and prolong service life, a substantial number of scientists of many research groups all over the world have joined the field [3-5]. In the last decade, the study of self-healing phenomena has been broadened from composites to the very active field of coatings, but also to metals, cement and ceramics, and even self-healing asphalt [6-9]. The various approaches developed for anticorrosive coatings differ by the external stimulus, applied to initiate a healing process in the coating, and healing chemistry [5]. Stimuli can be temperature, UV-light, pH, mechanical damage [10].

Presently, the focus of investigation is gradually shifting from prove of concept studies towards the critical assessment of healing capabilities of the approaches [11] and analyses of practical issues related to the use of coatings in real world situations [12].

The present aim of our research is to find out whether introduction of a capsule-based self-healing approach to an anticorrosive coating can compromise the overall performance of the coating.

3.1.1 Mechanism of self-healing and methods investigated

The investigation is carried out on a system utilising mechanical stimulus, which, judging from the number of recent publications [5], seems to be the most pursued route to truly autonomous self-healing coatings. The method is based on incorporation of microcapsules, filled with reactive chemicals, into a polymer matrix [2]. Microcapsules are spherical, sometimes elongated [13], particles with diameters of 10 – 200 µm depending on the application. As illustrated in Fig. 1, the capsules consist of a solid, impermeable polymeric shell and a liquid core, which is a healing material. The wall thickness is in nanometer range and varies very much depending on diameter of a microcapsule. When a microcrack propagates through the coating, capsules rupture and healing agents are released and react, forming a cross-linked network in the fracture plane. The mechanism of the microcapsule-based approach is illustrated in Fig. 2.
The investigation is divided into 3 parts: preparation of microcapsules, formulation of a coating containing microcapsules, and testing of a microcapsule-containing coating. The first part included a choice of polymer matrix and materials for encapsulation, development of experimental procedures, and optimisation. The objective of this first part was to synthesize microcapsules, which remain intact during coating formulation and application but rupture readily when a coating is damaged. Furthermore, the capsules must be compatible with the polymer matrix and exhibit good adhesion, be chemically stable, and filled with reagents possessing fast reaction kinetics in an industrially relevant temperature range. A previous paper [14] describes the first part of the research project and provides the results of an investigation with 4 different microcapsule synthesis methods, available in the literature [2,15-17]. The experiments were conducted to investigate the challenges associated with the synthesis of stable microcapsules and identify a ‘simple’ and robust technique allowing formation of stable microcapsules with an industrially relevant core material. It was found that the nature of the core material strongly affects the microcapsule stability and performance. Furthermore, it was evident that experimental procedures developed for certain core materials were not suitable for encapsulation of other compounds without modifications.

The second part of the study focuses on the coating preparation and has the following objectives:
• investigation of solvent resistance of the capsules;
• investigation of microcapsule dispersion (assessment of dispersion quality, microcapsule stability under stirring in viscous medium, and need and use of solvents and dispersing agent);
• estimation of a critical microcapsule volume concentration;
• modeling of healing efficiency of the coating,
• formulation and application of a microcapsule-containing anticorrosive coating.

The two first objectives are covered in the present paper.

The chosen model coating is an epoxy-based barrier coating, intended for above water heavy duty anticorrosion protection. The desired healing pair consists of an epoxy resin and an amine crosslinker. However, due to difficulties with viscous liquids encapsulation, described in [14], poly(urea-formaldehyde) capsules filled with linseed oil and poly(melamine-urea-formaldehyde) microcapsules filled with alkylglycidylether have been prepared and used, as a first approach, in the current investigation as model microcapsules. In a coating, microcapsules can be considered and treated as a filler material. Information obtained can be used for assessment of microcapsule performance and influence of capsules on coating properties. The data is needed for optimization of both microcapsule preparation and coating formulation processes.

The third part of the study will be dealing with investigation of self-healing ability of the formulated coating, as well as assessment of coating performance and comparison to a coating with pigments or fillers in place of the microcapsules and will be covered in a subsequent investigation.

3.2. Experimental

Poly(urea-formaldehyde) microcapsules filled with linseed oil and poly(melamine-urea-formaldehyde) microcapsules filled with alkylglycidylether were prepared according to the procedure described in details in [14]. Mean diameter of the linseed oil-filled microcapsules was about 220 µm and capsule density was 0.84 g/ml. Mean diameter of the alkylglycidyl-filled microcapsules was about 120 µm and capsule density was 0.80 g/ml.

Solvent resistance of microcapsules was studied through addition of microcapsules to xylene (≥99 wt %, Fluka), acetone (≥99 wt %, Sigma Aldrich), tetrahydrofuran (≥99.9 wt %, Sigma Aldrich) and artificial seawater (5 wt % as used in salt spray testing) and storage of the system
under ambient conditions. Aliquots of suspension were taken for examination of integrity of the shells under an optical microscope (Nikon eclipse ME600).

Investigation of the microcapsule stability during the formulation stage was performed by dispersing them at a concentration of 5 wt % in a pure Epicote 828 resin (Hexion) and in the Epicote 828 resin containing 10 and 20 wt % of solvent. A mixture of m-xylene and 1-butanol (≥99.7 wt %, Sigma Aldrich) in proportion 4:1 served as a solvent. A Diaf dissolver with a turbine stirring head of 3 cm diameter was used as dispersion equipment. 500 and 1100 rpm stirring rates were applied to the samples during 5, 15 and 30 minutes. Subsequently, the amount of broken capsules was estimated by optical microscopy analysis. Viscosities of the dispersion media were determined using a paddle viscometer (shear rate at 200 rpm) [18]. The viscosity of Epicote 828 resin was 1.5 kg/(m·s). The viscosity of diluted Epicote 828 resin was 0.2 and 0.05 kg/(m·s) for the mixtures containing 10 and 20 wt % of the solvent, respectively.

3.3. Results and Discussion

3.3.1. Solvent resistance and storage stability of microcapsules

Xylene has been chosen as a solvent for investigation due to its adequate solvent strength towards shell material and a wide use in heavy duty anticorrosive coatings production. Other solvents such as acetone, tetrahydrofuran, and artificial seawater were used mainly for comparison and for making generalizations. Observations on solvent resistance of linseed oil-filled microcapsules are summarized in table 1. The study has shown that shells of both kinds of microcapsules did not degrade in xylene during one month exposure. However, degradation was significant after 1 year exposure. Fig. 3 shows the great difference in appearance of linseed oil-filled microcapsules stored in different solvents during 3 weeks. Capsules stored in xylene do not show any signs of degradation, capsules stored in tetrahydrofuran are more degraded, and capsules stored in acetone are heavily degraded with very few intact microcapsules seen in the micrograph. Capsules stored in artificial seawater have small dents on their shells probably due to osmotic pressure. Degraded microcapsules show a tendency to agglomeration and have wrinkled shells. If degradation continues, capsules lose their spherical form and only the shells or even their fragments can be observed in the sample. Although no investigation of solvent resistance of linseed oil or tung oil-filled microcapsules was found in the literature [15,19,20], a stability study of poly(urea-formaldehyde) microcapsules performed by Tong et al. [21] revealed similar behavior of
microcapsule shells, being introduced to acetone, ethanol and “solutions with strong pH value”. Yuan et al. has demonstrated degradation of poly(urea-formaldehyde) shell and diffusion of epoxy resin core material from microcapsules exposed to acetone more than 1 day [17].

Table 1. Degradation of linseed oil-filled microcapsules in various solvents.

<table>
<thead>
<tr>
<th></th>
<th>Xylene</th>
<th>Tetrahydrofuran</th>
<th>Acetone</th>
<th>Artificial seawater</th>
</tr>
</thead>
<tbody>
<tr>
<td>Short term (3 days)</td>
<td>None</td>
<td>Very little</td>
<td>Severe</td>
<td>None</td>
</tr>
<tr>
<td>Long term (3 weeks)</td>
<td>None</td>
<td>Some; agglomeration</td>
<td>Severe; agglomeration</td>
<td>Dents on part of the capsules</td>
</tr>
</tbody>
</table>

Fig. 3. Optical microscopy images (5x magnification) of poly(urea-formaldehyde) linseed oil-filled microcapsules after 3 weeks storage in different solvents: A) in xylene, B) in tetrahydrofuran, C) in acetone, D) in artificial seawater.

Observation of microcapsules stored in dry form after syntheses, in closed jars, has revealed that poly(urea-formaldehyde) capsules filled with linseed oil get oxidized with time (after approximately 3 month they change color from yellow to reddish) and even form firm lumps of the microcapsules,
which are “glued” together perhaps by released and polymerized linseed oil. The difference in appearance of freshly made microcapsules and microcapsules stored 1.5 year is shown in Fig. 4. Poly(urea-melamine-formaldehyde) microcapsules filled with alkylglycidylether did not show any signs of degradation after two years of storage at the same conditions.

![Fig.4. Photos of poly(urea-formaldehyde) linseed oil-filled microcapsules A) stored 3 weeks after the synthesis and B) stored 1.5 year.](image)

3.3.2. Dispersion of microcapsules

In the available literature sources, dispersion of microcapsules has been conducted using laboratory mechanical stirrers and applying very low stirring rate – 200 rpm [15,20]. In this study an industrial disperser with a minimal stirring rate of 550 rpm was used. A stirring rate of 1100 rpm was also applied.

During the dispersion stage the most drastic decrease in number of intact linseed oil-filled capsules was observed during the first 5 minutes of stirring in undiluted epoxy resin. In Fig. 5, a visual comparison of the quantity of intact capsules in the sample before and after stirring in undiluted epoxy is given. Addition of 20 wt % solvent to the epoxy resin allowed the majority of microcapsules to stay intact 30 minutes under 550 rpm stirring rate. This confirmed that the lower viscosity (0.2 kg/(m·s) compared to 1.5 kg/(m·s) of undiluted epoxy) and therefore the lower share rate was more favorable for the microcapsule stability. During dispersion of microcapsules under the high stirring rate (1100 rpm) some capsules were damaged even in the diluted (20 wt %), low...
viscous sample. Eventually, 10 wt% solvent concentration and 550 rpm stirring rate were found to provide optimal conditions for dispersion of the capsules in the binder.

![Fig.5. Optical microscopy images of undiluted epoxy resin, containing poly(urea-formaldehyde) linseed oil-filled microcapsules before and after stirring. 5x magnification.](image)

The investigation has shown that dispersion of linseed-oil filled microcapsules, if capsules are produced in a good quality (free flowing powder that does not contain polymer particles) is very straightforward and can actually be done in the lab just by using a spatula and not a high stirring rate disperser. Meanwhile, if the microcapsules form a somewhat denser product, due to polymer nanoparticles formed in the synthesis [14], then stirring time of minimum 20 minutes was found as sufficient for breaking agglomerates without addition of dispersion agents. Moreover, it has to be pointed out that large (dimensions of a few millimeters) polymer particles, which are also formed in the synthesis, or microcapsule lumps formed during storage, could not be dispersed in the binder even after 1 hour of vigorous agitation. This sets additional requirements to synthesis, separation, and storage of microcapsules. It has also been found that capsules with poly(melamine-urea-formaldehyde) possess superior strength compared to poly(urea-formaldehyde) capsules and can be dispersed in undiluted binder.

3.4. Conclusions

The concept of self-healing anticorrosive coatings is a novel approach to long-lasting anticorrosion protection. Due to a number of complex property requirements of such coatings, practical development of the concept is a difficult task. Close attention has to be paid to stability of microcapsules, reaction chemistry of the healing agents, and to adhesion of both capsules to the coating matrix and the coating to the substrate.
Table 2. Results of investigation of dispersion of microcapsules in pure and diluted epoxy resin.

<table>
<thead>
<tr>
<th>Stirring rate</th>
<th>Poly(urea-formaldehyde) microcapsules filled with linseed oil</th>
<th>Poly(melamine-urea-formaldehyde) microcapsules filled with alkylglycidylether</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Pure epoxy</td>
<td>Diluted epoxy</td>
</tr>
<tr>
<td></td>
<td>(1.5 kg/(m·s))</td>
<td>(0.2 kg/(m·s))</td>
</tr>
<tr>
<td>550 rpm</td>
<td>Damaged</td>
<td>Intact</td>
</tr>
<tr>
<td>1100 rpm</td>
<td>Damaged</td>
<td>Damaged</td>
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</tbody>
</table>

In this work we are aiming for epoxy-based self-healing anticorrosive coatings based on reaction chemistry of epoxide groups for healing. So far, a prototype of those capsules was established: microcapsules filled with linseed oil and with alkylglycidylether. It was shown that both poly(urea-formaldehyde) and poly(melamine–urea-formaldehyde) microcapsules retained integrity of their shells during one month storage in xylene. Meanwhile, stability towards stirring in viscous medium was considerably higher for poly(melamine-urea-formaldehyde) capsules. Furthermore, it was shown that both kinds of microcapsules remain intact when viscosity of the epoxy resin was adjusted to an optimal value. Further investigations will be dedicated to a study of microcapsule performance and assessment of the capsule influence on coating properties and to attempts to go from the prototype core materials to more relevant healing materials. Critical capsule volume concentration will also be determined. Subsequently, a coating, containing microcapsules, will undergo adhesion and mechanical strength tests, and finally self-healing ability of the coating will be assessed.

Acknowledgements

Financial support of the Technical University of Denmark and J.C. Hempel’s Foundation is gratefully acknowledged.

References


Chapter 4. Reduction of capsule size, coating formulation and testing

In this chapter a systematic study on reduction of microcapsule size and practical issues related to formulation of a microcapsule-containing are discussed. Determination of a critical capsule volume concentration is performed via gloss measurements and performance of coatings with different microcapsule concentrations is investigated through a salt spray and impact testing.

The chapter is prepared for submission for publication in Progress in Organic Coatings with the title “Microcapsule-based self-healing anticorrosive coatings: capsule size, coating formulation, and exposure testing” (authors Tatyana Nesterova, Lars Thorslund Pedersen, Kim Dam-Johansen, Søren Kiil).

List of abbreviations

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
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<tbody>
<tr>
<td>CPVC</td>
<td>critical pigment volume concentration</td>
</tr>
<tr>
<td>PVA</td>
<td>poly(vinyl alcohol)</td>
</tr>
<tr>
<td>PVC</td>
<td>pigment volume concentration</td>
</tr>
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</table>

Abstract

Self-healing coatings is a rapidly growing research area, where focus has mainly been on development of new approaches to the mechanism of self-healing. However, there is a growing need for investigation of practical issues related to formulation, application, and testing of true self-healing coatings. In this work, ways of reducing the size of poly(urea-formaldehyde) microcapsules, filled with linseed oil and intended for a microcapsule-based self-healing anticorrosive coating (above water exposure), are explored. The influence of microcapsules on epoxy coating performance is also studied. The synthesis parameters investigated are stirrer geometry, agitation rate, temperature, and stabilizer concentration. It was found that an increase in stirring rate, correct choice of temperature, and a high stabilizer concentration all caused a decrease in microcapsule size but were accompanied by excessive formation of nanoparticles. Thus, isolation of too large microcapsules has been performed by filtration utilizing a novel low-energy fluoropolymer-coated steel sieve. An estimation of the critical pigment (microcapsule) volume concentration (CPVC) was conducted using gloss measurements and a PVC ladder and found to be about 30 vol % though it needs to be confirmed if this low value is the true CPVC value. Coating performance was evaluated using salt spray exposure and impact testing. Results of the impact testing showed that addition of
microcapsules to a binder matrix did not compromise resistance of the coating to mechanical damage and led to formation of fewer and shorter cracks compared to a filler-containing coating. Flaking of the coating was also reduced. Results of the salt spray testing (3 weeks exposure) showed that with an increase of microcapsule content, in the interval 30 to 50 vol %, the extent of corrosion and potential coating delamination decreased and was identical to that of a full commercial anticorrosive coating.

4.1 Introduction

Self-healing materials, including self-healing coatings, is a fast growing research area. A search in the internationally recognized data base Science Direct using the search term “self-healing coating” reveals that the number of articles have increased from 35 publications in the year 2000 to 204 publications in 2011 as illustrated in Fig. 1 [1]. The total number of publications with the search term as of March 1, 2012 is 1018. The remarkable interest in self-healing coatings is probably explained by the fascinating potential ability of such coatings to recover their structural integrity autonomously after occurrence of microcracks, which may arise due to release of internal stress in a coating or due to its mechanical damage. Functionality of this kind is expected to lead to less maintenance and associated cost reductions, which is of particular interest for Off shore constructions such as oil rigs and wind turbines. Although the field of self-healing polymeric materials goes back to the mid 1990s, interest to self-healing coatings has increased dramatically after Scott White and co-workers publication in 2001 of a study on microencapsulation of dicyclopentadiene for use in self-healing composites [2]. Since that time different concepts for self-healing coatings and various healing and capsule chemistries were proposed. Review papers, published in 2008 by Wu et al. [3], in 2010 by Murphy et al. [4], Burattini et al. [5], and M. Samadzadeh et al. [6], and in 2011 by Garcia et al. [7], have summarized the findings. Among the most recent approaches are ternary interpenetrating microvascular networks for fast and repeated healing [8], the use of encapsulated silyl ester, which can react with humidity and metallic substrates thereby removing the need for a cross-linker or a catalyst [9], and the use of grafted polymer multiarm architectures with low viscosity and high accessibility of functional groups responsible for healing [10].
In addition to continuous presentations of new approaches to self-healing coatings, reports with a critical appraisal of the already developed methods and assessment of their robustness, relevance, and practical usability have started to appear [7;11;12]. The present work is focused on three issues all of relevance to microcapsule-based coatings. The first one concerns the effect of synthesis conditions on size distribution of produced microcapsules and post-synthesis separation of the product into different size fractions. The second issue is to verify that addition of microcapsules to a coating does not compromise selected coating properties such as resistance to salt spray exposure and impact testing. Finally, determination of the critical pigment (microcapsule) volume concentration using gloss measurements and a PVC ladder is presented. Investigation of self-healing ability of a formulated coating was not aimed in this work and can be found in literature [13].
4.1.1 Methodology of synthesis investigation

Microcapsule-based self-healing coatings are based on incorporation of microcapsules, filled with reactive healing agents into the coating matrix. When a microcrack, originating from internal stress or a physical damage, propagates through the coating, the microcapsules rupture and release healing agents, which flow to the fracture plane due to capillary forces. The healing agents then start to react, form a polymer network, and ‘glue’ the crack.

A previous experimental study (not published), in which formulation and application of a microcapsule-containing coating was considered, showed that a number of difficulties were associated with the use of microcapsules of 220 µm mean diameter (distribution of sizes between 30 and 400 µm). The use of such capsules required high coating thicknesses (400 µm dry film thickness), panels with a substantial average roughness, manual application, and use of rheology modifiers to prevent sagging. An acceptable dry film thickness for a heavy-duty anticorrosive coating layer is 100-200 µm and this sets an upper limit on the microcapsule diameters than can be used. Benthem et al. [14] mention 60 – 150 µm as a typical and relevant size of microcapsules made from poly(urea-formaldehyde). If the microcapsules are too small, the content of healing agent will be too low. On the other hand, if capsule size exceeds the coating thickness then mechanical properties will be compromised. In the present work, capsules with a mean diameter of 150 µm are targeted.

A substantial number of articles on the synthesis of microcapsules have been published and in nearly all cases, the influence of process parameters on the properties of the microcapsules produced has been reported. In particular, Brown et al. [15], Yuan et al. [16], and Xiao et al. [17] have demonstrated an inversely proportional dependence of microcapsule size on agitation rate. Some authors have also shown that microcapsule diameter decreases with an increase of stabilizer concentration [18]. However, as it was pointed out by Nesterova et al. [11], the influence of a parameter change on microcapsule properties is complex and affects not only a single property of the capsules (size, for example), but the overall capsule performance including, for instance, mechanical strength, friability, and ease of filtration. Therefore, for production of capsules with a given specification, in addition to knowledge of general tendencies, optimization of every experimental procedure is required. In the present work, the synthesis aim was to produce intact microcapsules with diameters less than 150 µm that can be efficiently separated from polymer
nanoparticles and form a free-flowing powder upon drying. Polymer nanoparticles are the polymer particles of small (nano-) size, formed as a by-product due to occurrence of urea-formaldehyde polymerization reaction in a bulk solution and not on the surface of oil droplets. As a basis for further modifications and a useful model reference, the synthesis procedure for linseed oil encapsulation, proposed by Suryanarayana et al. [19] and earlier used and described in details by Nesterova et al. [11], was used. The following parameters were varied during the syntheses: stirrer type, agitation rate, stabilizer content, and temperature.

4.2. Experimental

4.2.1 Materials

Urea (99 – 100.5 wt %), 1-octanol (99+ wt %) and resorcinol (99 wt %) were from Sigma Aldrich. Heloxy modifier 8 (alkylglycidyl ether C12 – C14), Epicote 828 (bisphenol A epoxy resin, epoxy equivalent weight 175 – 210) came from Hexion. Formaldehyde (36.5 wt % aqueous solution) and ammonium chloride (≥ 99.5 wt %) were from Fluka. Triethanolamine (≥99 wt %) was from Sigma and Mowiol (poly(vinyl alcohol) with $M_w$ 61000 g/mol) was acquired from Aldrich. Soya lecithin (Corilec F-62) was purchased from Lasenor Emul S.L and talc (Minestron 230) from Luzenac. A 25 wt% solution of hydrochloric acid was from Riedel-de Haen. Linseed oil was ordinary food oil from Scandic Food A/S. All the materials were used without additional purification.

Polyester monofilament mesh fabric DPP47T (Yanpai South-west filter cloth company) with 150 μm mesh size has been used as a filter for vacuum filtration. For size-separation of microcapsules, Retsch sieves of 200 x 50 mm with the mesh sizes 180, 350, and 710 μm and a Retsch sieve with mesh size 200 μm, coated in a thickness of about 30 μm with ACCOFAL Ultra P336/54 by Accoat A/S (DK), were used.

4.2.2 Methods

4.2.2.1 Microcapsule preparation and separation

Poly(urea-formaldehyde) microcapsules filled with linseed oil have been produced following the procedure described in [11] with few corrections. 260 ml of distilled water was poured into a 1000 ml reaction beaker and placed in a silicon oil bath. 5 g of urea, 0.5 g of ammonium chloride and 0.5
82 g of resorcinol were added to the beaker under agitation. Then a portion of a 10 wt % stabilizer poly(vinylalcohol) (PVA) solution was introduced. The mixture was acidified down to pH 3.5 using 1 M HCl solution and a solution of triethanolamine. Under continuous agitation 30 ml of linseed oil was introduced to the reactor and left for 10 minutes for emulsion stabilization. Then 12.67 g of formaldehyde were added and heated to the targeted initiation temperature. Heating was performed in several steps: from ambient temperature to 35, 45, and 55 °C and further, if needed. 15 minutes were allowed for each of the stages for temperature rise and stabilization. Agitator types used in the experiment are shown in Fig. 2. Agitation speeds varied from 500 to 1200 rpm. Stabilizer content varied from 10 to 30 ml of 10 wt % PVA solution. Temperature of the synthesis varied from 40 to 80 °C. Synthesis was considered as being complete after 4 hours when the temperature reached the target value (or 3 h 45 min when 80 °C was applied).

![Fig. 2. Schematic illustration of the agitators used in the syntheses of microcapsules.](image)

One of the following procedures was applied for capsule separation:
1) suspension left to cool down and then filtered in the entire volume by vacuum filtration,
2) distilled water was added to the suspension for subsequent decantation and vacuum filtration of upper, floating layer, consisting of microcapsules and polymer nanoparticles,
3) decanted layer was centrifuged prior to vacuum filtration,
4) decanted layer was sieved prior to vacuum filtration.

Filtered microcapsules were washed with distilled water or acetone and left to dry in a fume cupboard for 48 hours. Integrity and surface morphology of capsule shells were examined using an optical microscope (Nikon eclipse ME600). Size distribution of microcapsules was analysed using an instrument, based on laser diffraction (Malvern Mastersizer S). For each set of experimental
conditions, the synthesis was performed twice and analysis conducted on two samples from each synthesis. By statistical evaluation of data, a mean diameter of the capsules and a confidence interval, valid for given synthesis conditions, were obtained.

4.2.2.2 Coating formulation and application

Coated steel panels with the following concentrations of microcapsules in the coating were prepared: 5, 15, 30, 40, and 50 vol %. The binder matrix was a stoichiometric mixture of Epicote 828 resin and Gaskamine 240 with a weight ratio 2:1. Microcapsules were added to the binder together with xylene-butanol solvent (4:1) and dispersing agent (0.05 wt %). Solvent concentration varied from 3 to 10 wt % for 15 to 50 vol % concentration of microcapsules. The coating was stirred using a Diaf dissolver for 10 min under 550 rpm with a 3 cm stirring head.

Panels of 7x15x0.3 cm³ dimensions, prepared from mild steel with a roughness profile BN 10 (Rugotest no. 3), were used as substrates. Coatings were applied using a doctor’s blade (manual application) and left for curing for 1.5 weeks at room temperature. Manual application was preferred for substrates of a high roughness because it was non-destructive for the capsules and required a modest amount of the material. Three types of reference panels were prepared using the same application procedure: commercial epoxy-amine based coating, pure epoxy-amine binder, and a filler-containing epoxy-amine coating. Talc was used as filler in 5, 15 and 30 vol % concentrations. Panels intended for a salt spray test were also coated on the backside and edges to avoid uncontrolled corrosion processes taking place on the steel surface.

The thickness of dry coatings was measured with Elcometer Model 355 Top, calibrated for 250 μm thickness. A drawback of manual coating application was that the thickness of the coating varied somewhat over the panel length with a decreasing thickness as the doctor’s blade moved across the panel. Therefore, two mean thicknesses were determined for a panel by averaging 5 readings of the instrument for each half of the coated panel. Gloss of the cured coatings was determined using a gloss meter from Gardner. Six readings were taken for each of the panels at 60°.

4.2.2.3 Coating testing

Salt spray test

A 50 mm vertical scribe of 2 mm width was made on the front of each panel by a special tailor-made pneumatic instrument, removing the coating down to the substrate. Subsequently, the panels
were exposed to mist of a 0.5 M solution of sodium chloride at an angle of 70 to 75° in the corrosion test apparatus Erichsen 608/400 for 7 days. During this time, electrolyte solution was kept at 35 °C during salt spray phase, lasting 48 hours, and cooled down to 28 °C during condensation phase, lasting 24 hours. Subsequently, the experiment was continued as a continuous salt spray test for 14 days. This exposure scenario was used to accelerate a potential coating degradation. The extent of rust creep was determined by removal of the coating around the scribe.

**Impact testing**

Impact testing was performed using an Erichsen variable impact tester, model 304. Metal substrates, of 3 mm thickness, were coated with either a commercial coating, a microcapsule-containing, pure binder, or a filler-containing coating. For testing, a sample was immobilized horizontally at the bottom of the impact apparatus and a falling hemispherical impact body (20 mm diameter, 2 kg weight) was then allowed to damage the coating and substrate. The ball impact was directed on the “back side” of the substrate for a convex deformation of the coating (extrusion). The substrate penetration depth of the impact body was set to 0. Starting from a low height and gradually increasing the distance, the minimum height, where damage of the coating starts, was determined for the commercial coating and repeated 5 times to confirm the value. Then, using the same height, the test was performed on other samples. For each of the panels, the test was repeated twice at a distance of 70 mm between the impacts as recommended in the instrument manual [20]. The type and character of deformations obtained were analysed and compared to reference samples.

4.3. Results and discussion

4.3.1 Reduction of size of microcapsules

The measures, described below, were taken to reduce size of the microcapsules and achieve capsules of less than 150 µm diameter.

4.3.1.1 Effect of stirring rate and stirrer geometry

The most direct way of reducing the size of microcapsules produced in the synthesis is to increase agitation rate. Initially, a 4-bladed metal propeller was used for stirring and the influence of agitation rate on size of microcapsules is shown in Fig. 3. Indeed, capsules do get significantly smaller because the size of emulsion droplets, upon which interfacial polymerization takes place, is
reduced. The smallest mean diameter, which was achieved by using a stirring rate of 1200 rpm was 157 μm (temperature was 80 °C, 10 ml of 10 wt % stabilizer added). A further increase in agitation rate was not possible because too vigorous agitation caused capsules to reside high up on the sides of the reactor thereby not participating into reaction anymore, not building up the required wall thickness and leaving the excess of shell material in the reaction mass. The increase in the stirring rate was accompanied by intensified production of undesired polymer nanoparticles, which at a certain point made capsule filtration impossible. Furthermore, a microscopic inspection revealed that some capsules, produced under 1200 rpm agitation rate, were of irregular shape or even cut into smaller pieces, suggesting that mechanical stability of the capsules was compromised and capsules became unacceptable for a coating use.

Other stirrer geometries were also tried in the synthesis, aiming at finding a geometry that would result in small and intact microcapsules. The first stirrer used, illustrated in Fig. 2B, was made of glass. It did not cause rupture of microcapsules, but the intensity of mixing was too low to produce microcapsules of sufficiently small diameters. Subsequently, to enhance agitation, a glass disc with holes along it and shown in Fig. 2C, was tried. Although stirring was more intense, microcapsules produced had multiple dents on their shells though not ruptured. As the final option, a 3-bladed metal propeller, shown in Fig. 2D, was used. It should be noted that this type of stirrer was employed by the majority of authors who reported the type of stirrer used in their work [15;13;21]. The 3-bladed propeller, perhaps due to the shape of the blades, was less aggressive for capsules than 4-bladed propeller and, at the same time, somewhat less efficient in reducing microcapsule size, as illustrated in Fig. 4. A rise in nanoparticle formation, when high stirring rates were applied, was similar to observations for the other stirrers used.
Fig. 3 Dependence of microcapsule mean diameter on stirring rate under the following synthesis conditions: 80 °C, 4-bladed propeller stirrer, and 10 ml of 10 wt % PVA. The error bars represent a confidence interval (95%).

Fig. 4. Dependence of microcapsule mean diameter on stirring rate under the following synthesis conditions: 80 °C, 3-bladed propeller stirrer, 10 ml of 10 wt % PVA. The error bars represent a confidence interval (95%).
4.3.1.2 Effect of stabilizer concentration

It was shown by Yuan et al. [16] that an increase in surfactant concentration leads to production of smaller capsules. In the present work, surfactants were not used at all because excessive nanoparticle formation was found to take place in the presence of these compounds. In Fig. 5 the results obtained with different stabilizer concentrations are shown. It is seen that higher stabiliser content gives some, but not a large decrease in the mean diameter of the microcapsules. However, stabilizer concentration significantly increases nanoparticle formation making it impossible to filter microcapsules by use of vacuum filtration and a cellulosic filter paper.

Fig.5. Dependence of microcapsule mean diameter on amount of stabiliser added under the following synthesis conditions: 80 °C, 3-bladed propeller stirrer, 800 rpm. The error bars represent a confidence interval (95%).

3.1.3 Effect of temperature

Initially, the experiments were conducted at 55 °C as in Nesterova et al. [11], and then the temperature was increased to 80 °C whereby 15 - 20 μm smaller capsules were obtained. However, knowing that emulsions are less stable at high temperatures, experiments at 40 °C were also
conducted. As Fig. 6 shows, that gave lower values for the capsule mean diameter. Formation of nanoparticles was negligible in this case. It should be noted, however, that the use of that low temperature requires very stable temperature control and may compromise yield of the synthesis.

Fig. 6 Dependence of microcapsule mean diameter on temperature under following synthesis conditions: 800 rpm, 4-bladed propeller stirrer, 10 ml of 10 wt % PVA. The error bars represent a confidence interval (95%).

4.3.1.4 Other techniques for reduction of microcapsule size

In all the cases where reduction of microcapsule size was achieved, the amount of nanoparticles grew significantly. In addition, with decreasing size of microcapsules, the size of the nanoparticles also decreased causing blockage of filter paper during vacuum filtration. For this reason, a number of separation techniques were employed.
4.3.1.4.1 Separation of capsules in a centrifuge

Centrifugation has been proposed as a possible mean for isolation of nanoparticles. Besides them larger polymer particles were also formed as by-products and either deposited on the bottom of the reactor right after the synthesis, if they were solid polymer pieces of several mm in size, or were floating, if they were smaller in size white flakes. Thus, in the synthesis with abundant formation of nanoparticles, the floating layer consisted of three parts, namely as relatively large polymer particles, microcapsules and nanoparticles, arranged from bottom of the layer to the top. The floating layer was decanted from the suspension after the synthesis and subjected to separation in a centrifuge. The fact that all the constituents were floating together suggests that they all have densities lower than water, which could negatively affect separation process. Meanwhile, as it is seen in Fig. 7, a separation occurred and a white, glue-like deposit of polymer particles was formed on the bottom of a vial. However, the floating layer still contained small nanoparticles and was whitish in colour. Although it could be filtered by vacuum filtration on filter paper, the filtered product was a dense mass, not suitable for dispersion in coatings.

![Image](image.png)

Fig.7. Vial with reaction mass after separation in a centrifuge. Upper layer consists of microcapsules and nano-particles, bottom layer consists of sediment of polymer particles.

The use of a centrifuge for separation of microcapsules was also reported in the literature by T. Szabo et al. [22]. However, difference in a purpose of using centrifugation does not allow direct comparison with the observations of this work.
4.3.1.4.2 Sieving of microcapsules

The smallest mean diameter of microcapsules, for which capsules were not damaged by a stirrer, was 160 μm. To decrease size further, separation was thought to be performed by sieving or filtering the microcapsules through a filter or a sieve with a large mesh size. The aim was to remove microcapsules larger than 150 μm and then use the remaining microcapsules in formulating a coating of about 200 μm dry film thickness. Unfortunately, standard cellulose filters are not available with a mesh size larger than 30 μm, a Duran glass funnel with 100 μm porosity was therefore used for capsule separation. However, none of the capsules went through the glass membrane of the funnel. To make sure that this did not happen, due to other reasons than thickness of the membrane, a thin (120 μm) monofilament polyester mesh DPP47 was used tried next as a filter for vacuum filtration. A proper filter cake was quickly formed above the mesh and none of the capsules went through it. Then, Retsch steel sieves with different mesh sizes, all above 150 μm, were tried. However, sieving of dry microcapsules, wet microcapsules, or microcapsules in xylene with ultrasound vibration were not successful. None of the capsules went through the sieve with 180 μm mesh size and only very few of them did with a mesh size of 350 μm. Wet material formed lumps and became more yellow in colour, indicating rupture of some of the capsules and release of linseed oil. There were also traces of oil on the surface of the wash water, which the capsules from the sieve were washed in after the sieving. Dry capsules also did not go through the sieve and formed either a layer or several lumps on the sieve. However, intact capsules were observed under the microscope on the surface of those lumps. All three experiments testified that materials with high surface energies could not be used for fractioning of microcapsules also having high surface energies.

To reduce surface energy of the steel sieve, it was coated with a fluoropolymer-based coating and sieving of a decanted capsule layer could now be easily done. The separation process became straightforward, when a vacuum pump via a water trap was connected to a dish with a filtrate. When capsules of 156 μm mean diameter were sieved in a 200 μm mesh size sieve, a filter cake of 223 μm and a filtrate of 124 μm mean diameter microcapsules were formed. In Fig. 8, the size distributions of microcapsules before and after sieving are illustrated. In the case shown, microcapsule diameter in the original suspension was small enough for the capsules to be almost fully sieved. Only negligible amount of microcapsules formed a filter cake on the sieve. In comparison, just a very small, negligible fraction of microcapsules, produced with a mean diameter...
of 313 µm, went through the sieve. The PSDs of the filter cake and the particle-containing filtrate are also very different in this case as illustrated in Fig. 9. In both cases it is seen that the maximum particle size of the solids in the filtrate is about 300 µm, which is substantially larger than the mesh size of the sieve (200 µm). In Fig. 10, an optical micrograph of a sieve fragment (after sieving) and a microcapsule entrapped in one of the cells is shown. It is evident that the sieve cells have a square geometry and the cells indeed have sides of 200 µm in length. This means that spherical microcapsules larger than 200 µm in diameter cannot go through the sieve and, as prolongated capsules were not observed in the syntheses products, the particle-containing filtrate’ PSDs in Figs 8 and 9, with particles larger than 200 µm, can only be explained by the presence of large polymer particles. The latter apparently can go through the sieve cells because of their observed flaky morphology (note that the diagonal in the cells is almost 300 µm). It may be possible to separate the large polymer particles from the microcapsules using fluoropolymer-coated sieves with smaller mesh sizes, but this was not attempted. Therefore, when evaluating the results of this work it should be kept in mind that the microcapsules contain polymer particles as an impurity.

![Graph](image)

**Fig. 8.** Particle size distributions obtained before and after sieving of microcapsules. Mean diameters are 156, 124 and 233 µm for the capsules in the original suspension, the filtrate, and the filter cake, correspondingly. In the figure, “1” and “2” refer to repititions.
Fig. 9. Particle size distributions obtained before and after sieving of microcapsules. Mean diameters are 313, 159 and 335 µm for the capsules in original suspension, filtrate and filter cake correspondingly. In the figure, “1” and “2” refer to repetitions.

Fig. 10. Optical micrograph of a fragment of the fluoropolymer-coated sieve with a 200 µm mesh size (after sieving). Note the microcapsule entrapped in one of the sieve cells.
Thus, microcapsules with a desired mean diameter (less than 150 µm) have been achieved and could be used for formulation of microcapsule-containing coatings and their subsequent testing.

4.3.3 Testing of a microcapsule-containing coating

4.3.3.1 Estimation of critical pigment volume concentration

The critical pigment volume concentration (CPVC) of a coating is the pigment volume concentration (PVC) at which the binder just fills the interstices between the particle, including any particle porosity. The concept was introduced by Asbeck and Van Loo in 1949 [23] and CPVC represents a transition point at which some significant changes in coating properties, such as permeability and optical properties, take place. The concept is of great relevance for formulation of coatings, also microcapsule-based self-healing coatings, because the anticorrosive (barrier) and mechanical properties are expected to deteriorate when formulating above the CPVC [24].

The most common approach for estimation of CPVC is to determine the oil absorption value of a given pigment or pigment mixture (including any fillers), using linseed oil and a spatula, and from that number calculate the CPVC [25]. According to Wicks et al. [25], CPVC values generally vary from 18 to 68%. In the case of self-healing coating containing microcapsules, it seems most logical to treat the capsules, due to their particulate nature and size (10-150 µm), as a filler material. This means that the CPVC value of a self-healing coating is dependent on particle size distributions, and surface chemistries of capsules, pigments, and fillers. However, the oil absorption method is not useful for microcapsules because the required rubbing with a spatula breaks the capsules. An alternative method, used in this work, is based on gloss measurements. A so-called PVC ladder is produced by formulating coatings with an increasing volume concentration of capsules and measuring the gloss of these coatings. The CPVC value is measured where a sharp transition point appears. This way of measuring CPVC is easy, but does require a set of coatings to be prepared. The method has been criticized in the earlier literature (e.g.[26]) for not providing a sharp end point and thereby produce inaccurate data. However, Gibson et al. [27], Tang et al. [28], and Ding et al. [29] have verified the applicability of this approach by also measuring the CPVC of the same coatings using transparency and tensile strength of PVC ladders. In Fig. 11, the gloss-PVC ladder of the microcapsule-containing coatings of this work is shown.
The shape of the curve is similar to that obtained by Ding et al. [29] in their figure 1 and that of Tang et al. [28] in their figure 11. According to these references, the CPVC value should be taken as indicated with an arrow in figure 11 and the CPVC in this case is about 30%. The value is rather low, but the system is also unusual and does not contain any conventional pigments (e.g. TiO$_2$) or fillers (e.g. limestone), which coatings most likely will do for industrial applications. In addition to that, microcapsule size is much larger (average diameter of 150 μm), than that of fillers. The residual gloss number above the CPVC is also rather high (equal to 40). In the studies of Ding et al. [29] and Tang et al. [28] the residual gloss is only 5-15 gloss numbers. This might be explained by the fact that the capsules unlike the conventional pigments are organic materials of high gloss and are somewhat similar to the pure binder. They are of a much larger size than most conventional pigments giving fewer surface disturbances, and as it was pointed put in [26], both refractive index difference across the reflecting surface and pigment size affect gloss. According to Gibson et al. [27], gloss of a film (documented for a latex binder), may be either constant or actually increase again above the CPVC. It has to be also added, that due to a special nature of microcapsules (soft polymeric shell and a liquid core) an additional error can be introduced to CPVC determination if
micromachines are damaged during formulation. However, the above effects have not been confirmed for the studies of this work.

Summarizing, it seems possible to estimate the CPVC of a microcapsule-containing coating and, in the absence of other fillers or pigments, the value of CPVC is in the lower end of the expected CPVC range for coatings, when microcapsules of 150 μm diameter are used. This low value is in some contradiction to the results obtained using salt spray exposure (to be discussed in a later paragraph).

4.3.3.2 Impact testing

Mechanical properties are important characteristics of industrial anticorrosive coatings, which should not be compromised by addition of microcapsules. Apart from microcracks arising due to release of internal stress in the film, damages of coatings can occur due to falling or moving objects. Impact testing has been chosen as a way to simulate this kind of stress and to assess coating damage (cracking or flaking) from a falling standardised metal object [30]. According to the procedure in the standard ISO 6272-1:2002 [31], this method can be used either for a pass/fail test or as a classification test, to determine the minimum mass and drop height for which a coating damage is observed. The standard also gives a choice between concave (intrusion) and convex (extrusion) deformations, which may be used for assessment. In this work, convex deformations have been chosen, at which the impact object is directed onto the back side of the substrate. Although this kind of damage is less likely to happen to a coating in real life situations, it leads to cracking of a coating and illustrates well the difference between the materials tested. Impacts directly onto the coating form craters, which are difficult to compare. In the experiments performed, the results obtained for microcapsule-containing coatings were compared to those obtained for the reference samples, which consist of commercial coating samples (containing pigments and fillers, but no microcapsules), pure binder, and filler-containing coatings.

The minimum height, at which a visible damage of the commercial coating was observed, was 17.5 cm. The defects consisted of a small number of cracks of 3-4 mm. The photographs of the damages on all samples, taken using a camera macro lens, are shown in Fig. 12. All the photos are given in the same scale, which was chosen to see the longest cracks formed after the damage (found on the pure binder coated sample). Preferably, the comparison between coatings should be done based on a reduced PVC basis, but due to the uncertainty in the CPVC value of the microcapsules it
was done on a PVC basis only. The second longest cracks were observed on filler and microcapsule coatings with a particle concentration of 5 vol %. A tendency of decreasing crack length and increasing number of cracks with an increase in pigment volume concentration is observed for both filler and microcapsule-containing coatings. However, apart from formation of the long cracks, the filler-containing coatings were also flaking significantly upon damage. In summary, the results of the experimental series confirm that microcapsules do not compromise resistance of a coating to an impact stress and may even improve it compared to a coating with filler materials. This effect may be due to a higher elasticity of the microcapsules, having a polymeric shell and a liquid core, compared to hard filler particles.

4.3.3.3. Salt spray

Salt spray (fog) test is an accelerated weathering test. Although it has been reported (e.g. in [25]) that the correlation between results of the test and actual performance of coatings is doubtful and it cannot be considered as truly predictive, the experiment has been conducted as a preliminary test, giving an estimation of anticorrosive performance of the microcapsule-containing coatings in comparison to the reference coatings. In addition, the test is also widely used by the coatings industry. After 3 weeks of exposure to salt spray, none of the panels showed any delamination (adhesion loss) or blistering. To assess the rust creep, the coating around the scribes, made prior to exposure, was removed mechanically applying force with a special tool. The observed extent of corrosion on all the panels was so little that quantification and comparison of rust creep areas would not be informative. However, some qualitative observations could be made. The widest corrosion area was seen on the panels coated with pure binder. The extent of rust creep, for filler-containing coatings, first decreased with PVC growing from 0 to 15% and then increased somewhat for 30 vol % of the filler. For microcapsule-containing coatings, no difference was seen between 5 and 15 vol %, but at higher concentrations the corrosion area became even thinner and identical to the commercial coating. Thus, microcapsules, even at a very high concentration (50 vol %), did not ruin coating performance in terms of adhesion or permeability of corrosive ions. It has to be noted,
Fig. 12. Photographs of the damages of the coating films after the impact test (17.5 cm height, 2 kg falling weight). 1: commercial coating, 2: binder, 3: 5 vol % filler-containing coating, 4: 15 vol % filler-containing coating, 5: 30 vol % filler-containing coating, 6: 5 vol % microcapsule-containing coating, 7: 15 vol % microcapsule-containing coating, 8: 30 vol % microcapsule-containing coating, 9: 40 vol % microcapsule-containing coating, 10: 50 vol % microcapsule-containing coating. Two repetition damages are shown for each of the coatings. The scale is identical for all of the photos.
however, that surface of the panels with coatings containing 30 vol % or more of microcapsules were significantly less glossy compared to other panels and to their initial unexposed state. Moreover, before exposure the surface of the panels was a little greasy and after exposure felt and smelt as a film of cured linseed oil, what could be an evidence of ruptured microcapsules and linseed oil, released into the coating and, possibly, filled coating’s porosity.

The very good performance observed in salt spray for coatings with high concentrations of microcapsules is in contradiction with the CPVC value (about 30 vol %) determined (see earlier paragraph). For PVC values above CPVC, the coatings are porous and the permeability of corrosive electrolytes is expected to be high. Therefore, microcapsules either provide some protective function to the coating above CPVC or the CPVC value estimated from gloss measurements is not the true CPVC value. Using a marker, it was attempted to reveal any porosity in the coating containing 50 vol % microcapsules, but no porosity could be detected.

4.4 Conclusions

The aims of this work have been to formulate and test a microcapsule-based self-healing anticorrosive coating. Poly(urea-formaldehyde) capsules, filled with linseed oil, and an epoxy-based coating matrix were used as a basis in the study. Initially, a systematic study on the influence of different synthesis parameters on microcapsule size and properties has been conducted. In agreement with earlier investigations, it was shown that an increase in stirring rate and stabilizer content led to a decrease in microcapsule size. The effects of temperature and stirrer geometry on microcapsule size and properties have been also explored. It was found that the smallest capsules were produced at the lowest temperature at which reaction can proceed, but with a risk of a small yield due to insufficient reaction rate. It was also demonstrated that a 3-bladed propeller was the most gentle for microcapsules, but leads to formation of larger capsules than a 4-bladed propeller stirrer. In all the cases, where significant reduction of microcapsule size was achieved, excess formation of polymer nanoparticles (by-product) was observed. Nanoparticles complicated isolation of capsules by vacuum filtration and made the resultant product a dense mass, not suitable for dispersion in a coating. Both decantation and 1-stage centrifugation did not allow separation of nanoparticles from microcapsules and production of a free-flowing product after drying. This means that a compromise has to be found between size of the microcapsules and amount of produced nanoparticles, and other approaches to reduction of capsule sizes have to be used. It was shown that a very good separation of microcapsules, based on their diameters, could be obtained using a steel
sieve coated with a low-energy fluoropolymer. Thus, capsules with a mean diameter less than 150 µm have been prepared and used for coating formulation.

Based on specular gloss measurements and a PVC ladder, a CPVC value for microcapsules has been estimated to about 30 vol %. The value is within the common CPVC interval but significantly lower than anticipated. Using the CPVC concept has not been attempted for microcapsules (as opposed to pigments and fillers) before and therefore it needs to be confirmed if the obtained value is the true CPVC value.

Reverse impact test of microcapsule- and filler-containing coatings as well as a commercial coating and a pure binder have been performed. It was found that both filler-containing and microcapsule-containing coatings form smaller cracks compared to a coating of pure binder. In addition, microcapsule-containing coatings were found to form fewer and smaller cracks than coatings with the same amount of filler (ideally this comparison should be done based on a reduced PVC basis, but due to the uncertainty in the CPVC value of the microcapsules it was done on a PVC basis only). The enhanced resistance to impact of the microcapsule-containing coating might be due to higher elasticity of microcapsule polymeric material compared to hard inorganic filler particles. Finally, results of the preliminary salt spray exposure of coatings have shown that addition of microcapsules to the epoxy binder matrix does not compromise coating performance.

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References


Chapter 5. Modeling of healing efficiency of a microcapsule-based self-healing coating

Nomenclature

\( a \) 
- distance from the centre of a microcapsule to the crack plane

\( C_V \)
- volume concentration of microcapsules, vol %

\( d \)
- distance between centres of two microcapsules, mkm

\( E_{th} \)
- theoretical healing efficiency, %

\( F_S \)
- face separation, mkm

\( K \)
- capsule shell thickness, mkm

\( l \)
- length of the crack, mkm

\( N_{caps} \)
- overall number of microcapsules in the cell

\( N_{crack} \)
- number of microcapsules ruptured by crack

\( N_{CReaps} \)
- number of capsules per crack

\( N_H \)
- number of simulation cases for the certain data point, for which

\( N_R \)
- number of the simulation cases for the certain data point for which rupture of at least

one capsule occurred

\( N_S \)
- total number of simulations performed to obtain each data point

\( N_{VUcaps} \)
- number of capsules per volume unit

\( P_H \)
- probability of healing

\( P_C \)
- cracking probability

\( r \)
- radius of a capsule, \( \mu m \)

\( S \)
- area of triangle KLM, \( \mu m^2 \)

\( V_{caps} \)
- volume of a capsule, \( \mu m^3 \)

\( V_{cell} \)
- volume of the cell, \( \mu m^3 \)

\( V_{crack} \)
- volume of the crack, \( \mu m^3 \)

\( V_R \)
- volume of healing agent released from the microcapsules, \( \mu m^3 \)

\( V_{Tcaps} \)
- total volume of microcapsules, \( \mu m^3 \)

\( w \)
- width of the crack, \( \mu m \)

\( X_{cell}, Y_{cell}, \) and \( Z_{cell} \)
- linear dimensions of the representative volume element (cell), \( \mu m \)
5.1 Introduction

To formulate a self-healing microcapsule-based coating, the amount of a healing agent, which must be added to the coating to obtain a desired degree of healing or healing of a crack of a certain size, needs to be known. Knowledge of a maximum crack size, which can be healed, and effect of microcapsule diameter and concentration on the coating healing efficiency is also very useful for microcapsule-based coating development. An attempt to describe experimental data, obtained for healing of a crack in an epoxy matrix with encapsulated dicyclopentadiene, by a mathematical model has been performed by Rule et al. [1]. Later a numerical study of healing efficiency of both spherical and elongated capsules has been developed by Mookhoek et al. [2]. In this chapter a basic and statistical approaches to prediction of healing efficiency of smicrocapsule-based self-healing coatings are considered.

5.2 Basic approach

It is assumed that a free volume \( V_{\text{crack}} \) is formed in a coating when a crack appears. Shell thickness of the capsules is considered negligible, compared to the capsule diameter. For self-healing to occur, this free volume has to be filled with a healing agent of volume released \( V_R \) from the microcapsules. If, in the basic case, only microcapsules which fit into the volume formed are considered as ruptured and release healing agent, shown at Fig. 1, then the volume released from the microcapsules will always be lower than volume formed by the crack, and will be determined as

\[
(1)
\]

Thus, \( V_R \) in this case is only dependent on a volume of crack and a volume concentration of microcapsules \( C_V \) and is not affected by microcapsule diameter. As it follows from equation (1) under given assumptions the volume released is always lower than volume of crack because \( C_V \) is always lower than 1. This can be explained by the fact that only the volume of healing agent, which is released from capsules fully lying within the crack volume, is counted.
To improve the model with a capability of taking into account microcapsules intersected by crack but not fully lying within the crack volume, some changes to conditions of the model have to be made. Fig.2 illustrates a scheme of the modified approach. In this case, effective crack volume is introduced. Effective crack volume is volume of a crack, in which all linear dimensions are increased for 2 capsule diameters. The use of effective crack volume allows to count healing agent released not only from the capsules fully lying within the crack volume but from all the capsules intersected or touched by the crack. This approach with planar crack and effective volume was used by Rule et. al. [1].

Fig. 2. Schematic presentation of a modified basic approach to modelling of a microcapsule-based self-healing coating, utilizing term of effective crack size.
Such a model does take into account diameter of the capsules but does not effects of a crack geometry and crack and capsule position, especially if the crack in the model is represented by a plane going through the whole representative volume element. To see whether a crack geometry and a mutual position of a crack and microcapsules affect the results of predicted healing, a statistical model has been developed.

5.3 Statistical model

The model is based on Monte Carlo simulations and can be considered as the developed version of the model proposed by S. Mookhoek [2]. The prizmatic shape of the crack was added. The model allows taking into account not only the volumes of a crack formed and a healing agent released but also geometry of the crack and mutual positioning of microcapsules and the crack. In this model it is also assumed that when a microcrack propagates through the coating free volume is formed and needs to be filled by a reactive healing agent, stored in the microcapsules. Thus, the amount of healing agent released becomes dependent on the following parameters:

- dimensions and geometry of the crack as this determines how many microcapsules can be intersected;
- volume concentration of microcapsules as this determines number of microcapsules, which can meet the crack, and volume, which can be released from them;
- diameter of microcapsules as this both affects probability of rupture and the amount of healing agent released;
- microcapsule shell thickness as this has an influence on amount of healing agent available in microcapsules for healing.

The model allows estimation of volume of the crack which can be healed as well as its linear dimensions depending on microcapsule concentration, diameter and shell thickness. This contributes to finding optimal combination of those parameters and use it for formulation of an efficient self-healing coating.

The model is based on the following assumptions:

- Capsules are spherical and have uniform radii.
- Capsules are randomly homogeniously distributed within the cell volume.
- Capsules do not touch each other within the cell volume.
- Cell (representative volume element, RVE) has a form of a parallelepiped.
Crack is placed within the cell and has a form of a prism with the rhombic base.

- Crack propagates from surface of the cell and has a form of a prism with triangular base.
- Capsule considered as intersected when a crack reaches its shell.
- Healing agent is fully released from the capsule, when the rupture occurs.
- Free volume is formed in place of the microcapsules.

Schematic drawings of RVE with microcapsules and both kinds of crack are shown in Fig. 3.

![Schematic drawings of RVE with microcapsules and cracks](image)

Fig. 3. Representative volume elements with positioned in them microcapsules and cracks, propagating within the cell volume and from the cell surface.

### 5.3.1 Model Equations

The cell has dimensions $X_{cell}$, $Y_{cell}$, and $Z_{cell}$. Volume of the cell is determined as follows:

$$V_{cell} = X_{cell} \times Y_{cell} \times Z_{cell}$$

Capsules are defined by radii $r$ and coordinates of their centres $(X, Y, Z)$ which are randomly generated in such a way that all the capsules lay within the cell volume. Volume of a microcapsule is calculated as:

$$V_{caps} = \frac{4}{3} \pi r^3$$

For each of the loading capsules condition of it’s intersection with capsules already placed in the cell is checked. If

$$d > r_1 + r_2$$

where $d$ is a distance between centres of two microcapsules, Fig. 4A, then capsules do not touch each other. If intersection of the capsule with any of the already loaded ones is detected, the new coordinates of it’s centre are generated. If the new coordinates, at which microcapsule does not touch other microcapsules, are not found during 500 iterations then the volume is considered as full and no other capsule is placed. Thus, the overall number of microcapsules $N_{caps}$ placed in the cell is
determined by their concentration $C_v$, diameter (through the volume) and condition of loading assuring that they do not contact each other:

$$\text{(5)}$$

Fig. 4. Conditions of intersection of microcapsules with A) another microcapsule, B) with a crack.

A crack is defined within the cell by the horizontal rectangular crack plane which is set by the coordinates of two corners: $C_1X$, $C_1Y$, $C_1Z$ and $C_2X$, $C_2Y$, $C_2Z$, where $C_1Z = C_2Z$, $C_2X = C_1X + w$, and $C_2Y = C_1Y + l$, were $l$ is length of the crack, $m$ and $w$ is width of the crack, $m$. When a face separation is added ($FS$, $m$), crack becomes represented by the prism with a rhombic base, which vertexes are defined by the following coordinates, as illustrated in Fig. 5A:

A ($AX = C_1X; AY = C_2Y; AZ = C_1Z$)

B ($BX = C_1X, BY = C_1Y, BZ = C_1Z$)

C ($CX = C_1X + l/2, CY = C_1Y, CZ = C_1Z + FS/2$)

D ($DX = C_1X + l/2, DY = C_2Y, DZ = C_1Z + FS/2$)

E ($EX = C_1X + l/2, EY = C_2Y, EZ = C_1Z - FS/2$)

F ($FX = C_1X + l/2, FY = C_1Y, FZ = C_1Z - FS/2$)

G ($GX = C_2X, GY = C_1Y, GZ = C_1Z$)

H ($HX = C_2X, HY = C_2Y, HZ = C_2Z$)
The volume of a crack $V_{\text{crack}}$ is determined as

$$V_{\text{crack}} = \text{...}$$  \hspace{1cm} (6)

Distance $a$ from a capsule’s center with coordinates $\text{CapsX}, \text{CapsY}, \text{CapsZ}$ to the plane $ABCD$ of the crack is determined as a height of the triangle $KLM$, Fig. 5B, where $K$ is the capsule’s center with coordinates $(KX=\text{CapsX}, KY=\text{CapsY}, KZ=\text{CapsZ})$ and $L$ and $M$ are the points on the plane with coordinates $(MX=AX, MY=\text{CapsY}, MZ=AZ)$ and $(LX=BX, LY=\text{CapsY}, LZ=BZ)$. Distance $a$ is calculated as

$$a = \frac{S}{m}$$  \hspace{1cm} (7)

where $S$ is the area of the triangle $KLM$, $m^2$.

A capsule is considered as ruptured if the distance $a$ from the capsule centre to the rectangle plane is lower than capsule’s radius. The condition is checked for all planes and edges of the crack and is illustrated by Fig. 4B.

Volume of healing agent $V_R$ which is released from all the ruptured by crack microcapsules is determined as

$$V_R = \text{...}$$  \hspace{1cm} (8)

where $N_{\text{crack}}$ is a number of the capsules crossed by the crack, $K$ – capsule shell thickness, $m$.

Knowing volume of the crack formed and amount of healing agent which can be released from the microcapsules ruptured by crack, theoretical healing efficiency $E_H$ can be calculated.

$$E_H = \frac{V_R}{...}$$  \hspace{1cm} (9)

Probability of healing $P_H$ defines the probability of the crack to be healed and is calculated as
where \( N_s \) is a total number of simulations performed to obtain each data point, \( N_H \) is number of the simulation cases for the certain data point for which the following condition is fulfilled:

\[
(10)
\]

Cracking probability \( P_C \) defines the probability of at least one capsule in the cell to be ruptured and is determined as:

\[
(11)
\]

where \( N_R \) is number of the simulation cases for the certain data point for which rupture of at least one capsule occurred.

### 5.4 Results of modeling

A cell with 1000x1000x150 \( \mu \text{m} \) dimensions has been chosen as representative volume element for performing calculations. The cell is parallelepiped as opposed to a cube used by Mookhoek et al. [2] since it’s geometry is closer to a layer of a real coating. Height of the cell is set as 150 \( \mu \text{m} \) because it is close to the thickness of a layer of heavy duty anticorrosive coatings. Shell thickness was set as 3 \( \mu \text{m} \). Modeling has been performed for 2 kinds of crack: a rombic base crack, going through the coating volume and a triangle base crack, going from the coating surface of the coating. For each of the crack type two sizes were considered.

#### 5.4.1 Crack in bulk in form of the prism with rhombic base

The dependencies for the various parameters on capsules’ diameter obtained through the modeling for the crack in a shape of rhombic-based prizm are shown on Figs. 6-9. The results are presented for two volume concentrations of the capsules: 5 and 15\% and for the cracks of two sizes. First, noticed as “small”, is the crack with the following linear dimensions: \( l=100 \text{ mm}, W=50 \text{ mm} \) and \( FS=26 \text{ mm} \), where the face separation value has been adopted from Rule et al.[1], where it was an average experimental value. It models the case of the microcrack within the bulk of a coating. The “large” crack with linear dimensions of \( l=1000 \text{ mm}, W=200 \text{ mm} \) and \( FS=26 \text{ mm} \) represents the crack which propagates through the whole RVE. It is introduced for comparison with the results by Rule et al.[1].
The total released volume (8) as shown at Fig. 6 increases almost monotonously with the increasing diameter of the capsules. The larger concentration of the capsules and larger crack size provide more healing agent as crack propagates through more capsules.

Results for the theoretical efficiency of healing (9) at Fig. 7 are more interesting. The dependence obtained for a small crack and low capsule concentration does not show the monotonous increase of the EH. The value passes maximum of 65% at the capsule diameter of 60 \(\mu\text{m}\) and then decreases down to 29% at 70 \(\mu\text{m}\), and then begins to increase again. This shows that healing efficiency does not depend on a bulk released volume, but also on probability of the capsules rupture. Such a probability (12) dependence on capsules size as shown at Fig. 8 leads to unexpected conclusion. Despite the conclusion made by Rule et al.[1] that larger diameter of the capsules is always preferable, the graph shows decrease of a capsules rupture probability for a small crack and larger capsule diameters. The tendency is more pronounced for the low concentration case, so it also affects the dependence of theoretical healing efficiency.

Such behavior can be explained by the fact that larger capsules being placed into the RVE provide more free volume than smaller ones at the same volume concentration. Thus, capsule rupture becomes less probable for the small cracks. However, it has almost no effect for the cracks, propagating through the whole volume, as for them probability of intersection with at least one capsule is close to unity for all the cases.

The crack healing probability (10) was introduced to describe the healing as theoretical healing efficiency does not show the whole picture. As healing efficiency averages released volume by the number of simulations it can be assumed that for the large diameters of the capsules, when the volume of the single capsule exceeds the volume of the crack by the orders of magnitude, there are cases when low-probable rupture can provide enough healing agent volume to keep theoretical efficiency high. For the real cases probability of a crack to be healed is more meaningful as it shows the chances of the crack to be healed in every single case.

The dependence of healing probability on the capsules diameter shows the principal difference between the microcrack and large crack cases. Probability of healing for the large cracks increases monotonously with the increasing diameter as the rupture probability for them is close to unity and released volume increases monotonously with the diameter increase. Such behavior is in good agreement with the data obtained by Rule et al.[1].
The same dependence for microcracks obtained for both concentrations passes maximum at the capsules diameter of 60 \( \mu \text{m} \) and then probability of healing decreases. From the practical point of view this means that for the self-healing coating the optimal microcapsule diameter has to be chosen in order to reach the maximum efficiency. Self-healing function of the coating, containing capsules of the diameter greater than optimal, will be less efficient.

Another conclusion which may be drawn from the simulations made is that dependencies obtained from the experiments or modeling with the cracks propagating through the whole coating volume should not be transferred to the healing of microcracks, especially if concentration of microcapsules in a coating is low.

![Graph](image)

Fig. 6. Dependence of released volume of healing agent on diameter of the capsules.
Fig. 7. Dependence of theoretical healing efficiency on diameter of the capsules.

Fig. 8. Dependence of capsule rupture probability on diameter of the capsules.
Fig. 9. Dependence of crack healing probability on diameter of the capsules.

5.4.2. Crack from surface in form of the prism with triangular base

Range of calculations have been performed for modeling of healing of a crack propagating through the coating from the coating surface. Dimensions of the small crack were 100x26x50 µm, which corresponds to length, width (face separation) and depth, and dimensions of the large crack were 1000x26x150 µm.

The dependencies for all the parameters mentioned in previous subsection are shown at the Figs. 10-13. It is clearly seen that the graphs reproduce the general tendencies from the previous case, while the rupture probability and probability of healing for microcracks are lower for the cracks, originating form the coating surface compared to the cracks within the bulk of the coating. This can be due to a different geometry and a crack position, which allows less of the crack space to be in contact with microcapsules.

The conclusions drawn in the previous subsection for healing of crack, lying in a bulk of the coating, are also valid for the cracks, propagating from the surface.
Fig. 10. Dependence of the released volume on diameter of the capsules.

Fig. 11. Dependence of theoretical efficiency on diameter of the capsules.
Fig. 12. Dependence of capsule rupture probability on diameter of the capsules

Fig. 13. Dependence of crack healing probability on diameter of the capsules

5.5 Conclusions

3-D model based on Monte-Carlo simulations have been developed for describing of microcapsule-based healing in a coating. Two types of a crack have been considered: one in a bulk
coating and one, going from the coating surface. Both large cracks, propagating fully through the coating layer, and small cracks were analysed. The range of capsule diameters studied was 20 – 100 µm. Range of microcapsule concentrations used was 5 and 15 vol %.

By the results obtained, it was shown that size of microcapsule and geometry of the crack play an important role in coating healing. So, for healing of small cracks optimal diameter of microcapsule has to be chosen, as with an increase in diameter and volume of available healing agent, probability of healing significantly decreases as probability of hiding of loosely located large microcapsules by a small crack becomes very low. In case of a large crack the maximum possible microcapsule diameter has to be used for efficient healing as probability of rupturing capsules is close to 1 and healing depends only on amount of healing agent available. Cracks, propagating from the coating surface have less chance to be healed compared to the crack, located in a bulk of a coating, as it’s geometry decreases the probability of capsule intersection.

References
Chapter 6. Conclusions and further work

6.1 Conclusions

Self-healing anticorrosive coatings are smart materials which have been proposed as a way to long-lasting corrosion protection. A number of approaches to self-healing coatings have been developed since the early 2000s. The microcapsule-based approach, which is currently the most studied route and seems to be the most versatile and suitable for industrial use, has been chosen for investigation. It has been applied to development of an epoxy-based self-healing anticorrosive coating for above water heavy duty corrosion protection. Emphasis in the study was put on investigation of practical issues associated with development and use of this type of coating.

A laboratory investigation to identify the most suitable method for production of mechanically stable and forming a free-flowing powder upon drying microcapsules, filled with industrially relevant core materials, has been performed. Four different experimental procedures, available in the literature, have been used for encapsulation of 6 core materials, including epoxy resins, diluent and linseed oil. The following challenges of microcapsule preparation were identified: excessive agglomeration of microcapsules, core material-dependence of microcapsule stability, undesirable formation of nano-particles in bulk solution, and long synthesis time. Encapsulation of viscous liquids (viscosity of about 1.3 – 1.5 kg/(m·s)) was found to be difficult in all the methods. Generally, microcapsules produced with poly(urea-melamine-formaldehyde) shell were more robust than those produced with poly(urea-formaldehyde) shell. However, the former were accompanied by a significant amount of nano-particles being formed. Free-flowing powders of poly(urea-melamine-formaldehyde) capsules, filled with alkylglycidylether, and poly(urea-formaldehyde) capsules, filled with linseed oil, were prepared and used as model systems in further investigations.

The microcapsules produced have been tested for parameters important for use of the capsules in coating formulation. Solvent stability, stability towards stirring and storage of the microcapsules have been evaluated as well as ease of capsule dispersion. It was found that both kinds of microcapsules remained intact after 1 month storage in xylene, which is a very common solvent for solventborne anticorrosive coatings. Linseed oil-filled microcapsules on the other hand were damaged during 1 month storage in polar solvents and artificial seawater. Poly(urea-formaldehyde) microcapsules filled with linseed oil degraded during long term storage in a closed jar under ambient conditions, while poly(urea-melamine-formaldehyde) capsules were unaffected. Both kinds
of microcapsules were easily dispersed and remained intact in epoxy binder, diluted with solvent, under 550 rpm stirring rate, while poly(urea-melamine-formaldehyde) microcapsules could remain intact also during dispersion in pure epoxy, without any addition of solvent. Thus, microcapsules demonstrated different degrees of stability depending on core and shell materials.

Preliminary studies have shown that use of microcapsules with 220 µm mean diameter give difficulties in coating application and therefore a systematic study has been performed for reduction of size of poly(urea-formaldehyde) capsules filled with linseed oil. Results showed that any measure taken to reduce size of microcapsules (i.e. an increase in stirring speed or in stabilizer concentration, a temperature adjustment or a change of the stirrer geometry) enhanced nano-particle formation in the bulk solution. This complicated filtration and led to formation of a dense product after drying, possessing a need for finding a compromise between size of the microcapsules, which is desired, and amount of nano-particles. For obtaining a free-flowing powder of microcapsules, several means of mechanical separation of large and small microcapsules was tried out. Due to the high surface energy of the capsule materials, separation could only be done by sieving of capsules using a fluoropolymer-coated sieve. Large microcapsules were isolated as a filter cake, whereas small capsules could be obtained in the filtrate and used in formulation of a capsule-containing coating. A batch of coatings with 5 – 50 vol % of microcapsules was prepared and applied to steel substrates along with reference coatings. Impact and salt spray testing were conducted. It was clearly demonstrated that addition of microcapsules in a concentration up to 50 vol % did not compromise resistance of the coating to impact and, perhaps, owing to elasticity of microcapsules with a polymer shell and a liquid core, even reduces intensity of crack formation (both in number and length) compared to filler-containing coatings and prevents coating from flaking upon damage. In addition, 3-weeks exposure of panels to a salt spray did not reveal either any drawbacks from addition of microcapsules to an epoxy coating. Based on specular gloss measurements on a PVC ladder of microcapsule-containing coatings, CPVC was estimated to 30 vol %, which is in the lower end of expected CPVC values for coatings. The number needs to be confirmed especially because it seems to be in contradiction with results from the salt spray exposure test.

Finally, a 3-D model, based on Monte-Carlo simulations, was developed for prediction of healing efficiency of a microcapsule-based anticorrosive coating. Two kinds of cracks were considered: cracks accommodated within the bulk coating and cracks starting from the coating surface. The model takes into account volume of the crack formed, it’s geometry and linear dimensions as well
as diameter, volume concentration and shell wall thickness of the microcapsules, embedded in the coating. Simulations showed that diameter of microcapsules and crack geometry play an important role in self-healing of the coating.

6.2 Further work

Self-healing anticorrosive coatings possess a great potential for development of industrial heavy-duty anticorrosive coatings, however, to bring the concept to work a number of aspects have to be taken into account and thoroughly studied in collaboration of chemists, material scientists and coating engineers. Presently, there is still a demand for new self-healing approaches, applicable to industrial systems, but also for investigations of influence of the added self-healing functionality on other properties of the coating.

The present work can be continued with a more extensive laboratory study of microcapsule-containing coatings. Either model capsules or capsules with industrial relevant core materials can be used for that. Long-lasting corrosion tests are of particular interest.

An attempt to verification of the obtained CPVC value should be performed. In the repetition experiment amount of the solvent added to coatings with 30 and more vol % of microcapsules needs to be increased to prevent capsules from rupture.

The developed statistical model can be improved and perform simulations closer to a real microcapsule-containing coating, if a PSD will be used instead of a single capsule diameter.